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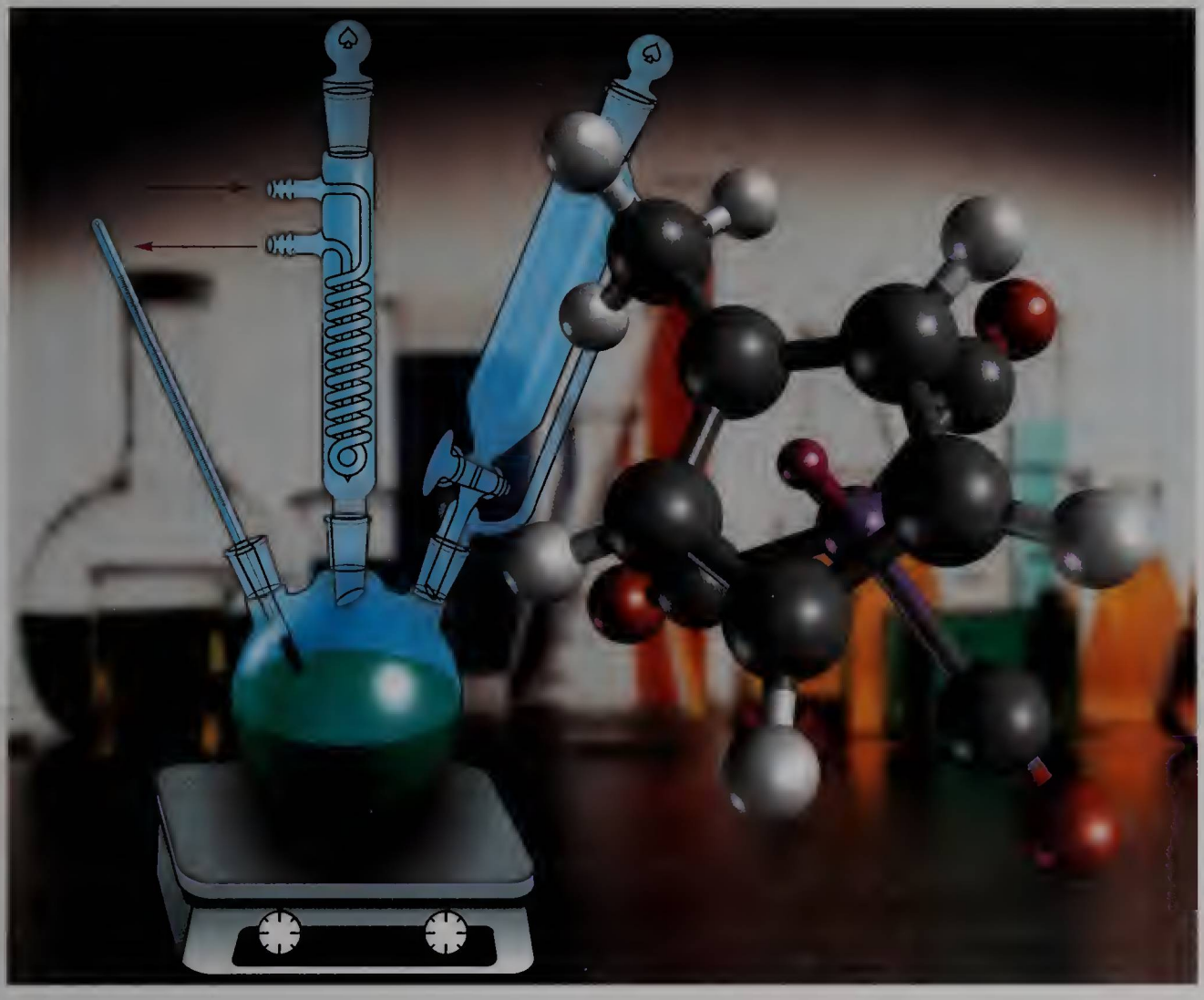
Inorganic Experiments

Third, Revised Edition



Inorganic Experiments

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To Alex, Philip, Robert and Timothy
for still "putting up with me"

Foreword to First Edition

I am delighted to write a foreword to this work, *Inorganic Experiments*. While many chemists may prefer to spend most of their time tapping on keyboards, I have always thought that making new compounds provides the real fun and enjoyment in chemistry.

While the experiments set out utilize known chemistry, any students who do even a modest selection of them should be given confidence to go into the laboratory not only to make starting materials but to do some original reactions with them as well.

Professor Woollins and the distinguished international group of contributors have provided a stimulating and instructive selection of experiments that should prove invaluable in teaching institutions.

Professor Sir Geoffrey Wilkinson
Imperial College, London

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1
Introduction

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1.1
Introduction

J. Derek Woollins

Chemistry remains a practical subject and for many of us the topics we recollect most sharply (and understand most thoroughly) are often derived from our own experiences in the laboratory. Meaningful experiments which develop laboratory skills, introduce interesting chemistry and are reliable are not always easy to find. This text seeks to address the problem for inorganic chemists. The following compilation of experiments in no way attempts to cover all of inorganic chemistry. However, I hope that there is sufficient range to demonstrate the majority of the important techniques in the context of some interesting and stimulating chemical examples. The experiments have generally come from laboratory courses where they have been tried and tested or they have been checked so we can optimistically assume that they 'work'. For convenience, the experiments have been classified (by me – not the authors) into 'introductory', 'intermediate' and 'advanced'. Clearly, laboratory course organisers must make their own assessment as to the level of difficulty of individual experiments in the context of their laboratory facilities, experience of the students, etc. In general, we have not described measurement methodology in great detail, again on the assumption that facilities differ from one laboratory to the next. Furthermore, some experimental arrangements differ depending on the origin of the submission. This is the case in research and in industry and I have made no effort to impose any house style, there is much to be learnt from the differences!

The experiments are usually prefaced by a section detailing any special safety precautions. Although this is an aid for the user, it should not be assumed that all aspects of safety have been dealt with – the laboratory course supervisor and the student performing the experiment **must** make their own assessment as to the hazards which the chemicals and procedures represent. Although we have made every reasonable effort to test experiments and to provide appropriate safety data and instructions, the authors and the editor do not assume any responsibilty or liability for any mishaps or accidents that may occur in the use of any part of this text as a laboratory manual.

In this revised edition, I have added 18 additional experiments, bringing the total available to just under 100. I am grateful to Petr Kilian, who has provided a brief chapter dealing with reporting of data. I have taken the opportunity to reorganise the order of the experiments into coherent groupings. Alert readers will

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also notice that there are possibilities to link together experiments, e.g. the synthesised Ph_3PO from Experiment 2.20 can be utilised in a coordination chemistry Experiment 2.14.

I wish to express my gratitude to all the authors who have so readily contributed experiments to this third edition.

1.2
General Spectroscopic Techniques and Report Writing

Petr Kilian

The following sections are derived from 'good practice' at St Andrews. They do not represent the only way to collect and report spectroscopic data, but it is hoped that they will serve as indications of good practice.

1.2.1
General Spectroscopic Techniques

1.2.1.1
Preparation of Samples for Infrared Spectroscopy

A) Use of NaCl (or KBr) Sample Plates

Note: Alkali metal halide plates used in IR spectroscopy must be handled only by their edges, never by their polished faces. They dissolve on contact with water!

The sample plates are mounted in a plate holder and placed in the sample beam of the spectrometer. After use, the plates are wiped clean with a tissue dampened with dichloromethane and stored in a tube containing silica gel.

a) Liquid Samples

For liquids, it is normally appropriate to measure IR spectra as thin films. A small drop of the substance is placed on a polished face of a sodium chloride plate. A second plate is placed on top and the two plates are squeezed firmly together. Any excess sample squeezed out is wiped off with a clean tissue.

b) Solid Samples

Solids may be run as a KBr disc or a paste in Nujor (Nujol mull).

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B) Nujol Mull Preparation

Nujol is a mixture of alkanes and therefore contains only C–C and C–H bonds; hence it has a comparatively simple spectrum (see Fig. 1.2-1), the principal absorptions of which are associated with C–H vibrations. These absorptions should be subtracted from the final spectrum to obtain the spectrum of the solid.

1. A small amount of the solid is placed in the agate mortar and ground thoroughly to a very fine powder.
2. A small drop of Nujol is added and the mixture ground again to give a thick paste.
3. The paste is placed on the polished face of a sodium chloride plate.
4. A second plate is placed on the first and the mull is squeezed between the plates until it appears to be a thin translucent smear between the plates.

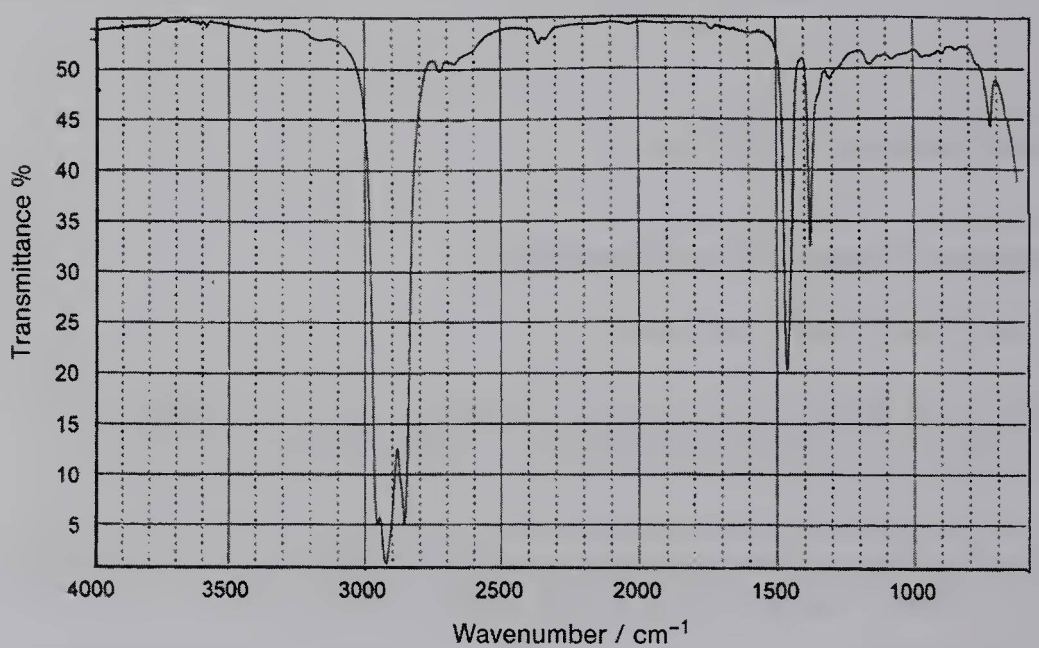

Fig. 1.2-1 IR spectrum of Nujol.

C) Use of a Mini-Press for KBr Pellet Preparation

a) Sample Grinding

Dried spectroquality potassium bromide (KBr) is used as the matrix. Thoroughly grind approximately 2–3 mg of solid sample (with experience you will see that this is enough to cover the tip of a microspatula) with 100 mg of KBr in a dry agate mortar and pestle. Grind thoroughly for 3–5 minutes, until the resulting powder is like talc.

b) Forming the Pellet

Place one dry bolt into the dry barrel and advance five full turns. Deposit ground matrix and sample on the surface of the bolt inside the barrel. Tap the unit gently to spread the sample uniformly over the lower bolt. Insert second bolt and advance until finger tight. Using two ring spanners, gradually exert pressure on each bolt. To operate more easily, the lower bolt may be placed in a bench vice and the top tightened with a wrench. Apply pressure for about 1 minute, then remove bolts. If one bolt holds tight in the barrel, use a vice on the flats of the barrel with wrench on the bolt.

c) Clean-Up

The pellet is best removed, and the barrel and bolts cleaned, using hot water followed by rinsing with acetone, blotting with a tissue, then oven drying for a few minutes. **Note:** Do not attempt to punch out the pellet or to drive it out with one of the bolts – this may damage the barrel or the polished die surface. Take care in the oven not to scratch the polished bolts. Ensure that the KBr is removed completely, then return the barrel and bolts to the desiccator. Ensure the clean-up is performed for the benefit of the next user!

The quality of spectrum is affected by the grinding and by the amount of sample in the matrix; see the example spectra in Figures 1.2-2 and 1.2-3.

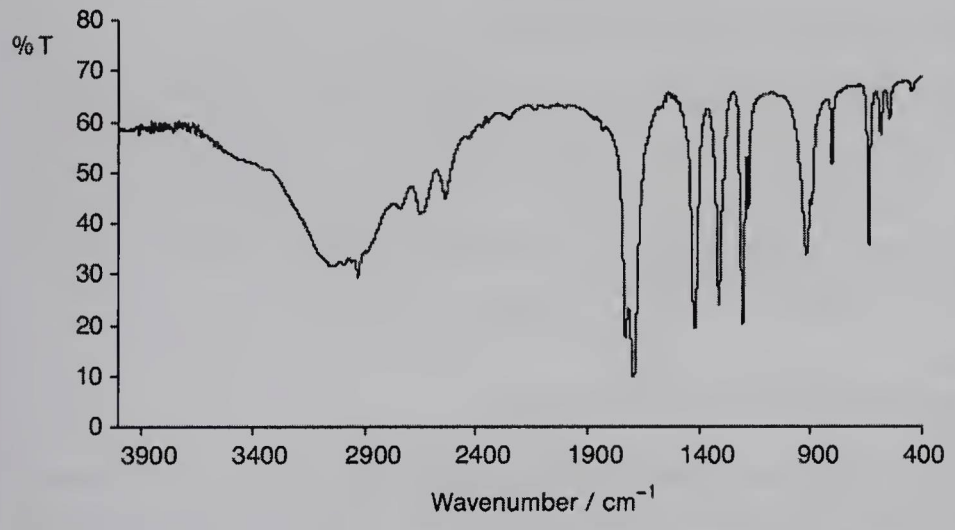

Fig. 1.2-2 Good-quality IR spectrum.

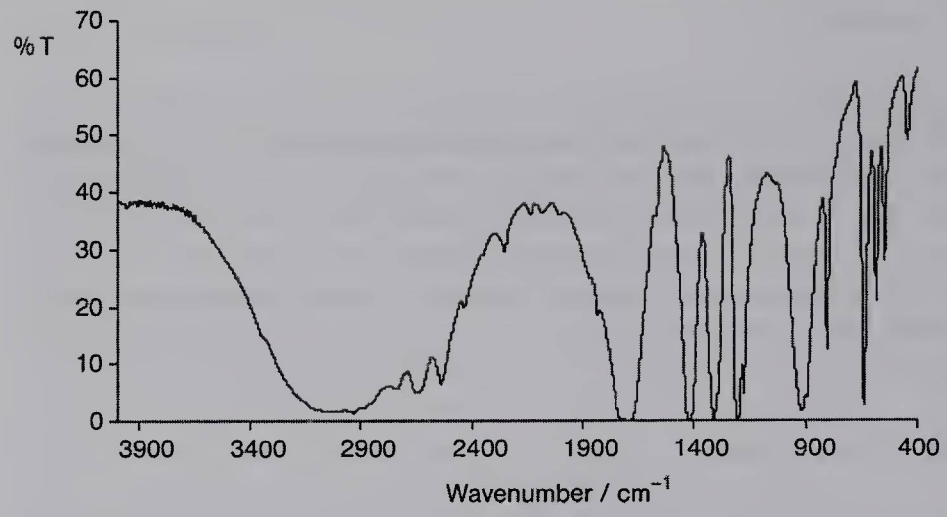

Fig. 1.2-3 Spectrum with too much sample in the pellet.

Further Reading (including help with assignments)

K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, Inc., New York, 1978.

1.2.1.2

Preparation of Samples for Raman Spectroscopy

Use of glass sampling accessories (e.g. melting point capillary) is possible in Raman spectroscopy, as the spectrum is usually obtained using a near-infrared laser beam which is not absorbed by ordinary glass. Seal one end of a melting point capillary using a Bunsen burner. Fill the capillary to *ca.* 10 mm height with your sample by scooping it from a sample vial and compact by gentle tapping. The open end of the capillary can be sealed using Blu-Tack.

1.2.1.3

Preparation of Samples for UV-Vis Spectroscopy

The sample concentration should be chosen such that the maximum absorbance of the band of interest does not exceed 2 and is preferably close to 1. Remember that the absorbance is usually proportional to concentration (Beer's law: $A = \varepsilon cl$, where ε (epsilon) is the extinction coefficient in units of $dm^3\ mol^{-1}\ cm^{-1}$, c is concentration in mol dm^{-3} and l is the pathlength in cm.

1.2.1.4

Preparation of Samples for ^{1}H NMR Spectroscopy

To run an NMR experiment, the sample compound must be dissolved in a deuterated solvent (normally $CDCl_3$) and transferred to an NMR tube. It is important to filter the sample prior to running the experiment since small solid particles can lead to a distorted NMR spectrum. The NMR tube must first be cleaned and thoroughly dried. You will soon find out that acetone is not as volatile as you think; it is the most common contaminant in NMR spectra. Wash tubes with water, then rinse with acetone and finally with dichloromethane.

For each ^{1}H spectrum, *ca.* 10 mg of sample is required. Note that it is not advantageous to put in more than this as this will reduce the resolution of the spectrum. The sample is dissolved in ca. 0.7 cm^3 of the appropriate deuterated solvent, usually deuterated chloroform ($CDCl_3$) unless otherwise instructed in the experimental procedure. If there is any undissolved material in the sample, then the solution **MUST** be filtered (through e.g. a cotton-wool plug in a disposable pipette) before it is placed in the NMR tube. The depth of sample is also very important; it has to be between 50 and 60 mm. It is also very important that the outside of the tube is clean, so give it a wipe with some tissue.

Make up your sample as instructed above and write a legible sample code on the side of the NMR tube (e.g. for J. A. Smith the code might be JAS001) and place the tube in the appropriate sample rack for your NMR queue. Add your name and details of the sample to the list. These details will be necessary for subsequent identification of your spectrum.

Remember when analysing the spectrum obtained from your sample to watch for the signal due to the solvent. The signal for residual $CHCl_3$ present in $CDCl_3$ is at 7.27 ppm. Further common contaminants include the solvent used in the reaction and work-up (e.g. hexane), water and vacuum grease. To help you identify these, a table of chemical shifts of residual protons in common deuterated solvents is given in Table 1.2-1.[1)]

Table 1.2-1 Chemical shifts of residual protons in common deuterated solvents.

	Proton	Multiplicity	$CDCl_3$	$(CD_3)_2CO$	C_6D_6	D_2O
Solvent residual peak			7.26	2.05	7.16	4.79
H_2O	OH	s	1.56	2.84	0.4	
Acetone	CH_3	s	2.17	2.09	1.55	2.22
Benzene	CH	s	7.36	7.36	7.15	
Chloroform	CH	s	7.26	8.02	6.15	
Dichloromethane	CH_2	s	5.30	5.63	4.27	
Diethyl ether	CH_3	t	1.21	1.11	1.11	1.17
	CH_2	q	3.48	3.41	3.26	3.56
Ethanol	CH_3	t	1.25	1.12	0.96	1.17
	CH_2	q	3.72	3.57	3.34	3.65
	OH[a)]	s	1.32	3.39		

1) H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* 1997, *62*, 7512–7515.

Table 1.2-1 (continued)

	Proton	Multiplicity	$CDCl_3$	$(CD_3)_2CO$	C_6D_6	D_2O
Ethyl acetate	CH_3CO	s	2.05	1.97	1.65	2.07
	CH_2CH_3	q	4.12	4.05	3.89	4.14
	CH_2CH_3	t	1.26	1.20	0.92	1.24
Grease	CH_3	m	0.86	0.87	0.92	
	CH_2	br s	1.26	1.29	1.36	
n-Hexane	CH_3	t	0.88	0.88	0.89	
	CH_2	m	1.26	1.28	1.24	
Methanol	CH_3	m	3.49	3.31	3.07	3.34
	OH	br s	1.09	3.12		
Silicone grease		s	0.07	0.13	0.29	
Toluene	CH_3	s	2.36	2.32	2.11	
	CH(*o*, *p*)	m	7.17	7.1–7.2	7.02	
	CH(m)	m	7.25	7.1–7.2	7.13	

a) The signals from exchangeable protons are not always identified.

1.2.1.5 Preparation of Samples for ^{13}C NMR Spectroscopy

The same rules apply for preparation of samples for ^{13}C NMR as for ^{1}H NMR analysis, the only difference being the concentration of the sample needed. As the sensitivity of ^{13}C NMR is two orders of magnitude lower than that of ^{1}H NMR, **very concentrated sample** is needed (the recommended amount to obtain a good spectrum is 100 mg). ^{13}C chemical shifts of common solvents as trace impurities are shown in Table 1.2-2.[2)]

Table 1.2-2 ^{13}C chemical shifts of common solvents as trace impurities.

	Carbon	$CDCl_3$		Carbon	$CDCl_3$
Solvent residual peak		77.16	Grease	CH_2	29.8
Acetone	CO	207.1	*n*-Hexane	CH_3	14.1
	CH_3	30.9		$CH_2(2$	22.7
Benzene		128.4		$CH_2(3)$	31.6
Dichloromethane		53.5	Methanol	CH_3	50.4
Diethyl ether	CH_3	15.2	Silicone grease		1.0
	CH_2	65.9	Toluene	CH_3	21.5
Ethanol	CH_3	18.4		C(*i*)	137.9
	CH_2	58.3		CH(*o*)	129.1
Ethyl acetate	CH_3CO	21.0		CH(*m*)	128.3
	CO	171.4		CH(*p*)	125.3
	CH_2	60.5			
	CH_3	14.2			

2) The signals from exchangeable protons are not always identified.

1.2.1.6
Conductivity

In brief, with the exception of H^+ or OH^-, which have hydrogen-bonding chain conduction mechanisms, most singly-charged ions have a molar conductivity of roughly 60 Ω^{-1} cm^2 mol^{-1} and thus a 1:1 electrolyte MX has a conductivity of around 120 Ω^{-1} cm^2 mol^{-1}. Comparisons with molar conductances of known ionic substances allow one to determine the number of ions present in a given salt. Slow-moving large or highly charged ions will give lower values; for complex ions this can reach the point where the determination becomes uncertain. Typically, 10^{-3} mol dm^{-3} solutions are used for measurements.

Typical molar conductances (Ω^{-1} cm^2 mol^{-1}) in water for various ion conductors are as follows:[3)]

	1:1	1:2	1:3	1:4
Λ_m	96–150	225–273	380–435	~540

1.2.1.7
Magnetic Susceptibility

Background

Magnetic susceptibility is a measure of the tendency of molecular magnets to align themselves with an applied field, and from the degree of paramagnetism observed we can assess the number of unpaired electrons in a sample. The effect is temperature dependent, since thermal vibration causes some magnetic randomisation and a number of other magnetic influences cannot be compensated for. Hence the result is approximate although generally unambiguous.

In the traditional Gouy method (after French physicist Louis Gouy), a cylindrical sample is suspended from a traditional balance, weighed, then partially immersed in a strong magnetic field by introducing a powerful magnet around it. The consequent displacement of the sample is registered on the balance: diamagnetic materials are forced away from the field and appear to become lighter; paramagnetic materials are pulled in and appear to become heavier.

In the *Johnson Matthey apparatus* or Evans' balance as it is sometimes called (Fig. 1.2-4), the same principles apply but, instead of the sample, the magnet is attached to one arm of a balance much more sensitive than the analytical balance. Introducing a sample causes a displacement of the magnet, which is restored to its original position by altering the current flowing through electromagnet acting on the opposite arm of the balance. The reading displayed digitally on the front of the instrument is proportional to the apparent change in weight that would have been observed using the Gouy method; that is, net diamagnetic materials repel the magnet, giving a negative reading, and net paramagnetic materials attract it, giving a positive reading.

3) *Source:* S. Girolami, T. B. Rauchfuss, R. J. Angelici, *Synthesis and Techniques in Inorganic Chemistry*, 2nd edn, Saunders, Philadelphia, 1997.

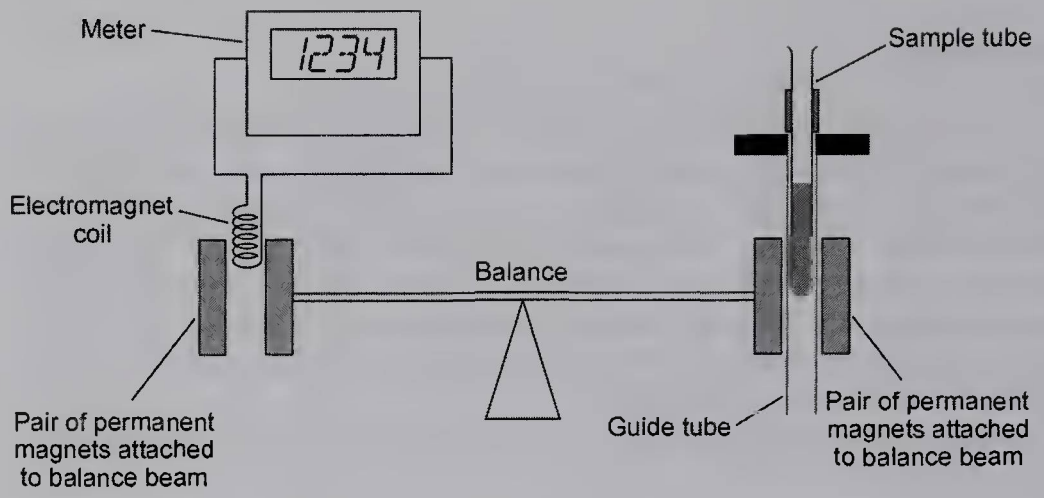

Fig. 1.2-4 Johnson Matthey/Evans' apparatus.

It is important that part of the sample remains outside the magnetic field – there is no net effect when it is fully immersed in the field. Since you cannot alter the position of the magnet in the Johnson Matthey apparatus, you must instead insert a sample of adequate height.

Further details of the Johnson Matthey balance, the method and the underlying theory are provided in manual available with the balance. Please note in particular:

- The balance is very sensitive! Moving the balance even slightly will alter the zero position and sudden movements may cause damage.
- The magnet is very strong! Ferromagnetic materials (including spatulas) should be kept away from the balance and must never be inserted.

Measurements

The method provided below applies for the magnetic susceptibility balance manufactured by Johnson Matthey, Catalytic Systems Division, UK. Although the following notes apply to all similar instruments, particular details may differ and should be checked against the manual supplied with your instrument.

The balances should be level and have been switched on for 10 minutes before any measurements are made.

1. With the sensitivity knob on the Johnson Matthey magnetic balance set at "×1", adjust the "ZERO" knob until the digital display reads "000".
2. Carefully insert a clean sample tube, then note the reading, R_0, which should be negative since the glass is diamagnetic. Keep the tube vertical to avoid damaging the very thin internal guide and draught shield. The rubber ring on the sample tube ensures the same height of sample is immersed every time in the magnetic field – check that the ring is 48.0 mm from the bottom of your sample.
3. Zero the analytical balance, then weigh the empty sample tube to 0.1 mg.

4. The greatest experimental error in this method arises from uneven packing. Grind your sample briefly (mortar and pestle) to obtain a small and regular grain size, but avoid creating a very fine powder, which tends to form clumps.
5. Fill the sample tube a few mm at a time to a depth of at least 1.5 cm and ideally 2.5–3.5 cm, compacting the powder by gently tapping the tube on the bench between additions. Note the room temperature.
6. Zero the magnetic balance, then insert the filled sample tube. Note the reading, R, carefully remove the tube, gently tap it on the bench a few times, then re-insert it. Repeat until consistent results are obtained.
7. Carefully remove the tube without disturbing the sample then measure the length, l, of the sample column to the nearest 0.5 mm.
8. Zero the analytical balance, then weigh the filled sample tube to 0.1 mg. Find, by difference, the mass of the sample, m.
9. Tap out the powder then repeat from step 4 or 5 to calculate an average R.
10. Clean the sample tube by tapping out the powder followed by careful use of water and a length of pipe cleaner. Rinse the tube with distilled water, followed by acetone, then blot dry internally with a clean length of pipe cleaner. Continue from step 4 with your next sample or return the clean tube and collar to the box.

Calculations

First, the *calibration constant*, K, for your instrument has to be determined by measurement of a sample with known magnetic properties. The K for your instrument is given by

$$K = \frac{\chi_g \times m \times 10^9}{l \times (R - R_0)}$$

where

l = length of the sample (cm)
R = the reading when a sample is introduced
R_0 = the reading for the empty sample tube
m = mass of the sample (g)

A standard, such as $HgCo(SCN)_4$ (a deep blue powder)m needs to be provided in order to determine K of your instrument. Compact the standard, then measure its R_0, m, l and R. The literature value of χ_g for $HgCo(SCN)_4$ is

$$\chi_g = \frac{4981 \times 10^{-6}}{283 + T} = 16.44 \times 10^{-6} \text{cgs}$$

at 20 C, where T is temperature in °C.

In the second step, proceed with measurements of your sample with unknown magnetic properties. Record its R_0, R, l and m in order to determine the **gram magnetic susceptibility**, χ_g:

$$\chi_g = \frac{K \times l \times (R - R_0)}{m \times 10^9}$$

The **molar susceptibility** of an unknown sample is obtained by multiplying χ_g by the molecular weight:

$$\chi_M = \chi_g \times M$$

Now correct for the diamagnetism of the sample by using the appropriate values of diamagnetic molar susceptibilities from the literature (a few examples are given in Table 1.2-3).[4)]

Table 1.2-3 Diamagnetic molar susceptibilities ($\chi_D \times 10^{-6}$ cgs units) for selected ions, molecules and atoms.

Co^{3+}	12.56	NH_3	22.62	H_2O	16.34
O (ether)	5.79	O (ketone)	2.17	SO_4^{2-}	50.39
H	3.68	NO_3^-	23.75		

Remember that diamagnetic corrections are **added**. This gives the **corrected molar susceptibility**, χ'_M:

$$\chi'_M = \chi_M + \chi_D$$

For a sample of known χ'_M the **magnetic moment**, μ, is given by the Curie law:

$$\mu = \frac{(3RT\chi'_M)^{1/2}}{N_A}$$

where N_A is Avogadro's number (6.023×10^{23} mol^{-1}). This equation (after substituting for the value of R converted to cgs units) gives μ in cgs units. A more convenient unit for μ is the Bohr magneton, the magnetic moment of a single electron, which has a value of $\mu = eh/4\pi m_e = 9.273 \times 10^{-24}$ A m^2, so that μ/μ_B represents the **magnetic moment in Bohr magnetons** (also known as μ_{eff}). Thus the previous equation eventually gives

$$\mu/\mu_B = 2.828\sqrt{\chi'_M T}$$

where T is in kelvin. This is then related, by the "spin only" approximation, to the **number of unpaired electrons**, n, per formula unit:

$$\mu/\mu_B = \sqrt{n(n+2)}$$

4) For extensive tables of molar susceptibilities of molecules, ions and atoms, see R. C. Weast (Ed.), *Handbook of Chemistry and Physics*, 53rd ed, CRC Press, Cleveland, OH, 1972, p. E-108.

This can be solved as a quadratic equation, where the positive (real) solution is

$$n = \sqrt{(\mu_{\text{eff}}^2 + 1)} - 1$$

The value of n is often non-integral. Nonetheless, the experimentally obtained μ_{eff} value serves as a practical means of determining the number of unpaired electrons in a complex.

1.2.1.8 Cyclic Voltammetry (CV)

The CV technique is useful for surveying the position (volts) of the redox potentials of molecules in solution and also gives a measure of the relative stability of the different oxidation states. The potential of an electrode is swept over as wide a range as possible while the current at the electrode is simultaneously monitored. A positive current flow indicates that the molecule is being oxidised, while a negative current flow indicates reduction.

The theoretical cyclic voltammogram for a single one-electron oxidation process is shown in Figure 1.2-5. The first process seen is an upward peak (e.g. oxidation of Fc to Fc^+) and a reverse peak (e.g. due to reduction of the Fc^+). The upward peak arises because diffusion is slow on the electrochemical time-scale and during the scan the product Fc^+ builds up near the electrode, blocking the diffusion of unoxidised Fc to the electrode, leading to a fall in current. The standard sweep rate is 100 mV s^{-1}, although faster/slower scans can be used when we wish to investigate the kinetic stability of the Fc^+.

Many laboratory classes record the cyclic voltammograms of ferrocene and its derivatives. Detailed instructions on actual measurement are specific to the potentiostat. Usually nowadays the measurement is fully automated and driven by a PC. The software will determine the quantities E_p^a, i_p^a, E_p^c and i_p^c and calculate the redox potential

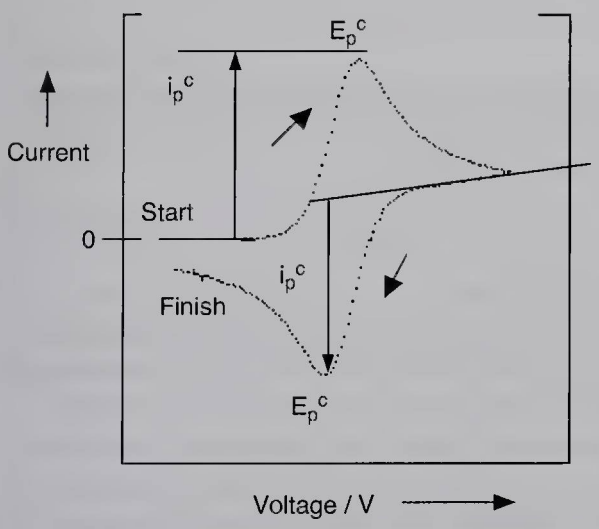

Fig. 1.2-5 Theoretical cyclic voltammogram for a single one-electron oxidation process.

(E) by taking the average of the peak voltages. Calculate the difference in peak positions $E_p^a - E_p^c$, which should be $59/n$ mV, where n is the number of electrons transferred in the redox process. Your measured $E_p^a - E_p^c$ will be somewhat larger than expected for a one-electron process (this is due to resistance effects).

1.2.1.9 Polarimetry

Optical rotation, α, is usually measured using the sodium emission wavelength (589 nm). Solutions of two concentrations (e.g. 0.01 and 0.025 mol dm^{-3} solutions) are measured and the average value of optical purity from the two measurements is taken. Read the instructions provided with your instrument and obtain α values for both solutions.

Calculate the specific rotation of your complex at 589 nm [ϕ] from

$$[\phi]_{589} = \frac{\alpha}{lc}$$

where l = pathlength of sample in decimetres and c = concentration in g cm^{-3}.

Knowing the specific rotation of pure enantiomer $[\phi]_{pure}$ (e.g. +60°), it is possible to estimate the *optical purity* (= enantiomeric excess, *ee*) for your product as an average of the two values obtained from the two solutions of differing concentrations:

$$\text{optical purity (\%)} = 100[\phi]_{obs}/[\phi]_{pure}$$

Knowing optical purity, calculate how much of each isomer (Λ and Δ) is in your product (in %).

1.2.2 Laboratory Reports

All reports should be **concise**, organised and tidy. They may be typed (strongly preferred) or hand-written, with (preferred) or without the use of chemical structure drawing software, such as ChemBioDraw or IsisDraw.

The following information should be included in a typical report:

1. Name of the experiment (as heading) and date.
2. Short abstract of the experiment. The abstract should include a brief description of syntheses performed and summarise characterisation methods and the most important findings (possibly including brief answers to questions posed in the manual).
3. A fully balanced equation for each reaction should be included for every experiment.
4. Detailed experimental procedure: write what you actually did and do not simply copy the procedure out of the manual. Details of the equipment used and of stan-

dard procedures, such as sublimation, are not required (see below); the degree of detail provided should be such that an experienced experimentalist will be able to reproduce the experiment based on your description. Note that for quantities of reagents and starting materials employed in a procedure *both* the mass (or volume) *and* the number of moles must be quoted, e.g. (0.25 g, 10 mmol).

5. Yield of product, i.e. actual weight and percentage yield. Calculation of the yield should be based on limiting component, which should be indicated.
6. Physical properties of product:
   - colour, state;
   - melting point (m.p.); or
   - boiling point (b.p.)/pressure.
7. Spectral and chromatographic data (e.g. IR, NMR and GC) with assignments and interpretation. The NMR and IR data should be given in the format which is discussed in more detail later. Spectra should be clearly labelled and attached to the report.
8. A short discussion of the spectral data (if there are some interesting trends, any unusual patterns in spectra, how the signals were assigned, etc.) and answers to any questions posed in the manual.

Generally, a good report will not be longer than three pages (12 point font size, 2.5 cm margins each side). The number of additional pages with spectra and other attachments is not limited.

Samples of each product must also be submitted with every report. They should be packed in sample tubes and clearly labelled with the following information:

- name of the student,
- experiment number,
- name or structure of the compound.

A more detailed example of a report is given below (covering points 1, 2 and 4–7) (remember to also include points 3 and 8). The idea of using this format is to give you practice in the way in which chemists write up their work for publication in the chemical literature.

Note that reports should be *CONCISE* and *NOT* of excessive length.

1.2.2.1 Example Report

Preparation of Ferrocene

Abstract

Ferrocene was prepared by the reaction of iron(II) chloride with cyclopentadiene in the presence of base (KOH). Crude ferrocene was purified by sublimation and was characterised by m.p., IR, UV-Vis, ^{1}H and ^{13}C NMR spectroscopy. Ferrocene was reacted with acetic anhydride in the presence of phosphoric acid to afford acetylferro-

cene. Acetylferrocene was purified by column chromatography on alumina and by recrystallisation from cyclohexane; it was characterised by m.p., IR, UV-Vis, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy and by cyclic voltammetry. The presence of the electron-withdrawing/donating acetyl group on one of the cyclopentadienyl rings of ferrocene resulted in the shift of E by xx V. In contrast to ferrocene, acetylferrocene was not oxidised to the corresponding ferricenium (Fe^{III} ion) on addition of concentrated sulfuric acid as determined by UV-Vis spectroscopy.

Experimental Procedure

Ferrocene

A three-necked flask equipped with magnetic stirrer, reflux condenser, dropping funnel and nitrogen inlet was charged with 1,2-dimethoxyethane (30 cm^3) and flake potassium hydroxide (15 g, 0.27 mol). Cyclopentadiene (2.75 cm^3, 34 mmol), prepared by cracking of its dimer, was added with vigorous stirring. Stirring was maintained as a solution of finely powdered iron(II) chloride tetrahydrate (3.25 g, 16.3 mmol) in degassed dimethyl sulfoxide (25 cm^3) was added dropwise over 30 min. The exothermic reaction resulted in gentle boiling. The reaction mixture was stirred for an additional 30 minutes, after which time it was neutralised with HCl (6 M, 45 cm^3) and ice (50 g). Ferrocene, as an orange precipitate, was collected by filtration, washed with water and dried in air (5.3 g, 25%). Purification by sublimation yielded orange crystalline material, which was used for spectroscopic characterisation, m.p. 174–176 °C.

Spectral Data

Ferrocene

IR:	ν_{max} (Nujol mull)/cm^{-1} 3050m (υCH), 1118s, 1002s, 835vs.
^{1}H NMR:	δ_H (300.0 MHz, $CDCl_3$, Me_4Si) 4.18 (10H, s, CH).
^{13}C NMR:	δ_C (67.8 MHz, $CDCl_3$, Me_4Si) 123.3 (s, CH).
MS (exact mass):	m/z (EI) 186.0134 (M^+); $C_{10}H_{10}Fe$ requires 186.0132.

1.2.2.2

Writing Up Spectral Data

A more detailed explanation of the format to be used for reporting the spectroscopic data is given in this section. The spectroscopic data can be listed in several ways, but here the standard format is that required for publication in *Dalton Transactions*. An important part of this laboratory class is to learn how to do this in the correct way. If unsure, consult Guidelines for Layout of Articles for Submission at RSC webpage (www.rsc.org).

Below is an example of data in the correct format.

Infrared Data

ν_{max} (Nujol mull)/cm^{-1} 3350 m (O–H stretch), 1670 s (C=O stretch), 1000 s, 850 m (aromatic C–H deformation).

Notes: List the peaks in decreasing order. List only major or significant peaks (typically this will be 3–10 peaks). You must record how the spectrum was run, most commonly as a Nujol mull or KBr disc (for solids) or a thin film (for oils and liquids). One of the main points is not to go overboard with assignments. The most important functional groups observed by IR are OH and NH, carbonyl groups (where we can often tell the type of carbonyl compound from the position), C–O bond and whether the compound is aromatic from strong peaks at the lower end of the spectrum (850–700 cm^{-1}) due to aromatic C–H deformations. C–H stretches for aromatics are at >3000 cm^{-1}, whereas for aliphatics they appear at <3000 cm^{-1}. The type of signal (s, m, w, vs, br) should be indicated by appended letters (e.g. 1670 s). Do NOT give IR data with excessive accuracy. Peaks should only be reported to the nearest whole number.

Raman Data

The same format as for IR can be used to list Raman data.

^{1}H NMR Data

δ_H (300.1 MHz, $CDCl_3$, Me_4Si) 7.50–7.30 (2 H, m, Ar-H), 7.23–7.12 (2 H, m, Ar-H), 7.16 (2 H, d, J 5.0 Hz, H-5), 6.58 (1 H, s, =CH), 4.30–4.10 (2 H, m, CHS), 4.05–3.97 (2 H, m, CHS), 3.84 (2 H, s), 3.82 (12 H, s), 3.43 (1 H, q, ^3J 2.5 Hz, H-3), 3.38 (1 H, br s, N–H), 2.68 (1 H, d of t, ^3J 10.2, ^4J 2.6 Hz, H-7) and 1.86–1.72 (1 H, m, H-6).

Notes: We start by giving the frequency at which the spectrum was run, the solvent employed and reference compound. Then list the chemical shifts of the peaks in numerical order starting from one end of the spectrum. For ^{1}H NMR, an accuracy of two decimal places is normal for δ and one decimal place for J. In parentheses after each, first put the number of protons (from the integral trace) then the form of the peak (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), then if possible the coupling constant J in Hz and finally the assignment. A ppm range must be given for a complex multiplet arising from more than one proton, whereas only the centre value is given for a simple signal.

^{13}C{^{1}H} NMR Data

δ_C (75.5 MHz, $CDCl_3$, Me_4Si) 164.4 (s, C=O), 144.9 (s, 4ry, C-1), 127.3 (s, CH, C-3,5), 127.2 (s, CH, C-4), 124.2 (d, $^3J_{CP}$ 2.5 Hz, CH, C-2,6), 79.1 (d, $^1J_{CP}$ 60.5 Hz, 4ry, C-7), 65.2 (s, CH, C-9), 54.8 (s, CH_2, C-10) and 52.4 (s, CH_3, 9-OMe).

Notes: As for ^{1}H NMR spectra, we start by giving the frequency at which the spectrum was run, the solvent employed and reference compound. Then list the chemical shifts of the peaks in numerical order starting from one end of the spectrum. For ^{13}C NMR, an accuracy of one decimal place is normal for both δ and J. In parentheses after each put the assignment. The form of the peaks (s, d, t, etc.) can be omitted if all peaks appear as singlets (e.g. no heteronuclear coupling such as from P or B is present). The number of carbon atoms cannot be determined from integral trace in $^{13}C\{^{1}H\}$ NMR spectra and therefore is usually not listed.

$^{31}P\{^{1}H\}$ and ^{31}P NMR Data

δ_P (121.5 MHz, $CDCl_3$, 85% H_3PO_4) 25.3 (s). In the non-decoupled ^{31}P NMR spectrum the signal was split into a doublet, $^{1}J_{PH}$ 121.0 Hz.

Notes: As for ^{1}H NMR spectra, we start by giving the frequency at which the spectrum was run, the solvent employed and reference compound.[5] Then list the chemical shifts of the peaks in numerical order starting from one end of the spectrum. For ^{31}P NMR, an accuracy of one decimal place is normal for both δ and J. The non-decoupled experiment provides information on PH coupling constants; the number of bonds between the two coupled atoms should be indicated if known (e.g. $^{1}J_{PH}$, $^{2}J_{PH}$).

2D NMR Spectra

The 2D correlations are supplied to help you with the assignment of the peaks observed in 1D spectra; there is no need to list peaks found in these in your report.

Mass Spectrum (Normal Resolution)

m/z (EI) 670 (M^+, 47%), 655 (M^+ – Me, 4), 488 (23), 368 (21), 306 (10), 279 (12), 248 (80), 222 (100), 220 (88) and 149 (62).

Notes: Remember to give the ionisation technique used (EI, ES) and mode in case of ES (positive or negative). List the peaks in decreasing order. For the molecular ion peak, put in parentheses M^+ and the relative intensity (100% is defined as the largest or base peak – in our example *m/z* 222). List the other main peaks up to a maximum of 8–10 with their intensities and, where known, assignments. Remember in ES, not only ($M + H^+$) but also other clusters such as ($M + Na^+$) and/or ($M + K^+$) are often observed.

5) In contrast to Me_4Si, often used as an internal standard in ^{1}H and ^{13}C NMR, 85% H_3PO_4 is rarely used as an internal standard. Instead, a sample with reference compound is measured in a separate experiment (hence external standard).

Mass Spectrum (Exact Mass Measurement)

Exact mass measurement can be reported as follows:

m/z (EI) 186.0134 (M^+), $C_{10}H_{10}Fe$ requires 186.0132

For your own PC, a very useful piece of freeware, Molecular Weight Calculator, is available from http://ncrr.pnl.gov/software/. It is very convenient for calculations of molecular weights, including isotopic weights (for exact mass measurement). Molecular weight, exact mass and isotopic patterns can also be calculated conveniently using the 'Analysis' tools in ChemBioDraw software.

2
Introductory Experiments

Inorganic Experiments, Third Edition. Edited by J. Derek Woollins

ISBN: 978-3-527-32472-9

2.1
Preparation and Investigation of Some Coordination Compounds

Manfred Bochmann

Special Safety Precautions

1. Ammonia solutions are irritating to skin and eyes, and the vapour must not be inhaled. Wear rubber gloves and safety spectacles when handling ammonia solutions and work in a fume cupboard. If ammonia is splashed on your skin, wash it off with plenty of water. Provided you do this immediately there is no cause for alarm.
2. Oxalic acid and oxalates are toxic and must not be ingested.
3. Hydrogen peroxide can cause burns, and skin contact must be avoided. Wear rubber gloves.

Note on the concentration of hydrogen peroxide. Bottles of hydrogen peroxide are traditionally labelled "20 vol", "100 vol", etc., meaning that one litre of the solution, when decomposed according to the equation $2H_2O_2 = 2H_2O + O_2$, yields 20 (etc.) litres of oxygen gas, at standard temperature and pressure. "20 volume" hydrogen peroxide contains *ca.* 6% H_2O_2 by weight.

If you are supplied with hydrogen peroxide labelled in this way, be sure to select the correct bottle. In your notebook, take care to record the concentration in the form specified on the label. In your report, however, be sure to mention the molar concentration as well as the "vols".

2.1.1
Experimental

2.1.1.1
Instructions for Course Organisers

1. Do **not** use "100 vol" hydrogen peroxide, 10 or 20 vol is sufficient.
2. Laboratory Technical staff need instructions to make saturated oxalic acid.
3. Supply references to the standard inorganic text book used in your course.

Inorganic Experiments, Third Edition. Edited by J. Derek Woollins

ISBN: 978-3-527-32472-9

a) Hexaamminenickel(II) Tetrafluoroborate $[Ni(NH_3)_6](BF_4)_2$

Dissolve about 3 g of hydrated nickel chloride, $NiCl_2 \cdot 6H_2O$, in 5 ml of warm water, and filter if necessary to remove any insoluble matter. Then slowly add 5 to 6 ml of concentrated aqueous ammonia (specific gravity 0.88 g cm^{-3}), stirring until all the initial green precipitate of nickel hydroxide has dissolved. The clear deep blue liquid now contains a copious crystalline deposit of the violet nickel hexaammine chloride. If this does not appear, leave it to stand for 5 minutes in a beaker of ice. If the solution is not clear blue add another 1 ml of 0.88 ammonia.

Redissolve the crystals by careful addition of a minimum (less than 8 ml) of cold water, added in 0.5 ml portions with continuous stirring. Take care not to hydrolyse the complex with excess water. Finally, filter off any small insoluble residue.

Dissolve approximately 2.5 g of ammonium tetrafluoroborate in dilute aqueous ammonia (ca. 2 mol dm^{-3}) and add this to the solution of the nickel ammine chloride. The sparingly soluble hexaaminenickel tetrafluoroborate is immediately formed as a crystalline precipitate. Filter by suction and wash the precipitate with aqueous ammonia until the filtrate (solution) is colourless. Finally, wash with acetone. Allow the mauve crystals to dry in a desiccator. Record the yield in your notebook.

b) Potassium Tris(oxalato)ferrate(III)

Dissolve 15 g of ammonium ferrous sulfate $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ in 50 ml of hot water acidified with dilute sulfuric acid. Add a hot solution of 7.5 g of oxalic acid in 50 ml of water. Cautiously heat the mixture to boiling and then allow the yellow precipitate of iron(II) oxalate, $FeC_2O_4 \cdot 2H_2O$, to settle. Cool the solution. Wash the precipitate with 30 ml water by decantation. Repeat the washing two to three times.

Now add a warm solution of 10 g of potassium oxalate monohydrate $K_2C_2O_4 \cdot H_2O$ in 30 ml of water. Add slowly, with a teat pipette, 25 ml of '20 volume' hydrogen peroxide (see *Special Safety Precautions*), stirring the solution continuously and keeping the temperature below 40 °C. Any effervescence indicates that the solution is too hot. Then heat the mixture, which now contains some ferric hydroxide, to nearly boiling. The precipitate is now brown. Add a saturated solution of oxalic acid until the precipitate just redissolves. Filter the solution whilst still hot and finally add 30 ml of methylated spirits. Leave to crystallise in the dark.

When green crystals of the complex have appeared (probably the next day) filter the solution and wash the crystals in acetone. Allow them to dry at room temperature in the dark. Store the product in a glass specimen tube, wrapped in aluminium foil.

N.B.: *Be sure to attach the label to the glass, and not to the foil!*

2.1.2 Chemical Properties

The object of the following tests is to give you experience in observing and identifying the products from reactions of transition metal complexes. Make notes in your laboratory notebook of your observations, as you make them. In your report, summarise your observations and try to write equations and explanations for the reactions.

Thermal decomposition of hexaamminenickel(II) tetrafluoroborate. Heat 0.3 g of your product carefully in a large dry test tube and record your observations (colour changes, gas evolution, etc.). Test both the residues and the sublimates for both boron and fluorine. Suitable tests can be found in Vogel's *Qualitative Analysis.* (6th ed., revised by G. Svehla. Longman Scientific). Note that any test which might involve the evolution of HF must be carried out on a small scale and in a fume cupboard. Account for your results. Write an equation that satisfactorily describes the decomposition.

The following test is designed to compare the lability of the ammonia in the hexaamminenickel(II) and hexaamminecobalt(III) and cobalt(II) complexes. Obtain a sample of $[CoNH_3)_6]Cl_3$ from the chemical shelf. Add some sodium hydroxide solution to a little of the nickel(II) and cobalt(III) complexes in test tubes and cover each with a piece of moistened indicator paper. Observe what happens over several minutes and then reduce the cobalt(III) complex to cobalt(II) by adding a little aluminium powder to the alkaline solution. In which complex is the ammonia least labile?

Investigate the equilibria which are present in a solution of potassium ferrioxalate by testing separate portions with potassium thiocyanate for ferric ion and barium chloride for oxalate. What happens when an excess of a sodium oxalate or an ammonium fluoride solution is added to the ferrioxalate solution containing thiocyanate? Note your observations carefully and write equations to describe the equilibria you have found. Is ferrioxalate a labile complex?

2.2
Gravimetric Analysis of Hexaamminenickel(II) Tetrafluoroborate $[Ni(NH_3)_6](BF_4)_2$

Manfred Bochmann

The quantitative determination of a material by precipitation followed by isolation and weighing a precipitate of known composition is called gravimetric analysis.

The success of the method depends upon several factors, especially the completeness of precipitation of the elements being analysed and the selectivity of the precipitation process. In addition, the precipitate should be readily collected and easily filtered. The conditions required for producing a pure precipitate of large granular particles which are easy to filter have been well investigated (see Van Weimann, *Chem. Rev.* **1925**, *2*, 207 and A. I. Vogel, *Quantitative Inorganic Analysis*, 3rd ed., Longman, **1966**).

It is essential that the precipitate obtained be pure, otherwise an accurate determination is not possible. If the precipitate is composed of very small crystals, the surface area of the precipitate may introduce appreciable errors. Furthermore, occlusion of 'foreign' ions during the process of crystal growth may occur, particularly if the precipitate is formed rapidly. The contamination of the precipitate by substances normally soluble in the mother liquor is termed *co-precipitation*. Because the size of the crystallites is, in general, larger the smaller the rate of precipitation, it is apparent that the effects of co-precipitation can be reduced by a slow rate of precipitation. As an added bonus, precipitates composed of larger crystallites are usually much more easily filtered than precipitates composed of fine particles. It is for these reasons that it is common practice to add a dilute solution of precipitating agent slowly, with stirring — the rate of precipitation depending on the amount by which the material to be precipitated exceeds the saturation value. The process of *digestion* (heating the precipitate and mother liquor on a steam bath for several hours) often decreases the effect of co-precipitation and gives more readily filterable precipitates, though it has little effect upon amorphous or gelatinous precipitates. An elegant method of maintaining only a small degree of supersaturation (giving large crystallite size) is *precipitation from homogeneous solution*, in which the precipitant is not added as such, but is slowly generated by a homogeneous chemical reaction within the solution. It is this technique which is to be used in the following experiments. The slow hydrolysis of urea that occurs in boiling aqueous solution will be used to slowly raise the pH of the solution by the generation of ammonia (Eq. 1).

$$CO(NH_2)_2 + H_2O \rightarrow CO_2 + 2\,NH_3 \qquad (1)$$

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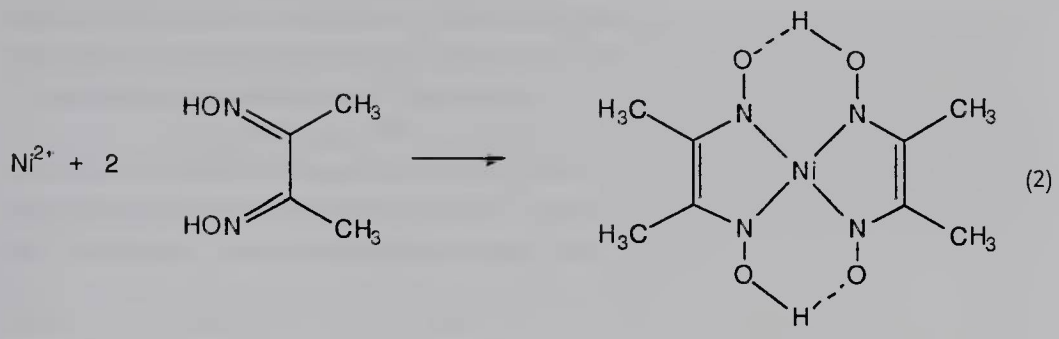


(2)

Bis(dimethylglyoximato)nickel

Nickel(II) will be precipitated quantitatively by the organic reagent dimethylglyoxime. The nickel ion is chelated by 2 molecules of demethylglyoxime, the overall reaction being given in Eq. (2) Protons are released and the stability of the complex is such that at low pH, the equilibrium is displaced to the left while at pH above 5, it is displaced to the right. If the two reactants are mixed at pH 3, no precipitation takes place. Addition of urea and slow heating will raise the pH of the solution slowly, by virtue of Eq. (1), and the nickel dimethylglyoxime complex will slowly form. A beautifully crystalline precipitate can be obtained in this way.

2.2.1 Experimental

2.2.1.1 Weighing Bottle

Prepare the weighing bottle by removing all dirt and grease, then wash it with tap water and distilled water, dry it in the oven (130 °C) and cool it for 10 minutes. Chemicals should be removed from a weighing bottle by careful tipping, the use of a spatula is undesirable as this is another source of error and possible contamination. Where several weighings are to be carried out, weighing by difference means that for n samples, only $n + 1$ weighings are required. It is useful to know the approximate weight of the empty bottle. *Never stopper a hot weighting bottle* since after cooling, it will be found to be difficult to open without causing breakage.

2.2.1.2 Gravimetric Analysis

Use a sample of $[Ni(NH_3)_6](BF_4)_2$ prepared in Experiment 2.1. Be sure to write down in your notebook what you do, and all your weighings, at the time of the experiments.

Wash your weighing bottle with distilled water and dry in the oven for 10 minutes. Weigh accurately (to 4 decimal places) *two* samples of the nickel ammine salt (about

0.08 g) and dissolve each in 30 ml of distilled water. Adjust the pH to 2 or 3 by dropwise addition of 1 to 15 drops of conc. (12 M) HCl. Check the pH between drops with pH paper. Prepare 100 ml of a 1% solution of dimethylglyoxime solution in 1-propanol. Take 10 ml of this solution and heat it to 80 °C on a hotplate.

Add 4 g of urea to the Ni sample and place the solution on a hotplate at 80 to 85 °C. Check that the pH remains below 3. Slowly add the dimethylglyoxime solution to the nickel solution making sure that the pH remains below 3. If it rises, add 12 M HCl, dropwise. Cover the beaker with a watch-glass and heat for one hour at 80 to 85 °C. A red precipitate will form. Whilst waiting for this precipitation to occur, prepare the sinters for weighing (see below). After this period, check the pH to see whether it is above 7. If not, add a drop of ammonium hydroxide and check again. Having obtained a precipitate, remove the beaker from the hotplate and cool to room temperature by standing it in cold water. If a white precipitate appears here, it will be dimethylglyoxime. Dissolve it by adding 4 ml of 1-propanol and heating to 60 °C.

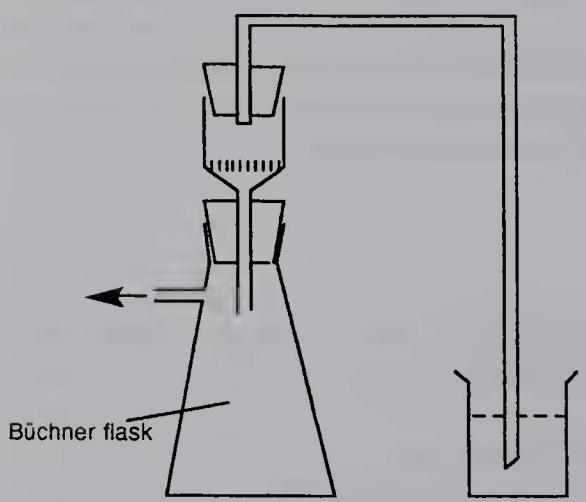
2.2.1.3

The Sintered Glass Crucible

While the above reaction is in progress, start preparing the crucible as follows. Insert the sinter into the adaptor supplied, push the adapter through a rubber bung, and insert the rubber bung into the top of a 400 ml Büchner flask.

With the filter pump, suck a little concentrated nitric acid through the sinter. Turn off the pump and allow the acid to sit in the sinter. Suck plenty of distilled water through the system, followed by a little concentrated aqueous ammonia. (NB: Remove nitric acid from the Büchner flask first). A glass siphon with a small rubber bung should than be fitted into the top of the filter crucibles, as indicated in the diagram. Wash again with distilled water.

Remove the sinter with a pair of tongs and heat in an oven at 130 °C to constant weight. (Place the sinter in a large boiling tube, which has been labelled with your name, and place the tube in one of the test tube racks in the oven set at 130 °C). The



hot crucible must be allowed to cool for 10 minutes before weighing is begun. Two consecutive weighings must agree within 0.2 mg.

Filter the solution on the prepared crucible using the siphon. Wash all the precipitate over with distilled water. If necessary, use a 'policeman' to dislodge particles adhering to the beaker. Remove the crucible with tongs, place in a boiling tube which carries your name on the test tube rack and dry for 1 hour at 130 °C. Allow to cool for 10 minutes and weigh. Repeat weighings until constant.

2.2.2 Calculation

Collect your results into a table as shown in Table 2.2-1. Calculate the percentage of nickel in nickel dimethylglyoxime, assuming the formula $Ni(C_4H_7O_2N_2)_2$, and thence calculate the percentage of nickel in your complex, following the procedure indicated in Table 2.2-2.

Table 2.2-1 Gravimetric determination.

	First determination	Second determination
Weight of clean dry weighing bottle		
Weight of bottle + complex		
Weight of complex		
Weight of sinter		
(i)		
(ii)		
(iii)		
(iv)		
Final weight		
Weight of sinter complex		
(i)		
(ii)		
(iii)		
(iv)		
Final weight		
Weight of complex		

Table 2.2-2 Calculations.

	First sample	Second sample
Weight of $Ni(dmgH)_2$ obtained		
Weight of Ni in the $Ni(dmgH)_2$		
Weight of ammine sample used		
Percentage of Ni in ammine sample		

Summarise your experimental procedure and make clear any difficulties. Set out your results and calculations concisely, *in tabular form.*

Estimate sources of error and give your final recommended value of the percentage of Ni in the ammine salt. Compare this with the theoretical percentage based on the formula given above.

2.3
Analysis of an Iron(III) Oxalate Complex

Manfred Bochmann

Iron(III) is nearly always determined by reduction to the divalent state followed by titration with permanganate or dichromate. Oxalate, however, would interfere and must be determined first. After titration of the oxalate with permanganate, two methods are available for the determination of the iron. The solution may be reduced with zinc amalgam in the presence of sulfuric acid, and the iron(II) titrated with permanganate; or the reduction may be effected by tin(II) chloride ('stannous chloride') and hydrochloric acid, and the iron(ii) determined with dichromate. (Reduction of Fe^{III} by Sn^{II} is rapid only in hot solution in the presence of hydrochloric acid). Permanganate, a more powerful oxidising agent than dichromate, cannot be used, even in the cold, in such solutions owing to oxidation of the chloride to chlorine (a process which is catalysed by iron compounds). The stannous chloride method will be employed here.

Special Safety Precautions

1. Wear eye protection at all times. Concentrated hydrochloric acid is highly corrosive and causes severe burns to skin and eyes. Wear rubber gloves when handling it and work in a fume cupboard.
2. Potassium permanganate soluton is a powerful oxidant and the dilute solution is a disinfectant. Avoid skin contact, but if you do spill it on yourself, simply wash with cold water. Any remaining brown stain will soon disappear.
3. Mercury(II) chloride is highly toxic, as are mercury compounds in general. Mercury waste must be collected in specially labelled bottles as hazardous heavy metal residues.
4. Oxalic acid and oxalates are toxic and must not be ingested.

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2.3.1 Experimental

2.3.1.1 Notes for Course Organisers

The potentiometric titration apparatus consists of a standard calomel electrode (commercial) and a bright platinum electrode made from a small (1 cm^2) piece of Pt foil joined to a short length of Pt wire which, in turn, is fused into a glass tube. The potentiometer is a digital voltmeter capable of reading to 20.1 mV. The "equipment" for photolysis is an ordinary 'Anglepoise' lamp!

2.3.1.2 Determination of Oxalate

The complex was prepared in Experiment 2.1. Weigh accurately about 0.35 g of the complex and dissolve it in dilute sulfuric acid. Heat the solution to about 60 °C and titrate when hot with the approximately 0.02 M solution of permanganate provided. Preserve the resulting liquid for the determination of iron.

The permanganate solution should be standardized against sodium oxalate in the following manner. Weigh accurately two portions of about 0.2 g of 'AnalaR' sodium oxalate into conical flasks. Dissolve each in water, acidify the solutions with suphuric acid and titrate with permanganate as above, at 60 °C.

Calculation

The half-reactions are

$$M^{VII} + 5\,e^- = Mn^{II}$$
$$2\,CO_2 + 2\,e^- = [C_2O_4]^{2-}$$

Hence the overall reaction may be written

$$Mn^{VII} + 2.5\,[C_2O_4]^{2-} = Mn^{II} + 5\,CO_2$$

Set out your calculations in tabular form as indicated below.

Standardisation			
Run	1	2	
Weight of sodium oxalate taken			g
Amount of sodium oxalate taken			mol
Amount of $[MnO_4]^-$ required			mol
Volume of $[MnO_4]^-$ solution used			ml
Concentration of $[MnO_4]^-$			mol dm^{-3}

Determination			
Run	1	2	
Volume of $[MnO_4]^-$ solution used			ml
Amount of $[MnO_4]^-$ consumed			mol
Amount of $[C_2O_4]^{2-}$ in sample			mol
Weight of $[C_2O_4]^{2-}$ in sample			g
Weight of sample			g
% of $[C_2O_4]^{2-}$			%

2.3.1.3

Determination of Iron by Potentiometric Titration

To the solution obtained above, add 15 ml of concentrated hydrochloric acid. Heat the solution to the boiling point and add some stannous chloride solution *dropwise* until the yellow colour of the iron(III) complex is discharged; then add 2 to 3 drops of the reductant in excess. Cool the solution to room temperature and add quickly, in one portion, 10 ml of mercuric chloride solution. (The resulting precipitate of mercury(I) chloride should be pure white in colour). After use, all solutions containing Hg should be returned to the mercury waste bottle.

The potentiometric titration apparatus should already be set up in the laboratory. Wash the iron solution into a 400 ml beaker, put in a magnetic stirrer bar and place the beaker on the magnetic stirrer. Lower the standard calomel electrode and platinum disc electrode into the solution. (NB: Rinse the electrodes with distilled water after removing them form their storage solutions). Record the potential using the digital voltmeter. Now add 10 ml of 40% phosphoric acid while stirring and record the potential again. In your report, comment on any difference between the two potentials you have recorded.

Add 10 drops of sodium diphenylamine sulfonate indicator and titrate with the standard dichromate solution provided. Record both the potential *and* the colour of the solution in a table after the addition of each aliquot (0.5 to 1 ml) of dichromate. Plot a graph of potential against volume of titrant, *while the experiment is in progress.* Use the plot to decide the size of each successive aliquot to be added. As you approach the endpoint, you will get an early warning as the graph will begin to curve upwards. Take particular care in the region of the endpoint, where a large swing in potential will occur. Continue taking readings until the potential has levelled off appreciably beyond the equivalence point. Determine the equivalence point from the graph, and also from the colour change of the indicator.

NB: *It is essential to plot the graph, point by point, at the time you take the readings. Do not just list the numbers and plot them all up afterwards. If you do, you will almost certainly miss the endpoint.*

Calculation

The half reactions are

$$Cr^{VI} + 3e^- = Cr^{III}$$
$$Fe^{III} + e^- = Fe^{II}$$

Hence the overall reaction may be written

$$Cr^{VI} + 3Fe^{II} = Cr^{III} + 3Fe^{III}$$

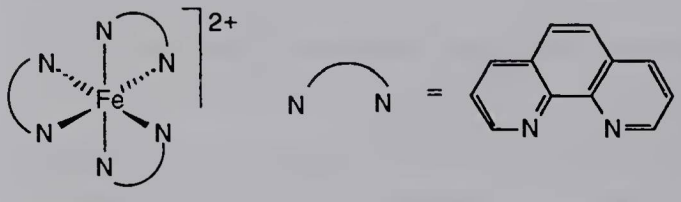
Set your calculations in tabular form as indicated below. Do not forget that one mole of dichromate contains two moles of Cr^{VI}!

	Using end point from graph	Using end point from colour change	
Volume of Cr^{VI} solution required			ml
Amount of Cr^{VI} used			mol
Amount of Fe reacted			mol
Weight of Fe			g
Weight of sample used in titration			g
Percentage of Fe in sample			%
Mean and error			

2.3.1.4

Determination of Iron by Colorimetry

Colorimetry may be used to directly estimate the amount of ferric ion in the complex. The salt is first photoreduced to form ferrous ions; then a reagent (1,10-phenanthroline, another chelating ligand) is added which will bind to the metal, forming an intense red colour. The intensity is compared with those of solutions of known concentrations of iron.



iron(II) tris(phenanthroline) complex

Accurately weigh a portion of about 0.120 g of potassium ferrioxalate. Dissolve it in distilled water and make up to 250 ml. Label this solution 'A'. Take 2 ml of solution A and add 5 ml of 0.5% phenanthroline solution, plus 5 ml of pH 4 buffer.

Make this up to 20 ml with distilled water and label this solution 'B'. Mix solution B well and transfer a portion to the colorimetry tube provided. Photoreduce the iron(III) by exposing to normal light for at least 1 hour. The equipment for this is set up in the laboratory. Prepare the five ferrous standards as follows. Take 2 ml of 0.0005 M $FeSO_4$, add 5 ml of the phenanthroline solution and 5 ml of the buffer solution. Make up to 20 ml with distilled water. Repeat this using 2, 3, 4, 5 and 6 ml of 0.0005 M $FeSO_4$. Label these solutions 'C2', 'C3', 'C4', 'C5', and 'C6' respectively.

Compare the colour intensities of all the solutions using the colorimeter. For each solution, first set the absorbance reading to zero with the tube out of the light beam, then read the value with the tube in the light beam. Move the tube out of the beam and reset the absorbance to zero if necessary. In this way, measure three readings of absorbance for each sample. Tabulate the results in your notebook as you go along and calculate the average absorbance of each solution. Plot a graph of absorbance, *A*, against iron concentration, [Fe], for the five solutions C2 to C6. *Be sure to plot this graph while the experiment is in progress.* It is expected to be a straight line, or at any rate a smooth curve. If some points deviate significantly, you may consider it advisable to either repeat the measurement or make up fresh solutions.

Calculation

From your graph, read off the concentration of solution B. Hence, calculate the concentration of solution A, the amount of iron in solution A, the weight of iron and the percentage of iron in the complex.

Summarise your procedures and indicate any difficulties, set out your results neatly in tables and discuss the sources of error. Compare your final values for percentage of Fe with each other. Calculate the mole ratio of oxalate to iron in the complex. Calculate the percentage by weight of potassium in the complex by a) assuming the mole ratio K/Fe = 3 and b) assuming $K/C_2O_4 = 1$. Do the totals of Fe, C_2O_4 and K add up to 100%?

2.4
Characterisation of a Copper Oxalate Complex $K_aCu_b(C_2O_4)_c \cdot dH_2O$

Andrew W. G. Platt

The copper(II) ion is mildly oxidising and can be used as the starting material for the synthesis of complexes of copper(I) as well as copper(II). Since the chemistry of the copper ion is modified by the presence of the surrounding ligands, in this experiment, you will prepare and characterise the complex and investigate the effect of the oxalate ligands on the chemistry of the copper ion.

2.4.1
Experimental

Dissolve 6 g of copper(II) sulfate pentahydrate in 15 cm^3 of hot water and add to this a solution of 17.6 g of potassium oxalate hydrate in 100 cm^3 hot water. Allow to cool to room temperature and finally to about 10 °C in ice. Filter the product by suction and dry thoroughly in air. Record the weight obtained.

2.4.1.1
Determination of the Oxalate Content

Weigh accurately about 0.25 g of your product into a conical flask and add 50 cm^3 of dilute sulfuric acid. Heat to boiling and tritrate with 0.02 mol dm^{-3} potassium permanganate solution. Note that during the initial stages of the titration the solution is cloudy due to undissolved complex. This clears during the titration. Ensure that the solution is still hot as the endpoint is approached. Heat to boiling if the reaction appears to be slow. Take care not to overshoot the endpoint as the presence of a large excess of permanganate makes the copper determination difficult.

2.4.1.2
Determination of the Copper Content

Ensure that the solution obtained above contains no excess permanganate by boiling until the purple colour is discharged. To the cooled solution, add 2 g of potassium iodide and titrate the liberated iodine with 0.05 mol dm^{-3} sodium thiosulfate. When

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the colour of the resulting suspension is pale yellow, add a few drops of starch and continue titrating until the blue colour begins to fade. Add 0.5 g of potassium thiocyanate and swirl the contents. The blue colour should intensify as iodine, adhering to the solid CuI, is liberated. Continue the titration until a white suspension is obtained. Note that the addition of the potassium thiocyanate should be carried out very near to the endpoint.

Repeat both determinations until consistent titres per gram are obtained and hence calculate the copper to oxalate ratio in the complex. From these results deduce the likely values of *a*, *b*, *c* and *d*. You will have to deduce the oxidation state of the copper to do this. You have seen several indications of this already, but the qualitative tests below, and a determination of whether the complex is paramagnetic or diamagnetic will help to confirm this.

Use the equations below to help in the calculations.

$$2\,Cu^{2+} + 2\,I^- + 2\,e^- \rightarrow 2\,CuI$$
$$2\,[S_2O_3]^{2-} + 2\,e^- \rightarrow [S_4O_6]^{2-}$$
$$2\,CO_2 + 2\,e^- \rightarrow [C_2O_4]^{2-}$$
$$I_2 + 2\,e^- \rightarrow 2\,I^-$$
$$[MnO_4]^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$$

2.4.1.3
Qualitative Work

Prepare a solution of the product in distilled water and add a few drops of potassium iodide solution. Test for the presence of iodine by adding a little chloroform and shaking the tube. Acidify with dilute sulfuric acid and shake the tube.

Compare the above with the reaction of a dilute solution of copper sulfate. Account for the differences in terms of the structure of the complex ion.

2.5
Synthesis of $[NH_4][BF_4]$ and Synthesis and Titrimetric Analysis of $[Zn(NH_3)_4][BF_4]_2$

Michael A. Beckett

The boron trihalides BX_3 (X = F, Cl, Br, I), well-known for their Lewis acidic properties, readily form adducts of general formula $BX_3 \cdot L$ with a variety of neutral Lewis bases (L). Halide anions also react with boron trihalides to give tetrahaloborate anions $[BX_4]^-$. The halides BCl_3, BBr_3, and BI_3 and the corresponding tetrahalide anions are all rapidly hydrolysed by water. However, BF_3 and $[BF_4]^-$ are much more stable, BF_3 forms isolable adducts with water and $[BF_4]^-$ and can even be prepared in aqueous solution from boric acid, $B(OH)_3$ (*vide infra*). The hydrolytic stablity of $[BF_4]^-$ has led to its widespread role as an inert, non-coordinating counterion in many inorganic systems. Metal cations generally exist in aqueous solution as their aquo complexes *e.g.* $[M(H_2O)_n]_{m+}$. Reaction of these aquo complexes with aqueous concentrated NH_3 solutions results in ammine complexes in which aquo ligands have been displaced by NH_3. In this experiment you will prepare $[NH_4][BF_4]$ and a cationic zinc(II) coordination complex $[Zn(NH_3)_4]^{2+}$. Addition of $[BF_4]^-$ (aq.) to a solution of this cation results in an immediate precipitate of $[Zn(NH_3)_4][BF_4]_2$ which you will be able to isolate by filtration. You will then determine the amount of NH_3 (% mass) in your product by a titrimetric method.

Special Safety Precautions

Chemicals: *conc.* H_2SO_4 – highly corrosive and causes severe burns, vapour extremely irritating to eyes and lungs. If swallowed causes severe internal damage. *conc.* NH_3 *(aq.)* – highly corrosive and causes severe burns with vapour irritating to eyes and lungs. If swallowed causes severe internal damage. $B(OH)_3$ – irritating dust, may be harmful if ingested in quantity. NH_4F – dust can irritate skin, eyes, and lungs, and poisonous by inhalation and ingestion. $ZnSO_4 \cdot 7H_2O$ – harmful if ingested in quantity, irritating to eyes. *HCl (aq.) (0.1 M)* – corrosive. *NaOH (aq.) (0.1 M)* – corrosive. NH_3 *(aq.) (2 M)* – corrosive with vapour irritating to eyes and lungs. *Acetone*, CH_3COCH_3 – highly flammable, vapour/air mixture explosive. Keep away from naked flames. Degreases skin and may cause dermatitis. $[NH_4][BF_4]$ – corrosive and harmful by ingestion. $[Zn(NH_3)_4][BF_4]_2$ – toxic.

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Risk Control: Wear eye protection at all times. The syntheses of the two $[BF_4]^-$ compounds should be undertaken using a well-ventilated fume-hood and gloves should also be worn. The NH_3 analysis of the Zn complex may be safely performed on the open bench. Wash your hands after completing the experiment.

2.5.1 Experimental

a) Preparation of $[NH_4][BF_4]$

Carry out this preparation protected by a well-ventilated fume-hood. In a small beaker (100 cm^3) containing H_2O (20 cm^3) CAUTIOUSLY add *conc.* H_2SO_4 (10 cm^3). To this acidic solution add powdered (mortar and pestle) $B(OH)_3$ (3.00 g). Dissolve as much of the boric acid as is possible (~90% should dissolve) by heating the acidic solution on a boiling water-bath. Allow this acidic suspension/solution to cool slightly but whilst it is still hot add $[NH_4]F$ (7.50 g) in small (~1 g) portions. Swirl the reaction mixture in the beaker between each addition of $[NH_4]F$. The remaining suspended $B(OH)_3$ should dissolve and a clear solution should result. Allow the reaction to complete by heating the mixture on a water-bath for a further 20 min. Ensure that the liquid level does not drop during this period by replacing, if necessary, any evaporated solvent with H_2O. Cool the reaction solution under cold running water, and then in an ice-bath to precipitate out the *product* as white crystals. Filter the product by suction, wash it with acetone (15 cm^3), and finally dry it in air. Record the weight of your product and using Eq. (1) calculate your percentage yield.

$$B(OH)_3 + 4[NH_4]F + 3H_2SO_4 \rightarrow [NH_4][BF_4] + 3[NH_4][HSO_4] + 3H_2O \quad (1)$$

b) Preparation of $[Zn(NH_3)_4][BF_4]_2$

Carry out this preparation protected by a well-ventilated fume-hood. Dissolve $ZnSO_4 \cdot 7H_2O$ (1.00 g) in the minimum amount of water (1–2 cm^3) and then add DROPWISE *conc.* NH_3 (aq.) until the white preciptate which initially formed redissolves – this should take a total of ~25 drops. Take some of your $[NH_4][BF_4]$ (1.50 g) and dissolve it in dilute (2 M) NH_3 (aq.) (10 cm^3). Add the tetrafluoroboate/ammonia solution to the zinc(II)/ammonia solution and allow the mixture to stand (10 min) for complete precipitation of the product to occur. The precipitated colourless product is difficult to observe in the reaction mixture as its refractive index is almost identical to that of the solution. Filter the *product* by suction, wash it with a small volume of acetone (5 cm^3) and dry it *thoroughly* in air. Record the weight of your product and calculate your percentage yield based on Eq. (2).

$$Zn^{2+}\,(aq) + \textit{conc.}\ NH_3\,(aq.) + 2[BF_4]^-\,(aq) \rightarrow [Zn(NH_3)_4][BF_4]_2\,(s) \quad (2)$$

c) Analysis of $[Zn(NH_3)_4][BF_4]_2$

An analysis of the NH_3 content of your complex may be undertaken at your bench in the following way. Weigh out accurately (four decimal places) about 0.25 g of your *dried* product and place it in a conical flask (250 cm^3) and dissolve it in EXACTLY (use a pipette) 50.00 cm^3 of 0.1M HCl (aq.). You may need to warm the solution slightly to ensure that all the complex dissolves reasonably rapidly. The acid will react with all the ammonia present in the complex to form ammonium ions. Titrate the residual acid with 0.1 M NaOH (aq.) using methyl red as the indicator. You should have prepared enough of your complex to repeat this analysis. From your results calculate the percentage ammonia (by weight) in the complex.

2.5.2 Additional Exercises

1. Why are BF_3 and $[BF_4]^-$ so much more stable towards hydrolysis than the other boron trihalides and tetrahaloborates?
2. Explain the chemistry associated with how boric acid functions as an acid in aqueous solution.
3. What is the precipitate which is initially formed upon addition of aqueous concentrated NH_3 to Zn^{2+} (aq.) and why does this redissolve upon continued addition of the aqueous concentrated NH_3 solution. Write balanced chemical equations for these reactions.
4. Calculate a theoretical value for the NH_3 content (% mass) of $[Zn(NH_3)_4][BF_4]_2$. Compare your experimental analytical results with this calculated value. Comment on your results.

Further Reading

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2.6
Iron(II) and Lead(II) Formates

Francisco J. Arnáiz, María R. Pedrosa, and Rafael Aguado

Metal formates are important compounds in inorganic and organometallic chemistry as sources for finely divided metals, oxides or carbonates, and in processes involving CO and CO_2 (1,2). They are usually prepared by crystallising the aqueous solution obtained from formic acid and the appropriate metal oxide or carbonate, or from metathetic reactions involving other formates. More recently the preparation from formic acid and the metal acetates has been reported (3). Here we describe the synthesis of the iron(II) and lead(II) formates, to illustrate how the basic chemical principles can be managed to devise simple synthetic strategies.

The reaction between iron and formic acid provides a pure iron(II) solution from which the formate can be crystallised, as previously reported (4). The method here proposed takes advantage from the low solubility of the iron(II) formate in ethanol to precipitate the product before significant oxidation takes place.

Lead(II) formate can be conveniently prepared by the usual procedures. However, we propose the synthesis from Pb_3O_4 and formic acid. The method is based in the oxidising power of lead(IV) and the facile oxidation of formic acid to carbon dioxide and water, as well as solubility variations of numerous lead salts as a function of the temperature.

Special Safety Precautions

1. Formic acid is corrosive, volatile and toxic. Use safety gloves and goggles, avoid inhalations of vapours and conduct the synthesis in a well-ventilated hood.
2. Lead compounds are toxic. Avoid inhalation of dust.

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2.6.1
Experimental

2.6.1.1
Iron(II) Formate Dihydrate

In a 25-ml conical flask place: a stirring bar, ca. 0.25 g (4.48 mmol) of finely powdered iron, 10 g of water and 1 g (21.51 mmol) of 99% formic acid. Heat the mixture, with gentle stirring, progressively (to control frothing) below the boiling point until just a trace of iron powder remains undissolved. Place 25 ml of 95% ethanol and a stirring bar in a 50-ml conical flask immersed in an ice cold bath. Decant (filtration is rarely required) the green, warm solution of iron(II) formate (the use of an external magnet helps to hold the stirring bar and the iron traces inside the flask) on the cold ethanol while stirring. Stir gently the resulting mixture for 5 minutes. Separate the faintly green (apparently white) precipitate from the orange-yellow solution by filtration, wash with two 10 ml portions of 95% ethanol and dry in air. Calculate the yield and test for the presence of Fe(III) in the product with 0.1 M solutions of NCS^- and/or $[Fe(CN)_6]^{4-}$ (use drops of these reactants on small samples of product, instead of a solution of iron(II) formate). The test should be negative, even a few days after the preparation. In a typical run with 252 mg of pure iron powder (from the thermal decomposition of the carbonyl) 15 minutes were sufficient to dissolve the metal and 0.662 g (90% yield) of $Fe(HCO_2)_2 \cdot 2H_2O$ were obtained.

Further Suggestions

1. Calculate the volume of hydrogen produced at STP. (Capping the conical flask with a clean balloon during the dissolution process is advisable to avoid escapes by overheating or frothing).
2. Perform a simultaneous titration of iron(II) and formate with standardised $KMnO_4$.
3. Recover the ethanol from the mother liquor and washings by simple distillation, (the presence of some ethyl formate in the distillate does not cause problems when this ethanol is re-used for subsequent preparations).

2.6.1.2
Lead(II) Formate

In a 25-ml conical flask place: a stirring bar, ca. 1 g (1.46 mmol) of finely powdered Pb_3O_4, 15 g of water and 2 g (43.02 mmol) of 99% formic acid. Heat the mixture with stirring and boil it gently for 3–5 min, until the brown solution becomes colourless. Immerse the flask in an ice bath and stir until the solution cools to ambient temperature. Recover the solid produced by filtration, wash it with 25 ml of acetone and dry in air or in an oven at 60 °C for 15 minutes (in this case it is advisable to cover the solid with a piece of filter paper to avoid eventual spilling of the solid). Weigh the product and determine the yield. In a typical run 997 mg of minium afforded 1.048 g of $Pb(HCO_2)_2$, 80% yield. A second crop of product was obtained

(0.210 g, 16% yield) as a white microcrystalline precipitate when the acetone washings were mixed with the filtrate. Perform qualitative tests for lead(II) using a few mg of product and drops of 0.1 M Na_2S, Na_2CrO_4 and H_2SO_4 solutions.

Further Suggestions

1. Analysing the product: (i) Spread 100–200 mg of product, weighed to the nearest mg, on a watch glass, heat in an air-circulating furnace to 300 °C for 1 hr and reweigh (note how the grey lead powder initially formed oxidises to red litharge, PbO). (ii) Meanwhile, perform a volumetric analysis for lead (e.g.: in a 250 ml conical flask place 50–60 mg of product weighed to the nearest 0.1 mg, approx. 100 ml of water, 2 g of Na-K tartrate, a Eriochrome T tablet and 1 ml of 24% NH_3; titrate with 0.1 M EDTA, in a 5-mL microburette, from red wine to green; 1-ml EDTA accounts for 20.7 mg of Pb). Compare the results. It should be noted that if the air circulation in the furnace is very low, or the formate is not finely powdered, 1 hour might be insufficient for the complete conversion of $Pb(HCO_2)_2$ into PbO. Note also the difficulty to conclude from weigh difference that the red product is litharge instead of minium (Pb_3O_4), and devise simple discriminatory tests.
2. Recovery of the products: Most of the acetone from washings can be recovered by distillation. Among the ways to recover lead we suggest: (i) direct conversion of the remaining formate to PbO or Pb_3O_4 by heating in air, (ii) precipitation from solution with a saturated solution of sodium carbonate, since the resulting $PbCO_3.xPb(OH)_2$ is a convenient source for many lead compounds, and (iii) recovering the metal as large floating lead globules (5).

2.6.2 Exercises

Iron(II) Formate Dihydrate

1. Explain why a diluted solution of formic acid is used instead of the pure acid. Calculate the excess of formic acid used in the preparation. Predict the effect on the reaction time of using the stoichiometric amount of formic acid and iron turnings.
2. Explain why the formate is precipitated from the solution just before the last trace of iron is consumed. Explain also the colour of the mother liquor and predict the result if a deaireated peroxide-free ethanol is used. Do you think easy to isolate iron(III) formate? Draw the structure of a typical basic carboxilate species of a first-transition trivalent metal.
3. Write the balanced equation of iron(II) formate with $KMnO_4$ in diluted H_2SO_4 acid. Assuming that a 200 mg sample of $Fe(HCO_2)_2.xH_2O$ consumes 11.1 ml of 0.1 M $KMnO_4$ calculate the value for x.

Lead(II) Formate

1. Write the balanced equation between Pb_3O_4 and HCO_2H. Predict the effect of using PbO_2 instead of Pb_3O_4 in the preparation. Explain why no formic acid escapes during the boiling of the solution (see azeotropes). Mention other lead salts for which solubility in water changes markedly with temperature.
2. The quantitative conversion of minium into lead(II) acetate with acetic acid is difficult. Explain why by comparing formic and acetic acid.
3. EDTA is used to treat saturnism (lead poisoning). Explain how it works and discuss the benefits of using a Ca-EDTA complex instead of Na-EDTA salts.

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2.7
Ammonium Dichromate, Chromium(III) Oxide, Potassium Chromate and Potassium Tetraperoxochromate(V)

Antonín Růžička and Zdirad Žák

Conversion (double displacement) reactions are among the most common of the simple chemical reactions and bear a special importance in the preparation of inorganic salts. The method depends on the fact that not only do the solubilities of the salts change with temperature, they also change at different rates for different salts. In a solution, inorganic salts are always present in the form of simple ions. When the conditions of a solution containing two or more salts are changed (e.g. lowering the temperature, evaporating the solvent), the salt with the cation/anion combination which is the least soluble at the given conditions can be crystallised. It is therefore possible to find such conditions of temperature, concentration and solvent that allow, from a solution of two salts, the respective salts with mutually exchanged ions to be crystallised. The most simple examples of double displacement reactions are precipitations that lead to substances which are practically insoluble in a given solvent.

In the following experiment, we shall prepare ammonium dichromate by this conversion procedure. Ammonium dichromate decomposes to N_2 and Cr_2O_3 at temperatures above 185 °C and thus small quantities of pure chromium(III) oxide can be prepared. We shall demonstrate the formation of substances in an oxidising flux by the preparation of potassium chromate from Cr_2O_3. From K_2CrO_4, we shall further prepare a relatively stable compound of Cr(V): red-brown potassium tetraperoxochromate (V), $K_3[Cr(O_2)_4]$.

Special Safety Precautions

1. Chromates and dichromates are highly toxic and possibly mutagenic. Do not inhale the dust from these compounds, avoid the contamination of skin with their solutions.
2. Ammonium dichromate decomposes on heating.
3. Concentrated hydrogen peroxide is corrosive and can cause unpleasant burns. Always use rubber gloves.

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2.7.1 Experimental

a) $(NH_4)_2Cr_2O_7$

The conversion process can be expressed by Eq. (1).

$$Na_2Cr_2O_7 + 2\,NH_4Cl \rightarrow (NH_4)_2Cr_2O_7 + 2\,NaCl \qquad (1)$$

From the solubility curves of sodium dichromate and ammonium chloride in Figure 2.6-1, it follows that on cooling a suitably concentrated solution of $Na_2Cr_2O_7$ and NH_4Cl (molar ratio 1:2) to 20 °C, only $(NH_4)_2Cr_2O_7$ can crystallise from the solution.

Dissolve the appropriate amounts of $Na_2Cr_2O_7 \cdot 2H_2O$ and NH_4Cl required for the preparation of 20 g of $(NH_4)_2Cr_2O_7$ as determined from the solubility curves + 15 ml of water at 60 °C (see Note 1). Filter the solution through a heated filtration funnel (see Note 2) and cool the filtrate in an ice bath 0–2 °C. Filter the crystalline mass of $(NH_4)_2Cr_2O_7$ using a sintered glass funnel and a vacuum filter flask. Wash the product with 10 ml of ice water and suck the mother liquid well off. Dry in an oven at 100 °C.

Notes:

1. From the two salts, $Na_2Cr_2O_7 \cdot 2H_2O$ and NH_4Cl, the latter is less soluble. Therefore, the necessary amount of water is that as read from the solubility curve for NH_4Cl at 60 °C.
2. Make the heated funnel ready before you prepare the solution of $Na_2Cr_2O_7 \cdot 2H_2O$ and NH_4Cl. Be sure that both salts are completely dissolved.
3. Due to the toxicity of chromates, do not pour the mother liquid in a water sink. Dispose of as instructed by the supervisor.

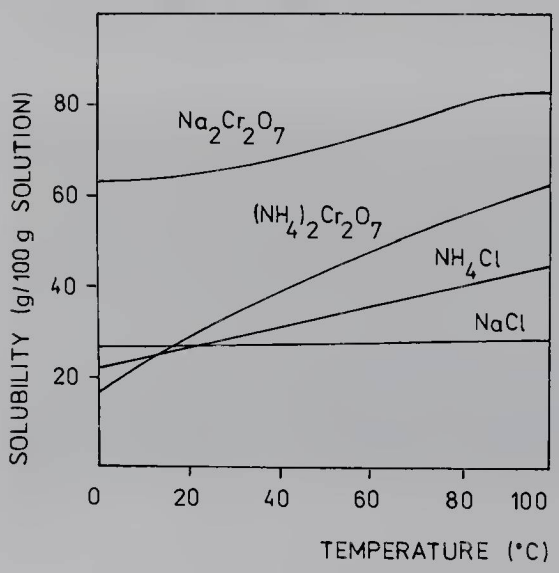

Fig. 2.7-1 Solubility curves.

Test for Cl^- ions: transfer a spatula tip of dry $(NH_4)_2Cr_2O_7$ to a test tube and dissolve it in 2 ml of water. Add a few drops of 5% solution of $AgNO_3$. By adding a few ml of diluted HNO_3 (conc. $HNO_3 : H_2O = 1:3$), dissolve the brown precipitate of $Ag_2Cr_2O_7$. If Cl^- ions are present in the sample, you will see a white precipitate of AgCl in a yellow solution.

b) Cr_2O_3

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O \quad (2)$$

Transfer 5 g of dry ammonium dichromate to a 500 ml Erlenmeyer flask. Cover the opening of the flask with a piece of Al foil and punch in it few small holes with a needle. This prevents finely dispersed Cr_2O_3 from being blown out of the flask by the stream of nitrogen and water vapours. Clamp the flask securely about the neck in a horizontal position so that all the dichromate is at the loweset part of the flask. Gently heat the part of the flask where the dichromate is collected with a gas burner. Keep the burner in your hand and remove it when the decomposition starts. After the flask has cooled down, add 300 ml of water, stir and allow to settle. Decant the supernatant, transfer the suspension of Cr_2O_3 to a Büchner funnel, wash on the filter with water and remove the liquid by suction. Dry in an oven at 100 °C. Although it takes up to several hours to dry Cr_2O_3 completely (why?), a still slightly damp oxide can be used for the preparation of K_2CrO_4.

c) K_2CrO_4

One of the methods for the preparation of alkaline chromates is an oxidation of chromium(III) oxide in a melt of alkaline nitrate or chlorate(V) and hydroxide or carbonate according to the Eqs. (3) and (4). In the laboratory, we can prepare a small amount of K_2CrO_4 by an oxidation of finely dispersed Cr_2O_3, prepared by the decomposition of $(NH_4)_2Cr_2O_7$ by air in a melt of KOH (Eq. 5).

$$Cr_2O_3 + 4KOH + 3KNO_3 \rightarrow 2K_2CrO_4 + 3KNO_2 + 2H_2O \quad (3)$$

$$Cr_2O_3 + 2K_2CO_3 + KClO_3 \rightarrow 2K_2CrO_4 + KCl + 2CO_2 \quad (4)$$

$$2Cr_2O_3 + 8KOH + 3O_2 \rightarrow 4K_2CrO_4 + 4H_2O \quad (5)$$

Transfer all of the prepared Cr_2O_3 to an iron or nickel crucible, add a stoichiometric amount of KOH (on the assumption that the decomposition of ammonium dichromate gives oxide with a 100% yield), place the crucible on a clay triangle and heat intensively with a gas burner. Stir the melt frequently with an iron or nickel wire and heat for a further 30 minutes. The bottom of the crucible should be heated to a dull red colour during this period. Allow to cool, dissolve the product in 25–30 ml of water and filter into a beaker filled with 100–150 ml of ethanol. Filter precipitated K_2CrO_4 using a sintered glass funnel *in vacuo*, wash with ethanol (15 ml) and dry at 100 °C.

Iodometric titration: use standard procedure and calculate the percentage of the salt.

d) $K_3[Cr(O_2)_4]$

Potassium tetraperoxochromate(V) is formed by the action of hydrogen peroxide on potassium chromate(VI) in a strongly alkaline solution (Eq. 6).

$$2K_2CrO_4 + 9H_2O_2 + 2KOH \rightarrow 2K_3[Cr(O_2)_4] + O_2 + 10H_2O \quad (6)$$

Dissolve 2.0 g of K_2CrO_4 and 2.0 g of KOH in 25 ml of water in a 100 ml Erlenmeyer flask. Immerse the flask in a ice/salt cooling mixture (or dry-ice/alcohol mixture) and wait until the contents solidify into a slush. Without disrupting the cooling, add 13 ml of a 30% solution of H_2O_2 dropwise under intensive stirring. Allow to stand in the cooling bath for a further hour, stirring from time to time. After this time, remove the flask from the bath and allow to warm up until the contents melt. Using a sintered glass funnel, vacuum filter the precipitated red-brown salt, wash with ethanol (15 ml) and dry in air.

Qualitative determination of O_2^{2-} ions: hydrogen peroxide forms with chromates(vi) in an acid solution giving a blue colouration ("chromium blue") which can be extracted in ether. Perform the following experiment.

Transfer 5 small crystals of K_2CrO_4 to a test tube, dissolve them in 2 ml of water, add a few drops of diluted H_2O_2 (3%), 2 ml of diethyl ether and a few drops of dilute sulfuric acid (3 ml water + 1 ml conc. acid). Shake the test tube and watch the blue colouration of the ether layer.

Perform the same reaction with the prepared $K_3[Cr(O_2)_4]$, but without hydrogen peroxide.

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2.8
Vanadium Alum: An Experiment in Electrosynthesis

David T. Richens

Vanadium alum, $NH_4V(SO_4)_2 \cdot 12H_2O$, is a member of an extensive series of isomorphous complexes. Unlike most compounds of V(III), it is fairly resistant towards oxidation in the crystalline state.

The preparation involves two separate reductions: from V(V) to V(IV) using SO_2 and from V(IV) to V(III) in an electrochemical reduction apparatus. These steps are accompanied by characteristic colour changes.

2.8.1
Experimental

Required materials: NH_4VO_3, conc. H_2SO_4, SO_2 cylinder, magnetic stirrer, electrochemical reduction apparatus, 12 V d.c. battery charger, mercury (designated fume cupboard should be available).

Cautiously mix 8 cm^3 of concentrated sulfuric acid with water contained in a 250 cm^3 conical flask and dilute to about 60 cm^3. In the **fume cupboard**, clamp the flask and insert a broad tube delivering SO_2 from the cylinder so that the end of the tube is close to the surface of the liquid, i.e. just dipping below it. Consult a demonstrator about the operation of the SO_2 cylinder. Warm the solution to about 50 °C then add 12 g of ammonium metavanadate, NH_4VO_3, *in small portions* while constantly stirring using a magnetic stirrer. Allow each portion of the initally formed brick-red divanadium pentoxide to dissolve by reaction with SO_2 before further addition. When all the solid has been added, **boil** the deep blue solution of vanadyl sulfate, $[VO(H_2O)_5]SO_4$, to expel excess SO_2.

To set up the electrochemical reduction, begin by carefully pouring mercury into the base of the apparatus (with the tap shut!) to form the cathode (Fig. 2.8-1). The mercury pool should cover the bottom. Transfer the vanadyl sulfate solution to the reduction vessel and introduce the glass cooling coil within which is placed the anode. The anode is a piece of lead sheet dipping into dilute sulfuric acid in a porous pot. Run tap water through the cooling coil during the reduction and stir the solution occasionally. The electrolysis is carried out at a steady current density of about 0.1 A cm^{-2} Hg until the solution is **deep green** with no remaining tint of blue. Main-

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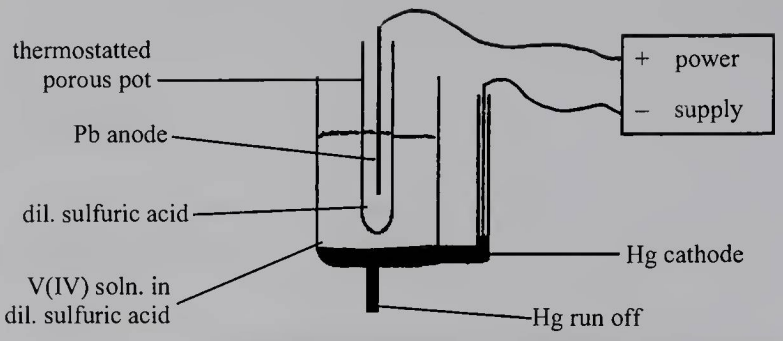

Fig. 2.8-1 Electrochemical reduction.

tain the bath temperature at 30 °C throughout. (A major cause of failure is incomplete electrochemical reduction – monitor by running a visible spectrum[1)] every 20 minutes on a sample of the reaction solution between 850 and 300 nm or until the absorption band of V(IV) at 750 nm has **disappeared**).

The mercury is then drawn off through the tap and put aside to be rinsed and returned to the prep room. The vanadium(III) solution is passed through a funnel containing a plug of glass wool and collected in a flask that can be stoppered. Making sure that no mercury droplets contaminate the solution, add 10 cm^3 of a **saturated** solution of ammonium sulfate and place the labelled flask in the refrigerator for a few hours (see a demonstrator) or preferably overnight. Seeding the crystallisation with a friend's sample sometimes helps.

The blue-violet crystals which separate are filtered at the water-pump and collected. The crystals are best dried on a piece of filter paper since desiccation over silica gel for more than 10 minutes can cause loss of lattice water and resulting efluorescence. Note the characteristic rhombic geometry of the alum crystals. The sample is to be submitted with your report when the magnetic and spectroscopic studies are completed. Record the yield and store in a well stoppered vial, but **not** a desiccator.

Magnetic susceptibility. Determine the magnetic moment of your sample as a fine powder.

Visible reflectance spectrum. Record the visible *'d-d'* spectrum of vanadium alum using a finely powdered sample in the form of a Nujol mull. Correlate the blue-violet colour of the alum with the reflectance spectrum you have recorded.

Report the yield and value of μ_{eff} and interpret the UV-visible and magnetic data in relation to the oxidation state and stereochemistry of the vanadium(III) ion.

1) Take out 1 cm^3 of solution and make up to 10 cm^3 with water (volumetric flask) before recording UV-visible spectra.

2.8.2 Questions

1. Why is SO_2 a particularly convenient reducing agent in the present synthesis?
2. What is the coordination environment of V^{3+} in the alum? Compare with the environment existing for V^{3+} in crystalline $VCl_3 \cdot 6H_2O$.
3. Why is a solid state UV-visible spectrum recorded using the crystalline alum, rather than the usual absorption spectrum measured in solution?

Further Reading

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2.9
Linkage Isomerism: An Infra-Red Study

David T. Richens and Christopher Glidewell

A number of ligands are **ambidentate**, that is, they can coordinate to a central ion in more than one way. Some examples are NCS^-, which can coordinate via N or S; NO_2^-, which can coordinate via N or O; and $acac^-$($(CH_3CO)_2CH^-$), which can coordinate via C or O. In this experiment, the ligand NO_2^- is investigated and a pair of linkage isomers having this ligand bonded to cobalt via both N and O is prepared and distinguished.

2.9.1
Experimental

Required materials: Cobalt(II) carbonate, ammonia solution, ammonium carbonate, ammonium chloride, HCl, sodium nitrite, diethyl ether, ethanol, pH meter plus electrode, dry KBr.

a) $[Co(NH_3)_5Cl]Cl_2$

Dissolve 5 g of cobalt(II) carbonate in 8 cm^3 of **hot** concentrated hydrochloric acid, filter, cool and add to a mixture of 60 cm^3 of 10% ammonia and 12 g of ammonium carbonate in 60 cm^3 of cold water. Draw a rapid stream of air[1)] through the solution for three hours, then add 38 g of ammonium chloride and evaporate the mixture on the rotary evaporator until a fairly thick sludge is obtained. Acidify the product with dilute hydrochloric acid, using a pH meter and a glass electrode, stirring constantly until carbon dioxide evolution has ceased. Neutralise with ammonia and add an excess (2 cm^3) of conc. ammonia solution. Warm the solution on the water bath for about half an hour, dilute to 100 cm^3 and add 75 $cm^3$of concentrated hydrochloric acid. Heat the resultant mixture on the water bath for 30–45 minutes and cool when the product separates. Filter off the product and wash with dilute hydrochloric acid and then with alcohol. Dry over silica gel in a desiccator and record the yield. Check

1) N.B.: The solution **must** be basic before bubbling air through; add more ammonia if necessary.

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the UV-visible spectrum in water against that of an authentic sample provided by the demonstrator.

b) The Two Linkage Isomers of $[Co(NH_3)_5NO_2]Cl_2$ (in Fume Cupboard)

Isomer I

Dissolve 1.5 g of $[Co(NH_3)_5Cl]Cl_2$ in 15 cm^3 of H_2O to which 5 cm^3 of 6 mol dm^{-3} ammonia has been added. Warm on water bath until salt dissolves[1], filter, cool and acidify with dilute HCl. Add 2 g of $NaNO_2$ and heat gently until the red precipitate first formed has dissolved. Cool and add 20 cm^3 of conc. HCl carefully since there is considerable effervescence. Cool the solution in ice, filter off the brown-orange crystals, wash them with alcohol and finally with ether. Dry in a desiccator over silica gel.

Isomer II

Dissolve 1.5 g of $[Co(NH_3)_5Cl]Cl_2$ in 25 cm^3 of water to which 5 cm^3 of concentrated ammonia has been added, warming gently if necessary.[1] Filter and add 6 mol dm^{-3} HCl dropwise until the solution is just neutral to universal indicator paper[2] (about 15 cm^3 is needed). Add 1.5 g of $NaNO_2$ to the cold solution plus 1.5 cm^3 of 6 mol dm^{-3} HCl and allow to stand for 1–2 hours in ice. Cool in ice, filter off the salmon-pink product as rapidly as possible, wash with ice water and alcohol and finally with ether, and then dry in a desiccator.

Record the IR spectra of both isomers immediately after preparation, and also of $[Co(NH_3)_5Cl]Cl_2$ using KBr discs. Do not grind the sample for too long a time – grind the KBr alone first, then add the sample and grind just long enough to mix thoroughly. Then expose small samples of each to (i) heat (oven), and (ii) bright daylight (sunlight if possible or use a UV lamp) for a few days. Record the spectrum of each after treatment.

Report the yields of all of your products and assign the IR bands as far as possible to vibrations involving the NH_3 and NO_2^- ligands. Identify the two isomers, determine which is the more stable thermodynamically, and explain the changes occurring. Propose a mechanism for the isomerisation.

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1) N.B.: It may be necessary to boil to ensure complete dissolution of the starting material.
2) It is important that this solution is not alkaline.

2.10
Preparation of Copper(I) Iodide

F. J. Arnáiz, M. R. Pedrosa, and S. Arnáiz

Copper(I) iodide is an important starting material for the preparation of organocuprates (1). It can be prepared by a variety of methods; most of them based on the treatment of aqueous solutions of cupric salts with an alkali metal iodide in the presence of a reducing agent (2, 3). One of the simplest procedures makes use of the reaction of $CuSO_4$ with KI and $Na_2S_2O_3$ (3, 4). In view that a growing effort is being made to devise, and to introduce in the chemistry curricula, procedures to minimise the production of wastes, here we propose a simple synthesis for CuI that fits these requirements when a freshly product is wanted. The procedure is based on the great difference in solubility of CuI in aqueous solutions as a function of iodide concentration, and it has been proposed for CuI purification (5). It is appropriate for the basic Inorganic Chemistry Lab since it allows the discussion of a number of basic principles (limiting reactant, solubility, acid-base, redox and formation of complexes). Ideally, no waste is produced as both the excess of copper and the alkali metal iodide are recovered quantitatively and can be reused for several times.

Special Safety Precautions

Iodine is a toxic, volatile and corrosive solid that attacks mucous membranes and adsorbs strongly to skin. Avoid prolonged exposure to its vapours and use rubber gloves. Spills are conveniently treated with some drops of a concentrated solution of sodium thiosulfate until discoloration, followed by water.

2.10.1
Experimental

In a 15 × 100 mm test tube place a small stirring bar, 0.5 g (197 mmol) of dry I_2, 5 g (33.4 mmol) of NaI, 5 g of H_2O and a drop of 4 M acetic acid. Take a copper wire (about 20–30 cm long, 1-mm diameter, such as those from waste electrical devices) and roll it 10–15 cm on one end. Weigh the wire to the nearest mg and hang it (assisted by a folding at the appropriate distance) on the edge of the tube with the

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rolling immersed in the NaI-I_2 solution, approx. 1 cm above the bottom of the tube (to allow for efficient stirring). Heat the tube at 80–100 °C with stirring (e.g. in a boiling water bath) until a colourless solution results (this takes about 15–20 min). Remove the copper wire and pour the warm solution in a 50 mL erlenmeyer flask containing 25 g of ice cold water. Precipitation of CuI is immediate. Stir the mixture for 10 min, filter the white precipitate, wash with water and dry in an oven a 110 °C for 30 min (alternatively, wash with acetone or ethanol and dry in air at room temperature). Wash and dry similarly the copper wire and re-weigh it.

In a typical run, using 502 mg of iodine and a 2.253 g copper wire, 678 mg of white (slightly grey) CuI is obtained (90% yield based on iodine). The weigh loss for copper amounted to 250 mg (calculated 251 mg). Characteristic tests can be performed by drop reactions on small samples of the solid: concentrated HNO_3 leads to the formation of a brown-black solid (iodine), evolution of NO_2 and formation of a blue solution of copper (II) nitrate (difficult to observe in the presence of iodine); concentrated ammonia in air dissolves CuI leading to a blue solution (formation of $[Cu(NH_3)_4]^{2+}$); heated to 350 °C in a capillary tube it turns yellow brown (thermochromic effect) without noticeable symptoms of decomposition.

2.10.2 Exercises

1. Explain the effect of adding a drop of acetic acid. Write the balanced equation of CuO, as well as that of $CuCO_3 \cdot Cu(OH)_2$, with the acid. Calculate how much CuO can be removed from a slightly oxidised copper wire with a 0.050 mL drop of 4 M acetic acid. Write the balanced equation between copper(II) acetate, sodium iodide and copper.
2. Explain why no iodine escapes, nor condenses in the upper cold part of the tube, while heating the mixture I_2-NaI-H_2O-Cu. Explain also why CuI is noticeably soluble in concentrated iodide solutions.
3. When the resulting 'diluted' NaI solution is concentrated and re-used for a further preparation of CuI, the yield eventually might go (apparently) beyond 100%. Explain why (remember that the yield in the procedure as described moves around 90%).
4. Explain why copper(II) and iodide are incompatible in acid media and compatible in ammonia media.
5. Predict the effect of adding PPh_3 to a suspension of CuI in CH_2Cl_2.

References

1 See, e.g.: R. J. K. Taylor (Ed.), *Organocopper Reagents: A Practical Approach*, Oxford University Press, New York, **1994**.
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3 G. B. Kauffman, R. P. Pinnell, *Inorg. Synth.* **1960**, *6*, 3.
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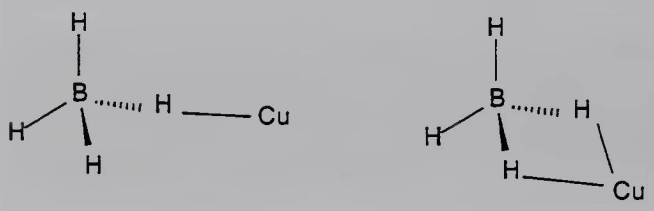
2.11
Deduction of the Coordination Mode of BH_4 in Bis(triphenylphosphine) Copper(I) Borohydride $(Ph_3P)_2CuBH_4$

Andrew W. G. Platt

This experiment involves the preparation and thermal decomposition of a copper borohydride complex, and infrared analysis of the complex and its decomposition products.

In principle the borohydride ion could be uncoordinated to the copper, i.e. have an undistorted tetrahedral structure or coordinate as a monodentate or bidentate ligand as shown below, or even as a tridentate ligand. Analysis of the infrared spectra of the compounds allows some deductions to be made about the coordination geometry.



Special Safety Precautions

Note that this experiment involves the use of flammable organic solvents. Ensure that all heating operations are carried out on a water bath and NOT over a naked flame. Dichloromethane is highly volatile and must only be used in the fumecupboard. Note also sodium borohydride is extremely toxic and liberates hydrogen on contact with acids. Avoid all contact and clean up any spillages immediately with a damp sponge.

2.11.1
Experimental

Mix 1 g of finely powdered hydrated copper sulfate and 5 g of triphenylphosphine in a beaker with about 80 cm^3 of methylated spirits. Heat and stir until all the triphenylphosphine and most of the copper sulfate has dissolved. It may be difficult to get all the copper sulfate into solution. Remove from the heat and cautiously add 1 g of

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sodium borohydride a **little at a time**. Sodium borohydride is best weighed out into a dry sample tube. Allow the effervescence to subside before each successive addition. Filter under suction and collect the crude solid product. Dissolve the crude solid in about 30 cm^3 of dichloromethane and filter by gravity through a fluted filter paper into a 100 cm^3 beaker. Rinse the filter with a little more dichloromethane. Heat the combined dichloromethane extracts on a steam bath in the fumecupboard and whilst this is evaporating slowly add 50 cm^3 of methylated spirits. When the total volume is about 60 cm^3 allow the mixture to cool. Filter the crystals and wash with a little ethanol and finally with a little ether and dry at the pump. Record the weight of the dry solid and calculate the percentage yield.

Record the infrared spectra of triphenylphosphine and of your product as KBr discs.

2.11.1.1
Thermal Decomposition

The thermal decomposition of the product proceeds according to the equation below:

$$(Ph_3P)_2CuBH_4 \rightarrow Ph_3PBH_3 + Cu + Ph_3P + H_2 \qquad \text{(not balanced)}$$

Place approximately half your sample in an sample tube and heat in an oven at about 200 °C for a few minutes. Do not leave the sample in the oven unattended. Take care when removing the reaction from the oven, use heat resistant gloves. Rubber gloves are not adequate. Extract the resulting solid with two 5 cm^3 portions of toluene. Filter the combined extracts directly into a small evaporating basin. On such a small scale this is best done by allowing the solution to run through a Pasteur pipette containing a small plug of cotton wool pressed firmly into the stem of the pipette. Once the solution has been filtered run a little more toluene through the pipette. Evaporate the toluene on a steam bath in the fumecupboard. Extract the remaining solid with 2 × 5 cm^3 of meths and filter by gravity into a small beaker, retaining both the filtrate and the undissolved solid.

To the Filtrate
Evaporate to dryness on a steam bath to obtain a solid material (solid (I)). You only require sufficient material for an infrared spectrum which should be recorded as a KBr disc.

To the Residual Solid
Wash with a little ether and dry at the pump to give solid (II). Record its infrared spectrum as a KBr disc.

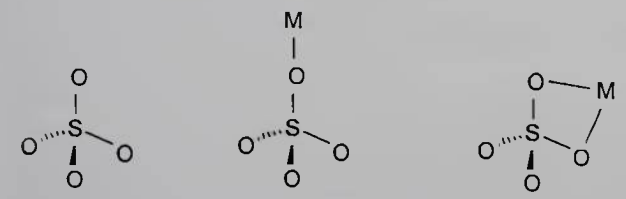
2.11.2
Complementary Work

1. Compare the infrared spectra of triphenylphosphine with that of the copper complex and assign the bands due to the BH_4 group. You may assume that any vibrations due to Cu–P are below 400 cm^{-1}.
2. By considering the local symmetries possible for the BH_4 group carry out a fragment analysis to deduce how many bands would be expected for each coordination mode, and hence assign a structure to the complex.
3. By analysing the infrared spectra of solids (I) and (II) deduce the identity of each, giving full explanations of your reasoning, this should include assignment of intense or characteristic bands in the spectrum where appropriate. What further experiment(s) could you carry out in the lab to confirm your deductions.
4. Describe the processes which are occurring in the thermal decomposition reaction. In particular consider the oxidation state of the metal and discuss how any changes in this have occurred. Balance the equation for the decomposition.
5. What are the two functions of the borohydride ion in the formation of the initial product?

2.12
Preparation and Identification of a Copper(I) Complex

Andrew W. G. Platt

The sulfate ion has a regular tetrahedral geometry. Its local symmetry is lowered on coordination to metals and thus analysis of the vibrational spectra can provide an easy means of identifying the different coordination modes. Some of the possible modes of bonding are illustrated below.



Special Safety Precautions

The preparation uses acetonitrile and diethyl ether which are volatile and flammable. All manipulations using these solvents should be carried out in an efficient fume cupboard. Concentrated sulfuric acid is extremely corrosive and must be used only in the manner described. Avoid all contact with the skin by wearing rubber gloves and wash any spillages with aqueous sodium carbonate solution. Copper compounds are generally considered to be toxic. Avoid all contact with the skin and wash any contamination immediately with plenty of running water. The compounds are all of low volatility and pose little hazard providing normal chemical precautions are taken.

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2.12.1 Experimental

2.12.1.1 Preparation

Dissolve 5.6 g triphenylphosphine in about 30 cm^3 acetonitrile with gentle warming on a steam bath. Suspend 0.5 g copper(I) oxide in 10 cm^3 acetonitrile in a wide test tube and add concentrated sulfuric acid **dropwise** with constant swirling until the red colour has discharged and most of the solid has dissolved. You should need no more than about 0.5 cm^3 for this. Add the copper solution to the triphenylphosphine solution and filter the mixture by gravity. Evaporate the filtrate to about 20 cm^3 on a steam bath in the fume cupboard and allow to cool to room temperature. Precipitate the product by adding diethyl ether slowly with constant stirring, about 50 cm^3 should suffice. Filter the product, dry at the pump and record the weight obtained.

Record the infrared spectrum of the compound as a KBr disc.

2.12.1.2 Analysis

Carry out fragment analysis using the S–O bonds as the basis set to deduce the number of S–O stretches expected in the infrared and Raman spectra of sulfate ion in the three coordination modes illustrated above. Compare these predictions with the infrared (and Raman if available) spectra of the complex and hence deduce the coordination mode of the sulfate ion. You will first need to assign the appropriate bands in your spectra and may find it helpful to run a spectrum of triphenylphosphine for comparison.

Deduce the composition of the compound using the following information. The compound is diamagnetic and has the elemental analysis C 72.19%, H 5.12%, Cu 7.06%.

Sketch a plausible structure for the complex and write equations for the reactions involved in its formation.

Compare the reaction of copper(I) oxide with sulfuric acid using water as the solvent instead of acetonitrile. This is conveniently done by adding a little copper(I) oxide to 2 M sulfuric acid and gently warming the tube. Account for any differences in the reaction compared with that observed in the first stage of the preparation.

Further Reading

D. M. Adams, *Metal Ligand and Related Vibrations.*
F. A. Cotton and G. Wilkinson: *Advanced Inorganic Chemistry.*
K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., Wiley, 1997.

2.13
Synthesis and Characterisation of a Metal Hydride Complex

Andrew W. G. Platt

Covalently bonded metal hydride complexes are known for all the transition metals. The complexes often contain the metal in a low oxidation state with phosphines, carbon monoxide, or cyclopentadiene groups as auxiliary ligands. Metal hydride complexes are important as intermediates in many catalytic processes such as alkene oligomerisation and hydrogenation.

In this experiment you will prepare a cobalt hydrido complex and deduce its composition from its nmr spectrum.

Special Safety Precautions

General good laboratory practice will ensure the safe completion of this experiment. Care should be exercised when using sodium borohydride which liberates hydrogen on contact with acids and water. Ensure that all apparatus, including the weighing bottle is dry before use. Note also that dichloromethane is highly volatile and must be used in the fume cupboard.

2.13.1
Experimental

A solution of sodium borohydride (0.5 g) in ethanol (10 cm^3) is added dropwise via pasteurre pipette, to a stirred solution of cobalt(II) nitrate hydrate (1.5 g) and triphenylphosphite (8.0 g) in ethanol (30 cm^3) at 25 °C. After 15 minutes the yellow solid is filtered, washed with ethanol, water and finally methanol and dried at the pump. Recrystallise the product by dissolving in dichloromethane as far as possible (about 30 cm^3). At this stage there will probably be some undissolved material which can be difficult to filter. Filter by gravity through a fluted filter paper. If difficulty is encountered in obtaining a clear filtrate, the solution can be filtered through a pipette containing a **small** plug of cotton wool. Once a clear dichloromethane solution has been obtained slowly add alcohol to precipitate the product. Record the yield and melting point.

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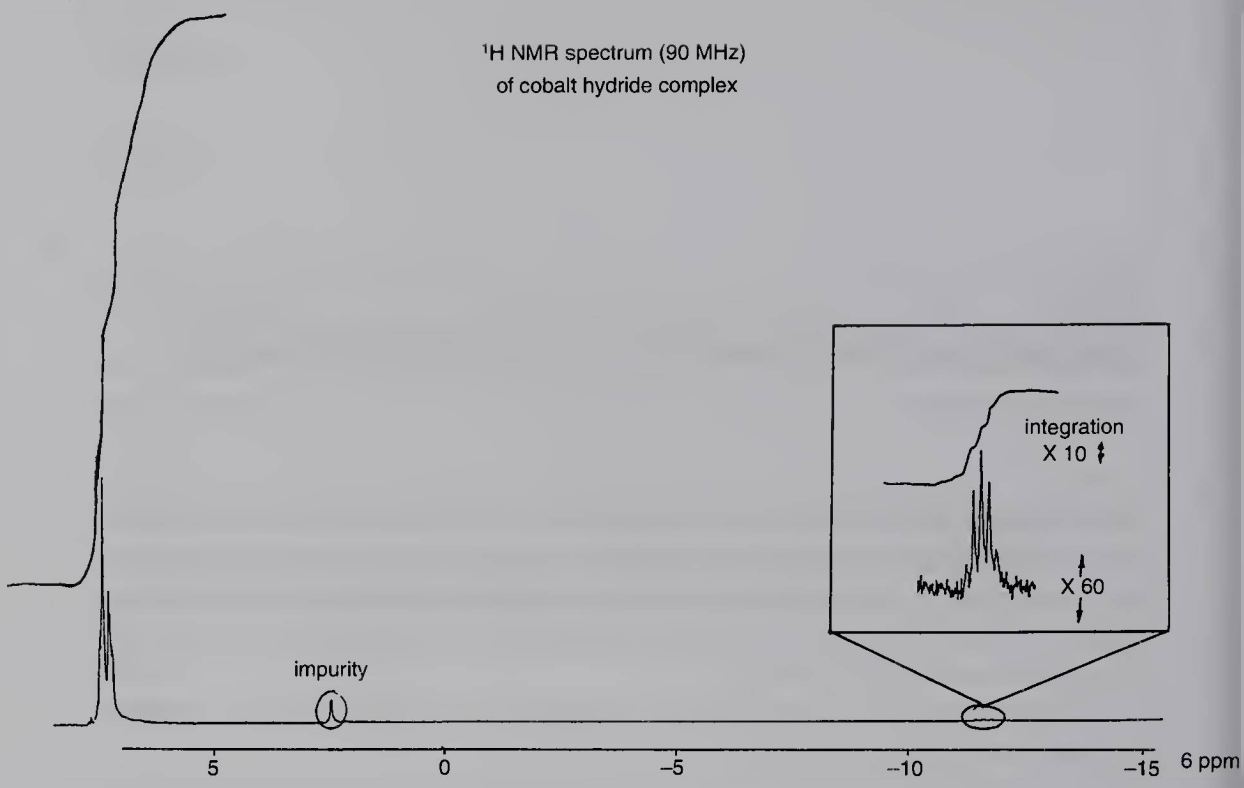

Fig. 2.13-1

2.13.2 Questions

1. Fully interpret the proton nmr spectrum of the complex, and from this deduce its formula.
2. What is the likely structure of the complex?
3. What are the possible oxidation states of the cobalt in the complex? Give full explanations of your answer.
4. Deduce whether or not the compound is an eighteen electron complex.

2.14
Reactivity of Triphenylphosphine and Its Oxide Towards $CuCl_2$

Paul F. Kelly and Martin B. Smith

Two important classes of compounds that contain phosphorus are the tertiary phosphines (PR_3) and tertiary phosphine oxides (OPR_3). Both compounds are two-electron Lewis bases that bind to metals. In this experiment you will explore the reactivity of both the parent phosphine and its oxide towards copper(II) metal ions.

Special Safety Precautions

Triphenylphosphine, triphenylphosphine oxide and copper(II) chloride should all be treated as toxic. Ethanol and diethyl ether are toxic and extremely flammable.

2.14.1
Experimental

2.14.1.1
Reaction of Ph_3PO with $CuCl_2$

Anhydrous $CuCl_2$ (0.12 g; note that this material should be brown – if it appears green due to partial hydration it should be dried in a hot oven for a few minutes until the green colour reverts to brown) is dissolved in absolute ethanol (5 cm^3) in a small beaker (use a stirrer bar/hotplate stirrer) and solid Ph_3PO (0.5 g) is added in one portion. The resulting mixture is stirred vigorously for 2 minutes, during which time the oxide should appear to mostly dissolve and a solid product appears. More absolute ethanol is added dropwise until just enough is present to solubilise the mixture fully and give a green solution (the total volume of ethanol present to achieve this should be a maximum of 10 cm^3 – do not add more than you need). After stirring this solution for a further 5 minutes, it is transferred into a round-bottomed flask and the solvent removed on a rotary evaporator. NB: This should be done with as little heating as possible – use only just enough heat to remove the ethanol in a sensible time-scale as too much heating may cause decomposition. The operation should be continued until some yellow solid is present (the residue does not have to

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be totally solid – some green oil will also be apparent), at which point diethyl ether (20 cm^3) is added and the mixture is stirred to give a finely divided yellow precipitate (if no solid but just a green solution is present after addition of the ether, this means that here is too much ethanol still there and you will have to evaporate down again).The yellow solid is collected by filtration, washed with ether (20 cm^3) and dried in air before storage in a sample vial (samples must be stored in a closed sample vial to prevent decomposition which occurs on longer exposure to air).

Measure the yield, melting point and IR spectrum of your product.

2.14.1.2 Reaction of Ph_3P with $CuCl_2$[1]

Ethanol (50 cm^3) and a stirrer-bar are placed in a three-necked 250 cm^3 round-bottomed flask; one of the side-arms is fitted with a glass stopper and nitrogen is then bubbled through the solution via the other side-arm for 5–10 minutes to deoxygenate the solvent (use a glass pipette connected to the nitrogen tap via a length of rubber tubing). While keeping a flow of nitrogen going, solid $CuCl_2 \cdot 2H_2O$ (1.7 g; make sure you use the hydrated and not the anhydrous material) and PPh_3 (4 g) are added to the flask, which is then fitted with a condenser, the side-arm is stoppered and a nitrogen bubbler is fitted to the top of the condenser with a slow stream of nitrogen passing through it. The mixture is heated until the ethanol begins to reflux – very vigorous stirring should be maintained during this period. Reflux is continued until the colour of the solution is discharged and a mass of white precipitate appears – this should take 20 minutes or less of refluxing. The resulting mixture is cooled and the precipitate collected by filtration, washed with ethanol (2×20 cm^3) and then diethyl ether (10 cm^3), and finally dried in air before being transferred to a sample vial (samples should be well sealed as prolonged exposure to air can result in decomposition).

Record the yield, melting point and IR spectrum of your product.

A sample of this product (0.5 g) is placed back into ethanol (50 cm^3, deoxygenated as before), PPh_3 (0.73 g) is added and the resulting mixture is refluxed under nitrogen with very vigorous stirring. Heating should eventually result in complete dissolution of all the solid to give a solution (which should be colourless, although it may be very pale green); once this has formed, it is heated for a further 5 minutes then cooled in an ice bath (NB: solid formation is often spontaneous before cooling, and indeed in some cases the fully dissolved solution phase does not last long, so careful attention must be paid). The resulting solid is collected by filtration, washed with cold ethanol (20 cm^3) and then diethyl ether (10 cm^3), and dried in air before being transferred to a sample vial (again, samples should be well sealed as prolonged exposure to air can result in decomposition).

Record the melting point of your product.

2.14.2 Observations and Discussion

Compare the IR spectra of PPh_3 and its oxide and account for any differences.

A full analysis of the product of the reaction of Ph_3PO with $CuCl_2$ reveals that the composition by weight is C 62.6, H 4.4, P 9.0, O 4.6, Cu 9.2, Cl 10.3%. Typically, a magnetic moment of ~2 BM is measured from samples produced in this experiment. Use these data and all your observations to assign a structure. What is the oxidation state of the copper?

A full analysis of the product of the reaction of Ph_3P with $CuCl_2$ reveals that the composition by weight is C 59.8, H 4.2, P 8.6, Cu 17.6, Cl 9.8%; mass spectrometry reveals a highest peak at *m/z* 1444 and magnetic measurements reveal it to be diamagnetic. Use these results and all your observations and measurements to assign a structure [1, 2]. What is the oxidation state of the copper in this case?

When this first material is then treated with further PPh_3, the resulting product shows a highest peak of *m/z* 885. What structure may we assign to this material? How might the geometry at the copper centre be confirmed by using ^{31}P NMR spectroscopy?

Account for the difference in reactivity of Ph_3P and its oxide towards $CuCl_2$ in terms of the products generated.

References

1 F. H. Jardine et al., *J. Chem. Soc. A*, **1970**, 238.
2 M. R. Churchill et al., *Inorg.Chem.* **1974**, *13*, 1065.

2.15
Synthesis of a Thermochromic Copper Complex

Iain A. Smellie

A substance is said to be thermochromic if it undergoes a colour change when the ambient temperature is raised or lowered. In this experiment, a tetrachlorocuprate(II) complex will be prepared before investigating its thermochromic properties.

$$CuCl_2 + 2(Et_2NH_2)Cl \rightarrow [Et_2NH_2]_2[CuCl_4]$$

Special Safety Precautions

2-Propanol, ethanol and ethyl acetate are volatile and highly flammable solvents. Copper(II) chloride hydrate ($CuCl_2 \cdot 2H_2O$) and diethylammonium chloride should be considered toxic.

2.15.1
Experimental

Place 2.20 g of diethylammonium chloride in a dry 100 cm^3 conical flask. Add, from a dry measuring cylinder, 15 cm^3 of 2-propanol. Similarly, weigh 1.72 g of copper(II) chloride hydrate into a 100 cm^3 conical flask and add 3 cm^3 of ethanol. Warm the solutions (gently, e.g. on a steam bath) until the solids dissolve completely (**keep swirling the solution**).

Prepare a 20% v/v solution of 2-propanol in ethyl acetate by mixing 2 cm^3 of 2-propanol and 8 cm^3 of ethyl acetate in a beaker. Add the diethylammonium solution to the copper chloride solution and heat the mixture on a steam bath for 3–4 minutes. Immediately add the 2-propanol–ethyl acetate mixture to the flask and allow the contents to cool to room temperature. Cool the mixture in an ice bath; green crystals should begin to form. If the crystals do not form, scratching the flask with a glass rod or the use of 'seed' crystals should initiate crystallisation of the product. After 10–15 minutes of cooling in ice, filter off the crystals using a Buchner funnel, wash any residual crystals out of the flask with ~10 cm^3 of ethyl acetate and suck the crystals dry for 10 minutes. Calculate a percentage yield for the reaction.

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Place a small amount of the product in a melting-point tube, use a hot-air blower to heat the bottom of the tube and note any colour changes. Place a second sample of the product in a melting-point tube and, using a melting-point apparatus, determine the temperature at which any colour changes take place. Determine the melting point of the product.

Further Reading

This section is based on S. Choi and J. A. Larrabee, *J. Chem. Educ.* **1989**, *66*, 774–776, which contains significant additional spectroscopic characterisation, making the experiment suitable for more advanced classes.

2.16
Preparation and Complexation of Tris(3,5-dimethylpyrazoyl)hydroborate

Manfred Bochmann

Binary boron hydrides are an extremely interesting class of compounds and form a multitude of structures. However, they are very difficult to handle. The simplest, BH_3, behaves as a Lewis acid and forms, for example, an adduct with THF. It also adds a hydride anion to give BH_4^-. In this anion the hydrogen has **hydridic** character, i.e. it reacts with a proton source to liberate H_2. This reaction principle is utilised in part a).

Special Safety Precautions

In this experiment hydrogen is liberated and carbon monoxide is used. All parts to this experiment should be performed in a fume cupboard.

2.16.1
Experimental

a) Potassium Tris(3,5-dimethylpyrazolyl)hydroborate

The tetrahydroborate anion reacts with the acidic hydrogen of pyrazole and its derivatives with liberation of H_2 and formation of B-N bonds. Bis-, tris- and tetra-pyrazolyl borates can be made which act as versatile anionic chelate ligands towards transition-metal ions. With 3,5-dimethylpyrazole, which we use here, steric crowding only allows substitution of a maximum of three hydrides (Eq. 1).

$$K^+BH_4^- + 3\,C_5H_8N_2 \rightarrow K^+[HB(C_5H_7N_2)_3]^- + 3\,H_2 \quad (1)$$

($C_5H_8N_2$ = 3,5-dimethylpyrazole)

The reaction is monitored by measuring the amount of H_2 evolved. Assemble the apparatus as in the following figure, consisting of a 100 ml flask with magnetic stirring bar, connected via a wash bottle (as a suck-back trap) to a water-filled 2 litre measuring cylinder in a half-filled bowl for the determination of the volume of

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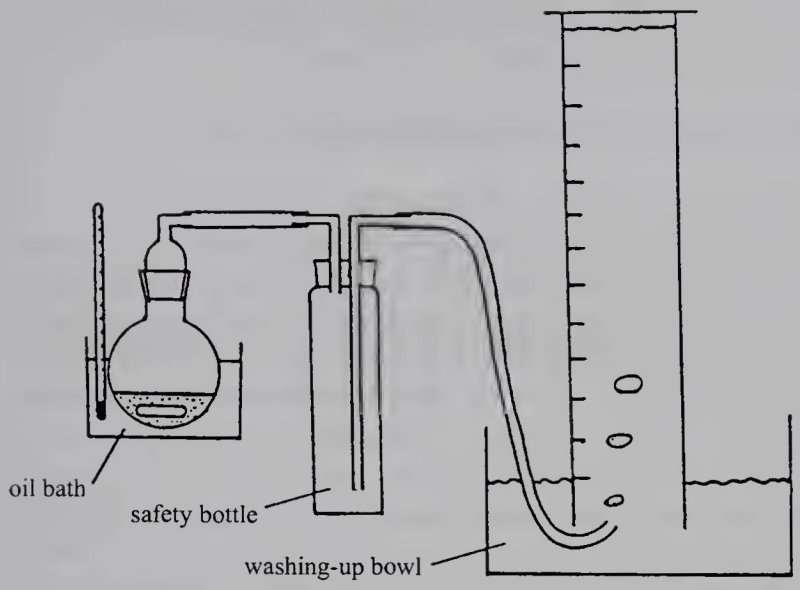

hydrogen gas evolved. Fill the bowl to between 1/3 and 1/2 full and the cylinder completely with water, cover the cylinder top with tight plastic or cling-wrap and quickly stand it upside-down in the bowl. Have suitable clamps ready beforehand. Now remove the plastic without letting air in. Mark the level of any air in the cylinder so that it can be subtracted later.

Caution: Hydrogen can be explosive – make sure no naked flame or sparks are in the neighbourhood. Work in an efficient fume cupboard. Is the safety bottle connected the right way around?

Quantities:

Potassium tetrahydroborate	(M_r =)	18.5 mmol =	g
3,5-Dimethylpyrazole	(M_r =)	73 mmol =	g
ml H_2 expected:	=	mmol H_2	
ml H_2 found:	=	mmol H_2	

Place powdered potassium tetrahydroborate (18.5 mmol) and 3,5-dimethylpyrazole (73 mmol) in the flask, connect to the wash bottle and heat on a silicone oil bath at 230 °C. The whole reaction should be completed within 1 to 1.5 hours. The stirred mixture melts at 130–140 °C oil bath temperature, and hydrogen evolves. Determine how many equivalents of H_2 you expect and how much you collect, ensure there are no leaks! Towards the end of the reaction, the product will solidify. Allow to cool to ca. 100 °C and add 50 ml toluene. Filter off while hot and wash the white crystalline residue with more toluene (2 × 50 ml) and finally with petrol (b.p.: 40–60 °C) to remove excess pyrazole. Dry *in vacuo* for 10–20 minutes (rotary oil pump).

Record the ^1H NMR spectrum (in D_2O) and the IR spectrum (Nujol mull). Assign the NMR spectrum and the significant bands of the IR spectrum.

Pyrazolylborates act as excellent chelating, mono-anionic ligands towards transition metals, and many complexes are known. In some cases, unusual complexes can

be stabilised in this way. The complex prepared in part b) is such an example. Generally, complexes of Cu(I) with carbon monoxide are very unstable.

b) A Copper Carbonyl Complex of Tris(3,5-dimethylpyrazolyl)hydroborate

Caution: CO is highly poisonous. Work in an efficient fume cupboard.

Stir 2 mmol of finely powdered copper(I) iodide in 50 ml acetone on an ice bath. Stopper the flask with a "suba-seal" and bubble CO through the inlet and outlet needles at a moderate rate for at least 5 minutes. It is important to keep the flask under CO and exclude air as much as possible during the reaction. Then quickly add 2 mmol of the $K[HB(Me_2pyr)_3]$ and continue CO treatment. The suspension soon becomes clear. Stop stirring, continue to bubble CO through until the mixture turns cloudy and crystals begin to form. Stop the CO stream, but leave the flask under a CO atmosphere on the ice bath for ca. 1 hour. Filter off the colourless crystals, wash with a little acetone and dry *in vacuo*.

Measure the ^1H NMR spectrum (in $CDCl_3$) and the IR spectrum. Assign the spectra and compare with the data obtained for $K[HB(3,5\text{-}Me_2pyr)_3]$.

Further Reading

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M. I. Bruce, A. P. P. Ostazewski, *J. Chem. Soc., Dalton Trans.* **1973**, 2433.

2.17
Tetraiodotin(IV) and its Triphenylphosphine Oxide Complex

Iain A. Smellie and J. Derek Woollins

Most of the heavier main group (p-block) elements have the capacity to expand their coordination number beyond that of their normal covalency by forming complexes with neutral ligands. The triorganophosphines (R_3P) are an important class of coordinating ligands, especially in the chemistry of the more electron-rich ('softer') metals. It is often found that complexation by a phosphine will decrease the reactivity of the metal species towards, for example, hydrolytic decomposition, as is the case here. The preparation features a convenient non-aqueous solvent procedure.

Special Safety Precautions

Tin compounds, iodine, phosphines and chloroform are all extremely harmful, and acetic acid and its anhydride are very corrosive. Do not inhale them or allow them to contact the skin. Perform all operations in a fume cupboard.

2.17.1
Experimental

a) Tetraiodotin(IV), SnI_4 (Stannic Iodide)

Weigh, using a top-pan balance, 1.0 g of tin metal and 2.5 g of iodine into a 100 cm^3 Quickfit round-bottomed flask. Add 10 cm^3 of toluene from a measuring cylinder and then add two or three anti-bumping granules. Connect a reflux condenser to the water supply **(ensure there are no leaks).** Place the flask in a heating mantle, secure it in place with a clamp and equip with a reflux condenser.

Heat the solution to the point where a violet vapour begins to condense in the reflux condenser. **Immediately** reduce the power setting by half and allow the solution to heat for ca. 30 minutes. The solution should initially be a violet colour and become orange as the reaction proceeds. When the heating period is complete, switch off the mantle and allow to the flask to cool to the point where the solvent stops condensing. Decant the hot solution into a 100 cm^3 conical flask (Care! Use a clamp to

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manipulate the flask), leaving the residual tin in the reaction flask. Add 10 cm^3 of 40/60 petroleum spirit to the conical flask and allow it to cool to room temperature. Wash the residual tin metal in the reaction flask with acetone (dispose of the washings in the appropriate waste bottle!) and leave it to dry on a watch-glass. Weigh the dried tin metal.

Orange crystals should begin to form as the contents of the conical flask cool. To maximise crystallisation, the flask should be cooled in an ice bath for a few minutes. Filter off the crystals using a Buchner funnel and wash them with 10 cm^3 of cold 40/60 petroleum spirit. Weigh your dried crystals. Record the melting point of your purified material.

Tests

To investigate the chemical properties of your product, you should perform the following tests and note down your observations:

1. Place a microspatula tip of product that you have obtained in the bottom of a test-tube. Add 2 cm^3 of water and gently shake the mixture.
2. Place a microspatula tip of the product that you have obtained in the bottom of a test-tube. Add 1 cm^3 of 0.1 M $AgNO_3$ solution and gently shake the mixture. **Dispose of all test residues into the appropriate waste bottle.**
3. Measure the melting point of your product.
4. Measure the mass of product and of the unreacted tin metal.

b) Tetraiodobis(triphenylphosphine oxide)tin(IV), $(Ph_3PO)_2SnI_4$

SnI_4 (1.0 g, 1.6 mmol) and Ph_3PO 0.95 g, 3.4 mmol are each dissolved in separate portions of dry chloroform (10 cm^3). The two solutions are then mixed and allowed to stand in a stoppered flask for about 25 minutes. The dark orange crystalline product is filtered off and dried in a vacuum desiccator.

2.17.2 Exercises

1. Write equations for the formation of SnI_4 and $(Ph_3PO)_2SnI_4$. Calculate your yields.
2. Rationalise your observations for the tests in a).
3. Draw the isomeric forms of $(Ph_3PO)_2SnI_4$. Suggest how you might differentiate between the different isomers.
4. Why are stannic halides rendered more inert by complexation?

2.18
Silicon Oxygen Compounds and Siloxane Polymers

Paul D. Lickiss

Since the 1940's, the interest in non-silicate silicon oxygen compounds (siloxanes and silanols) has grown enormously and they have been transformed from being laboratory curiosities to the products of a billion dollar a year industry. The interest in this type of compound stems from their useful combination of properties. The polysiloxanes, usually known as silicones (as their structure was initially thought to be $R_2Si=O$, i.e. analogous to ketones), may be prepared on a large scale and they are generally chemically and biologically inert, thermally stable, and have useful surface and electrical properties. These properties also vary by a relatively small amount with temperature, which allows them to be used over a wide temperature range. Although silanols are not bulk industrial products, the study of them is important as they are the intermediates from which polysiloxanes are made. The preparations below show how steric effects are important in the stabilization of silanols towards condensation and how rings and polymers containing Si–O bonds may be made.

Special Safety Precautions

1. Chlorosilanes R_nSiCl_{4-n} (R = alkyl, aryl, etc.; n = 1–4) hydrolyse readily in the atmosphere to give HCl which is highly corrosive. Hydrolytic reactions should, therefore, be carried out in a fume cupboard. This also applies to the opening of commercial bottles of chlorosilanes, which often have a simple screwcap lid. Spillages of chlorosilanes should be treated with sodium carbonate.
2. Dimethyldichlorosilane, diphenyldichlorosilane and the organic solvents diethyl ether, ethanol, hexane, toluene, ethyl acetate and *t*-butanol are all volatile and highly flammable and should be treated with appropriate care.
3. An oil bath at 200 °C is potentially dangerous. Check that the oil in the bath is suitable for using at such high temperatures for several hours without smoking. The smoke from such a bath may be toxic and should not be inhaled. A silicone oil bath is best for such heating, which is best carried out in a fume cupboard.

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4. Concentrated hydrochloric acid and sodium hydroxide solutions are both very corrosive and contact with skin, eyes, *etc.* should be avoided.

2.18.1 Experimental

a) Hydrolysis of Me_2SiCl_2

Prepare (in a fume cupboard) a solution of dimethyldichlorosilane (10 cm^3) in diethyl ether (20 cm^3) in a 100 cm^3 conical flask. Cool the solution in an ice-water bath and add water (20 cm^3) dropwise using a pipette or burette taking care to swirl the solution as the addition is carried out. Do not allow the solution to get warm. After the addition is complete, separate the two layers using a separatory funnel and then put the aqueous layer back into the separatory funnel and extract it with hexane or 60–80 petroleum ether (15 cm^3). Combine the two organic layers and neutralise the HCl in them with sodium bicarbonate solution. Then separate off the organic layer and dry it over $MgSO_4$. The drying agent should then be removed by filtration and the organic solution placed in a clean, dry and pre-weighed round bottomed flask for use on the rotary evaporator. Remove the volatile materials under reduced pressure and reweigh the flask to obtain the yield of the oily siloxane product.

Calculate the yield of oil and record its IR spectrum. Although the Si–Cl bond is strong, silyl chlorides are much more readily hydrolysed than alkyl chlorides. Why is this?

b) A High Molecular Weight Siloxane

Transfer the oil obtained in the experiment above to a 50 or a 100 cm^3 round-bottomed flask with a B24 neck (if it is not already in one) and add about 7% by weight of boric oxide and mix thoroughly for 2–3 minutes. Fit an air condenser or a water condenser with no water flowing through it to the flask and place the flask in a pre-heated oil bath at 200 °C for 3 hours. Allow the product to cool and then pour it out onto a preweighed watchglass, you may need to scrape the material out with a spatula.

Calculate the yield of the product. Roll the product into a ball and record its percentage bounce. Leave the material to stand (for several days preferably) and see what effect this has on its appearance and on the percentage bounce. What gives the polysiloxane its unusual properties?

c) Diphenylsilanediol

Prepare a mixture of toluene (2 cm^3), *t*-butanol (4 cm^3) and water (16 cm^3) in a 50 cm^3 round-bottomed flask and place it in a water bath at room temperature. Stir the mixture for 5 min, allowing it come to room temperature. Add a solution of to-

luene (2 cm^3) and diphenyldichlorosilane (4 cm^3) to the stirred aqueous mixture with a pipette at such a rate as to keep the reaction mixture below 25 °C. When the addition is complete, stir the reaction mixture for a further 5 minutes. Remove the white solid formed by filtration and wash it with water (3 cm^3) and diethyl ether (3 cm^3). Air dry the product.

Record the yield and melting point of the silanediol and record its IR spectrum for comparison with the product obtained from the hydrolysis of dimethyldichlorosilane. Diphenylsilanediol is an example of an organometallic compound that has some beneficial biological effects. It has been found to have anticonvulsant properties and it is an efficient antiepileptic agent. It does, however, like many drugs, have toxic side effects.

d) Octaphenylcyclotetrasiloxane

Add two drops of a 4 M aqueous sodium hydroxide solution to a solution of diphenylsilanediol (1 g) in absolute ethanol (10 cm^3). Boil the resulting mixture under reflux for 20 minutes during which time a white precipitate should form. Cool the flask to room temperature and remove the solid product by filtration. Crystallise the product using a minimum of warm ethyl acetate. Cooling the ethyl acetate solution with an ice-water/salt bath after removal of the first crop of crystals should afford a second crop of product.

Record the yield and melting point of siloxane and record its IR spectrum for comparison with the silanediol starting material.

e) Hexaphenylcyclotrisiloxane

Prepare a mixture of diphenylsilanediol (1 g), diethyl ether (15 cm^3) and concentrated hydrochloric acid (0.5 cm^3) and boil under reflux for three hours. Cool the reaction mixture to room temperature and remove the ether layer carefully with a Pasteur pipette and dry it over $MgSO_4$. Remove the drying agent by filtration and then remove the volatile materials from the remaining diethyl ether solution using a rotary evaporator to leave an oily white solid. Dissolve the product in a minimum of ethyl acetate and cool the product in an ice-water/salt bath to obtain crystals of the trisiloxane product.

Record the yield, melting point and IR spectrum of the product for comparison with the other materials made.

Further Reading

For a review of the preparations, properties and uses of silicones see F. O. Stark, J. R. Fallender, A. P. Wright, in *Comprehensive Organometallic Chemistry*, Vol. 2 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, Oxford, 1982, p. 305.

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For the X-ray crystal structure of $Ph_2Si(OH)_2$ see, J. K. Fawcett, N. Camerman, A. Camerman, *Can. J. Chem.* **1977**, *55*, 3631.

For a discussion of the biological effects of organosilicon compounds including $Ph_2Si(OH)_2$ see, R. Tacke, H. Linoh, in *The Chemistry of Organic Silicon Compounds, Part 2* (Eds.: S. Patai, Z. Rappoport), Wiley-Interscience, Chichester, **1989**, Chap. 18.

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For the X-ray crystal structure of $(Ph_2SiO)_3$ see, N. G. Bokii, G. N. Zakharova, Yu. T. Struchkov, *J. Struct. Chem.*, **1972**, *13*, 267 (English translation of *Zhur. Strukt. Khim.* **1972**, *13*, 291).

2.19
Preparation and NMR Identification of Two Phosphorus Esters

Christopher Glidewell

Phosphorus forms many oxo-acids, most of which form many esters. In this experiment, two esters are prepared and identified.

Phosporus(III) chloride reacts with alcohols in the presence of base to form trialkyl phosphites (Eq. 1). In the absence of base, the reaction between ROH and PCl_3 takes a different course. You are asked to identify the product formed (compound **A**) under these conditions when $R = CH_3$, and also to identify the reaction product of **A** with benzylamine and carbon tetrachloride (compound **B**).

$$PCl_3 + 3\,ROH + 3\,B \rightarrow P(OR)_3 + 3\,B\cdot HCl \qquad (1)$$

Special Safety Precautions

1. Phosphorus trichloride (PCl_3) is very moisture sensitive and is toxic by inhalation. Handle it **only** in a fume cupboard.
2. Carbon tetrachloride is toxic by inhalation or contact.
3. Carbon tetrachloride should be recovered and recycled by distillation.

2.19.1
Experimental

a) Preparation of A

Set up, in a fume cupboard, a 250 cm^3 3-necked flask equipped with a magnetic stirrer, ice bath, dropping funnel and condenser. Attach a tube from the top of the condenser to the water pump and fit a $CaCl_2$ tube to the dropping funnel.

Put 100 cm^3 CCl_4 and 9.6 g MeOH into the flask, and 13.7 g PCl_3 into the dropping funnel. Turn on the water pump with the release tap open. Add the PCl_3 dropwise with stirring. When addition is complete, continue stirring with the water pump still

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on for a further hour. Remove the solvent on the rotary evaporator. Distill under oil-pump vacuum to obtain **A**. Record the distillation conditions and the yield.

b) Preparation of B

Into a conical flask containing 100 cm^3 CCl_4, place 1.1 g of **A**, then 2.2 g of $PhCH_2NH_2$. Mix well and leave to stand overnight. Filter off the white solid (this is hygroscopic, so do not pump for too long), dry a small sample in a vacuum desiccator and record its melting point and infrared spectrum (Nujol). Attempt to identify it. Meanwhile, evaporate the filtrate to obtain **B** and record the yield. Check the purity of both **A** and **B** by GLC.

c) Spectroscopy of A and B

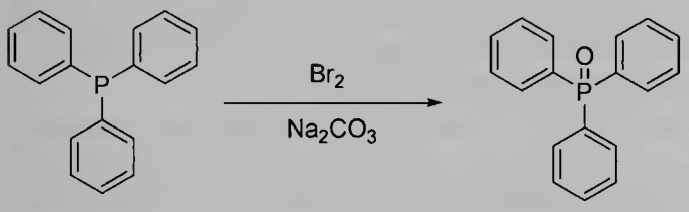
For each of your products **A** and **B**, as well as for an authentic sample of $(MeO)_3P$, record an infrared spectrum, a ^1H NMR spectrum in the range $-2 \rightarrow +13$ ppm, and ^{31}P NMR spectra (with and without proton decoupling) in the range $0 \rightarrow +200$ ppm. Assign all the NMR absorptions and identify **A** and **B**. Suggest a mechanism for the formation of **A** and **B** (the identity of the white solid discarded during the preparation of **B** may be helpful here).

Predict mechanistically the products of the reaction between MeBr and $P(OMe)_3$. There are two phosphorus containing products formed in the reaction between $PhCOCH_2X$ (X = halogen) and $P(OMe)_3$: predict mechanistically what these might be.

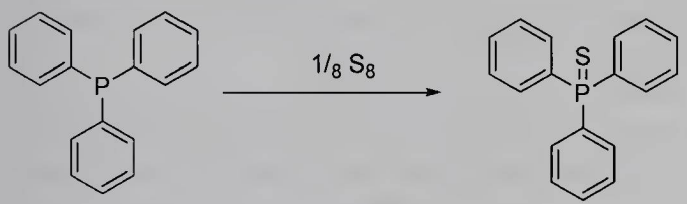
2.20
Synthesis of Triphenylphosphine Oxide and Triphenylphosphine Sulfide

Iain A. Smellie

In this experiment, triphenylphosphine will be used to prepare triphenylphosphine oxide (1) and triphenylphosphine sulfide (2). The exercise will introduce some of the analytical techniques that are used to characterise chemical compounds.



1



2

Special Safety Precautions

Bromine is volatile, toxic and causes serious burns on skin contact, and must be handled in a fume cupboard. Toluene, acetone and petroleum spirit are volatile and highly flammable solvents. Dichloromethane is harmful if inhaled or swallowed and is a suspect carcinogen. Powdered sulfur and triphenylphosphine are harmful if swallowed and are respiratory irritants.

Note: For large classes, it was found to be convenient for the instructor to distribute bromine from a burette mounted in a fume cupboard.

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2.20.1 Experimental

a) Preparation of Triphenylphosphine Oxide

Place 1.5 g of triphenylphosphine in a 250 cm^3 conical flask. Add 20 cm^3 of dichloromethane from a measuring cylinder and swirl the mixture until the phosphine dissolves. Add 0.5 cm^3 of bromine to the flask; this material is highly volatile and toxic (*handle with care! Do not leave flasks containing bromine on the open bench*).

Place the reaction flask on a stirrer hotplate, add a magnetic stirrer bar and start the mixture stirring. *Slowly* add 30 cm^3 of saturated aqueous sodium carbonate solution to the phosphine/bromine mixture using a Pasteur pipette (*you might observe some frothing, DO NOT allow the reaction to become too vigorous!*). On completion of the addition of the basic solution, allow the reaction mixture to stir until the solution turns from the initial red–brown colour to pale yellow. Stop stirring the mixture; this should result in the formation of two liquid layers.

Transfer the flask contents into a separating funnel, rinse the reaction flask with dichloromethane (20 cm^3) and transfer the washings into the separating funnel. Shake the funnel gently (*Care:* remember to hold the stopper and to release any pressure in the funnel!) to extract the product into the organic layer.

Run off the organic layer into a 100 cm^3 conical flask and dry over anhydrous magnesium sulfate. Filter the dichloromethane solution through a small cotton-wool plug directly into a clean, *dry* round-bottomed flask. Wash the cotton-wool with solvent and press dry with a glass rod. Remove the solvent using a rotary evaporator.

Transfer the crude product into a clean 100 cm^3 conical flask and recrystallise from *not more than* 10 cm^3 of toluene.

On cooling, white crystals should appear. When crystallisation appears complete, cool in an ice–water bath for 10 minutes. Filter off the crystals using a Buchner funnel and wash them with 10 cm^3 of cold light petroleum. Weigh the dried crystals and calculate a percentage yield. Record the melting point of the purified material.

b) Preparation of Triphenylphosphine Sulfide

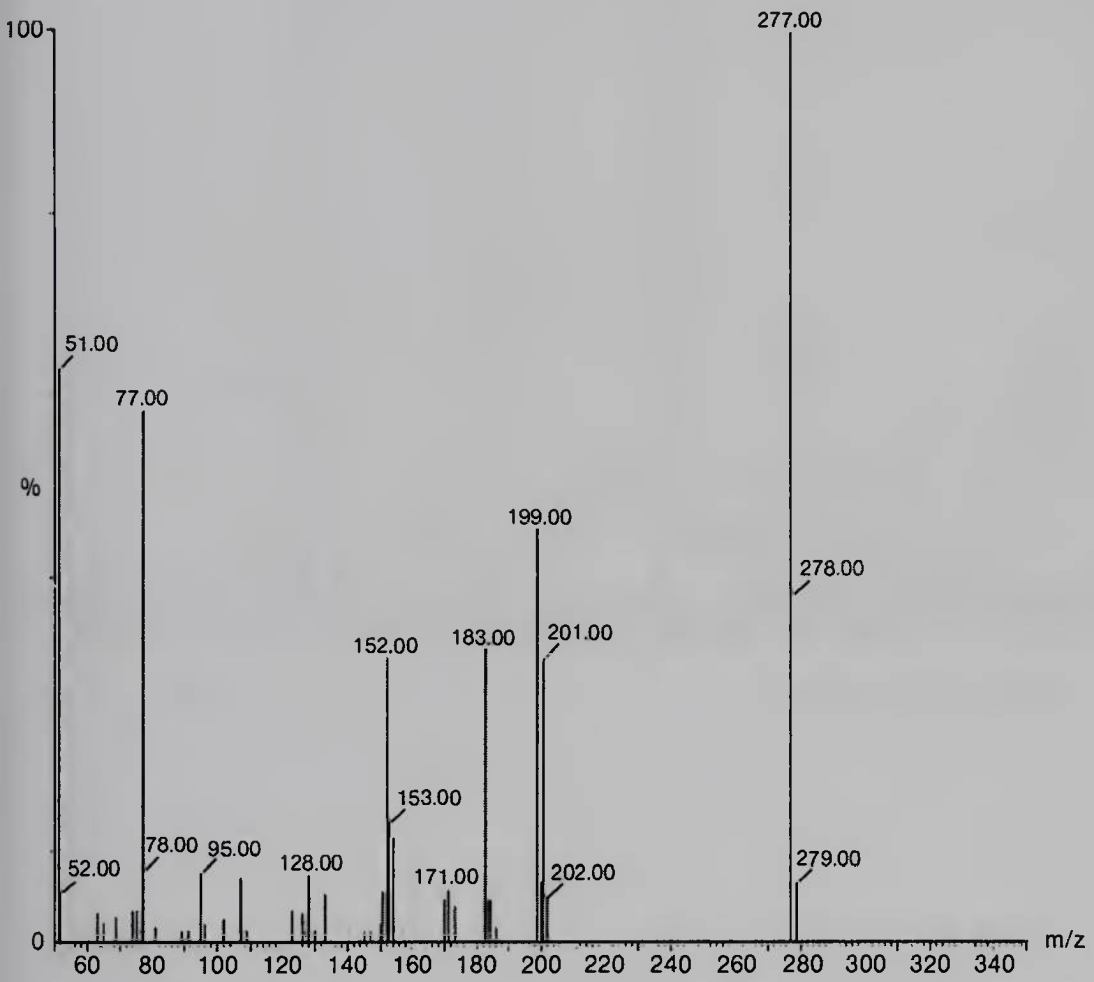
Add 1.25 g of triphenylphosphine and 0.16 g of elemental sulfur into a 100 ml round bottom flask. Add 20 cm^3 of toluene from a measuring cylinder and three or four anti-bumping granules. Connect a reflux condenser to the water supply. (*Ensure there are no leaks*). Secure the flask with a clamp and equip with a reflux condenser.

Heat the solution to reflux for 45 minutes. After the heating period is complete, remove the solvent (conventional distillation or rotary evaporator) and cool. Recrystallise the solid from a minimum volume of acetone. Weigh your dried crystals and calculate a percentage yield. Record the melting point of the purified material.

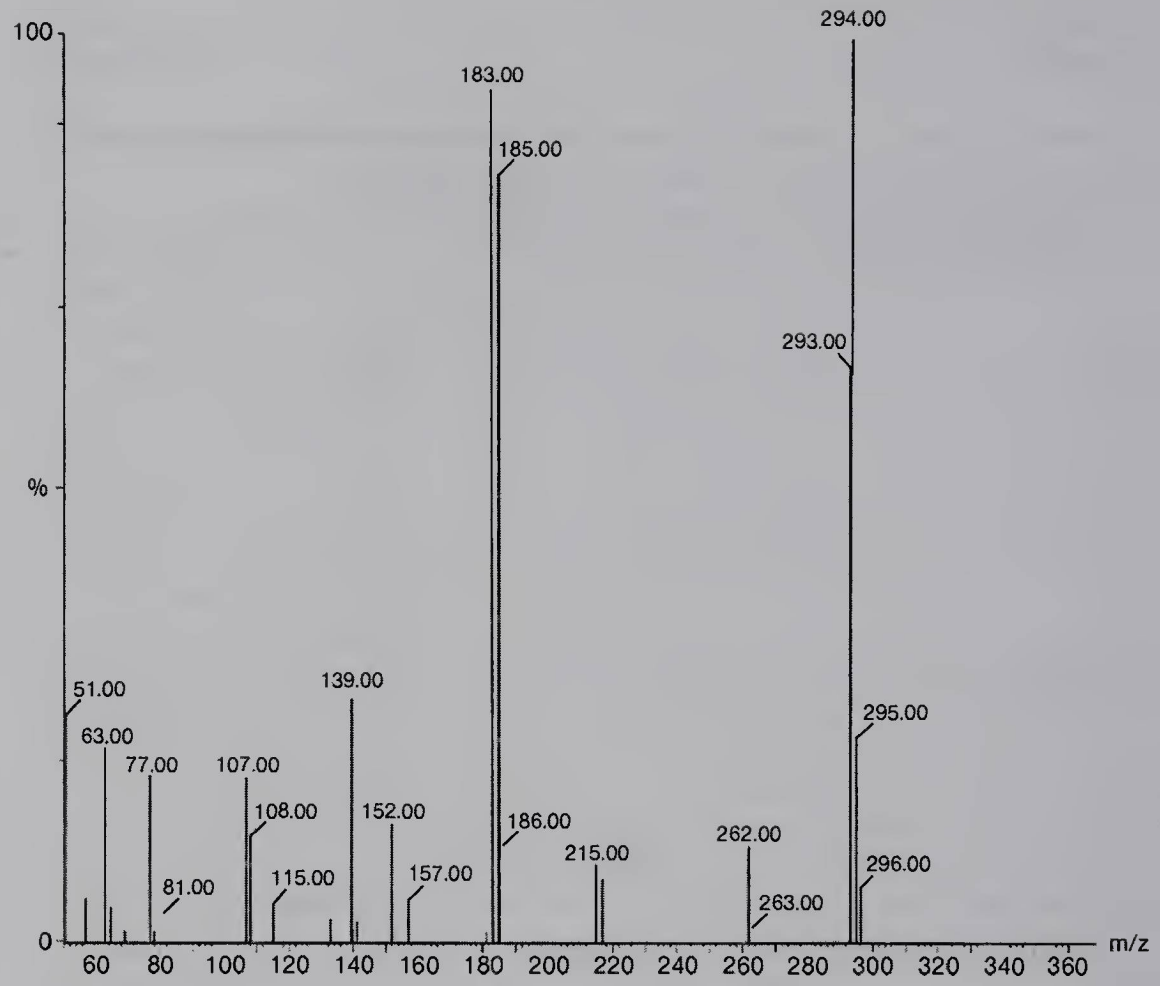
2.20.2 Exercises

Record IR spectra of triphenylphosphine and the oxide and sulfide that you made and compare the three spectra. Note any significant differences.

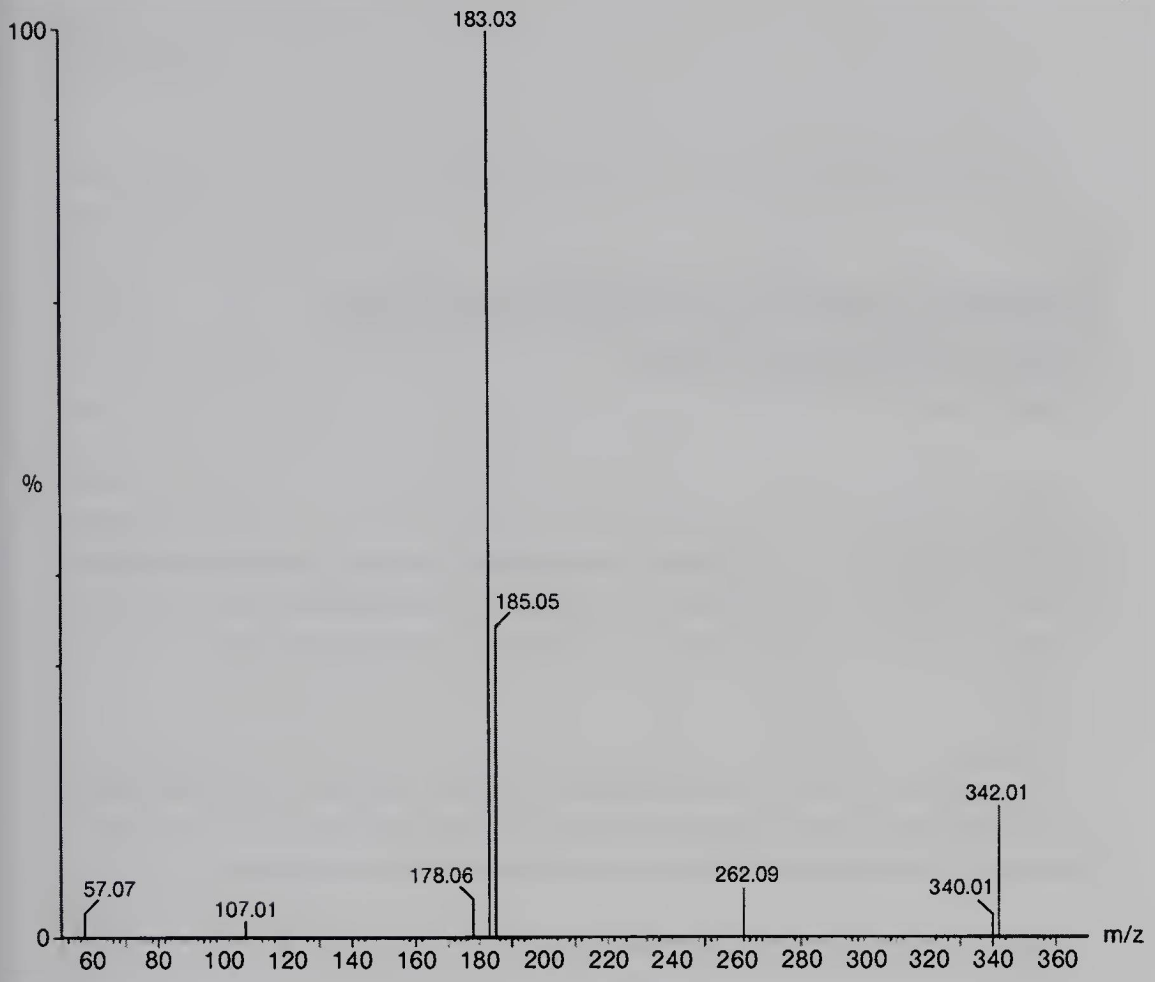
Interpret the mass spectra of the three compounds.



Mass Spectrum of $Ph_3P=O$



Mass Spectrum of $Ph_3P=S$



Mass Spectrum of $Ph_3P=Se$

2.21
Preparation of Sodium Trithionate, $Na_2S_3O_6$ and Potassium Trithionate, $K_2S_3O_6$

Andrew G. Platt

Polythionates are a class of compounds which contain the $[O_3S(S)_nSO_3]^{2-}$ ion. These ions are known for $n = 0-7$, although their stability decreases with increase in the number of sulfur atoms. The best know example of a polythionate ion is the tetrathionate ion, $S_4O_6^{2-}$, which is formed during iodine/thiosulfate titrations:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Many preparative routes to other polythionates give a mixture of products which have to separated. The preparation of trithionate requires the careful oxidation of thiosulfate with hydrogen peroxide according to the following equation:

$$2S_2O_3^{2-} + 4H_2O_2 \rightarrow S_3O_6^{2-} + SO_4^{2-} + 4H_2O$$

As can be seen from this equation, sulfate is also formed in the reaction and must be separated by fractional crystallisation to obtain a pure sample of sodium trithionate. Potassium salts are often less soluble than their sodium analogues and can be prepared by metathesis reactions. In the case of sodium trithionate with potassium acetate the potassium salt is precipitated:

$$Na_2S_3O_6 + 2CH_3COOK \rightarrow K_2S_3O_6 + 2CH_3COONa$$

Special Safety Precautions

This preparation requires the use of 30% hydrogen peroxide solution. This is a strong irritant and any contact with skin must be avoided. In the event of contact with the skin, wash immediately with plenty of running water. Take particular care when loading the burette, wear gloves and ensure that you do not raise the beaker of peroxide above head height. The reaction between thiosulfate and 30% hydrogen peroxide is strongly exothermic, and it is important that the addition is carried out in the manner described.

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2.21.1 Experimental

Place 15 g of sodium thiosulfate in a metal beaker equipped with a magnetic follower and add 10 cm^3 of water. Cool the beaker in ice–salt freezing mixture. Carefully clamp a thermometer so that its bulb is just below the level of the liquid and at the side of the beaker, well away from the magnetic stirring bar.

Measure 14 cm^3 of 30% hydrogen peroxide into a burette (*Caution*). Slowly add the hydrogen peroxide dropwise to the thiosulfate. *Caution*: the reaction is vigorous and care must be taken to keep the rate of addition such that the temperature stays below 15 °C. Monitor the temperature constantly and make sure that the cooling bath is replenished with more ice–salt when necessary.

Once the addition is complete, leave the mixture to stand for 1 hour in ice–salt. During this period, you should thoroughly rinse the burette to remove all traces of hydrogen peroxide. Filter the mixture from the precipitated sodium sulfate and wash the solid with 10 cm^3 of methanol. Retain the combined filtrate and washings. Add a further 25 cm^3 of methanol and store the filtrate in a refrigerator until the next practical session. During this period, further sodium sulfate crystallises. Filter off this solid and wash with 20 cm^3 of cold methanol, again retaining the combined filtrate and washings. Add the combined filtrate and washings to 100 cm^3 of methanol and cool in ice for 1 hour. Filter the sodium trithionate and wash with methanol and acetone and dry at the pump. Record the weight obtained and calculate the percentage yield. Record the infrared spectrum and assess the purity of the product, i.e. whether it is free from sulfate.

Dissolve the all the sodium trithionate in water (ca. 1 g of $Na_2S_3O_6$ in 2 cm^3 of water) and add to a solution of potassium acetate (1 g cm^{-3}). The volume of potassium acetate solution should be about half that of the sodium trithionate. A white precipitate should form on mixing. Cool the mixture in ice for 10 minutes and filter. Wash the precipitate with a little ice-cold water and finally with methylated spirits and dry at the pump.

Record the weight obtained and calculate the percentage yield.

2.21.2 Exercises

1. Why was it necessary to use a metal reaction vessel rather than glass?
2. Look up and sketch the structures of three polythionate ions other than trithionate.
3. Briefly describe using balanced equations two methods by which salts of the thiosulfate ion can be prepared.
4. The purity of trithionates can be assessed by reaction with Cu^{2+}:

$$S_3O_6^{2-} + Cu^{2+} + 2H_2O \rightarrow CuS + 2SO_4^{2-} + 4H^+$$

In an experiment to determine the percentage purity of a sample of sodium trithionate, 0.5014 g was reacted with an excess of copper sulfate to give 0.1912 g of CuS. Calculate the percentage purity of the trithionate sample.

Further Reading

This section is adapted from D. P. Kelly, A. P. Wood, *Methods Enzymol.* **1994**, *243*, 475.

2.22
The Preparation of Potassium Peroxodisulfate, $K_2S_2O_8$

Zdirad Žák and Antonín Růžička

One of the possible methods of the preparation of peroxo compounds is an anodic oxidation. In this experiment, we shall prepare potassium peroxodisulfate, $K_2S_2O_8$, by the anodic oxidation of a saturated $KHSO_4$ solution in dilute H_2SO_4 at 0–3 °C (Eq. 1).

$$2KHSO_4 - 2e^- \rightarrow K_2S_2O_8 + 2H^+ \quad (1)$$

Since peroxodisulfate is poorly soluble in this medium, it collects on the bottom of the electrolyser.

Special Safety Precautions

1. Concentrated sulfuric acid is a highly corrosive substance. Avoid contacts with skin, it can cause severe burns. Protective gloves and safety goggles should be worn all time.
2. Potassium peroxodisulfate is a strongly oxidising agent. Its contact with inflammable substances should be avoided.

2.22.1
Experimental

a) $K_2S_2O_8$

The solution of $KHSO_4$ will be prepared by dissolving K_2SO_4 in 38% H_2SO_4. Prepare 140 ml of 38% acid (*Warning:* pour acid in the water and not *vice versa!*) and dissolve 22 g of K_2SO_4 in the still hot solution. Cool the solution first with tap water and then in an ice bath to 3 °C. Excess $KHSO_4$ crystallises from the solution on cooling. Meanwhile, set up the electrolyser according to the drawing in the following figure. Place a 1000 ml beaker on a magnetic stirrer, insert the electrolyser (with mag-

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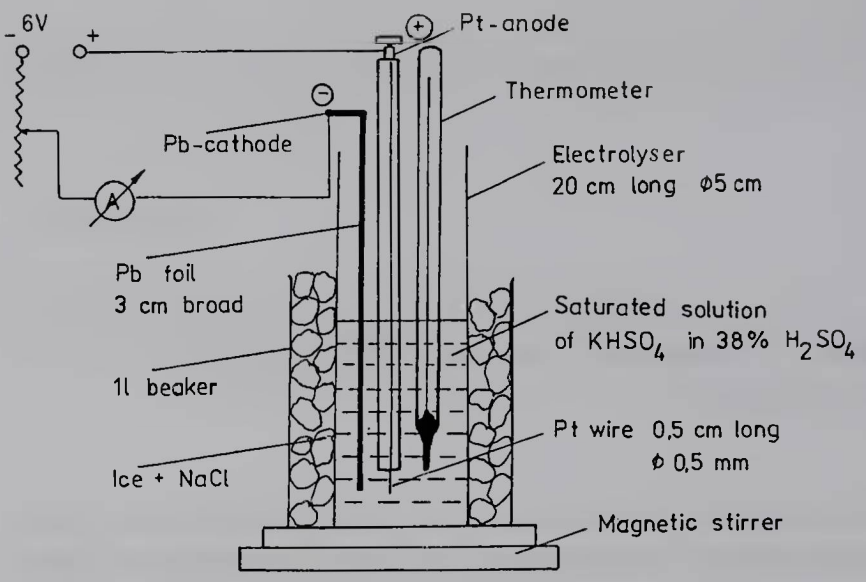

netic stirring bar) in the beaker and fill the space between the electrolyser and the beaker with an ice-salt mixture. Decant the cool saturated solution of $KHSO_4$ into the electrolyser (save the solid for further work) and switch on the electric source. Adjust the current through the electrolyser to approx. 1 A (the current density on the Pt anode should be ca. 10 A cm^{-2}). Under continuous stirring, allow to electrolyse for 90 minutes. Be sure that the temperature of the solution does not rise above 3 °C, supply fresh ice and salt if necessary. Disconnect the electric leads, take the apparatus apart and transfer the precipitated $K_2S_2O_8$ onto a sintered glass funnel and filter. Wash with ethanol (20 ml) and diethyl ether (20 ml) and dry in desiccator over anhydrous $CaCl_2$ *in vacuo*. Weigh the dried product and determine the contents of peroxodisulfate in the product by iodometric titration.

b) Determination of the $K_2S_2O_8$ Purity

Potassium peroxodisulfate is a strong oxidant. Water solutions of peroxodisulfates oxidise iodides (in the presence of NH_4Cl catalyst) to iodine which is determined by the titration with thiosulfate. The reactions can be described by Eqs. (2) and (3).

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2 \qquad (2)$$

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^- \qquad (3)$$

Insert 3–4 g KI and 3–4 g NH_4Cl in a 300 ml Erlenmeyer flask with ground stopper. Add 150 ml of water, dissolve and heat the solution to 30–40 °C. Quantitatively wash a weighed sample (see Note) into the lukewarm solution, close the flask with the glass stopper and allow to stand for 15 minutes. The solution will turn brown with liberated iodine. Open the flask, rinse off the stopper into the flask and titrate with a 0.1 M solution of $Na_2S_2O_3$ until faintly yellow. Add 5 ml of a starch solution

and continue the titration until the solution is completely decoloured. Calculate the percentage of $K_2S_2O_8$ in the prepared product.

Note: The amount of weighed sample should be equivalent to 15–20 ml of 0.1 M $Na_2S_2O_3$.

c) Recovery of K_2SO_4

Transfer the solid phase which remained after the decantation of the satured $KHSO_4$ solution in the electrolyser to a sintered glass funnel and vacuum filter. Wash with ethanol (20–30 ml) and ether (20–30 ml) and dry in a desiccator *in vacuo*. The isolated crystalline substance is not usually pure $KHSO_4$. Depending on the concentrations of K_2SO_4 and H_2SO_4 in the solution, it has a general composition $aK_2SO_4 \cdot bKHSO_4$. Detailed knowledge about the equilibrium between the solid phase and its saturated solution is obtained from the study of the $K_2SO_4/H_2SO_4/H_2O$ phase diagram. Weigh the dried salt and determine its exact composition by alkalimetric titration.

Weigh about 1.8 g of the salt to the nearest 0.1 mg and transfer it quantitatively into a 100 ml volumetric flask. Add 50 ml of water to dissolve the salt and then fill the flask to the mark. Stopper the flask and mix it by inverting at least three times. Pipette 20 ml aliquots (3n) and titrate each with 0.1 M NaOH. From the average consumption of NaOH, calculate the content of $KHSO_4$ in the salt. Calculate the amount of KOH necessary to neutralise all $KHSO_4$ to K_2SO_4 in the isolated salt. Dissolve the salt in a minimum of water in a 600 ml beaker and neutralise with a 20% solution of KOH. Cool with tap water and precipitate K_2SO_4 from the solution by addition of approx. 200 ml of ethanol. Filter and allow to dry in air.

Further Reading

H. Hecht, *Präparative Anorganische Chemie*, Springer-Verlag, Berlin, 1951.

2.23
Polyiodides, Me_4NI_x

Andrew W. G. Platt

There are many examples of polyhalide ions, anions containing halogen atoms only. These can be considered as being derived from a simple ionic halide, e.g. KI and a molecular halogen such as I_2 to give the triiodide ion I_3^-, pentaiodide I_5^-, etc. ions. Many other examples are known such as tribromide and trichloride ions and those which contain more than one type of halogen atom such as ICl_2^-, etc.

By far the most important polyhalide ion is the triiodide ion. The formation of I_3^- is responsible for the increase in solubility of iodine in water in the presence of iodide ions. The intense blue colour observed in iodine thiosulfate titrations is due to a complex formed between the starch and the triiodide ion.

Although I_2 forms the I_3^- ion in solution with any source of I^-, stable complexes can only be isolated in the presence of large cations. One of the reasons for this is that the lattice energies of solids which have a large anion (*i.e.* the polyhalide) and a small cation such as Na^+ or K^+ tend to be low compared with those of NaI or KI. Thus, attempted crystallisation of NaI_3 from solutions of iodine and sodium iodide tends to lead to isolation of either very unstable polyhalides, which decompose at room temperature, or of sodium iodide.

In this experiment, you will attempt to prepare polyiodides using the tetramethyl ammonium ion, $(CH_3)_4N^+$, as the large cation.

2.23.1
Experimental

a) Tetramethylammonium Triiodide

Finely powder 1 g of tetramethylammonium iodide and place in a beaker with 25 cm^3 of alcohol and add 1.3 g of iodine. Heat the mixture on a steam bath until all the white solid has dissolved. Allow to cool slowly to room temperature and finally cool in ice. Filter under suction, wash with a little diethyl ether and dry in air. Record the weight obtained and calculate the percentage yield.

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b) Analysis

One of the accepted ways for chemists to prove that they have made the compounds they claim is by obtaining satisfactory elemental analyses. This usually means determining the percentage by weight of one or more of the elements present in the compound. In the case of the compound you have synthesised, iodine is the easiest element to determine.

Weigh accurately about 0.2 g of the product into a flask and add about 20 cm^3 of ethanol. Swirl the contents of the flask and add 50 cm^3 of a 0.05 M silver nitrate solution in 10 cm^3 portions. After the addition, the mixture consists of a fine yellow precipitate of silver iodide which must be coagulated before filtration. This is done by heating the mixture on the steam bath until all the precipitate has settled and the supernatant is clear. Filter the silver iodide into a dry preweighed sintered glass crucible, ensuring that all the precipitate is collected. Make a note of the number etched onto the glass for identification. *Do not stick labels or write on the crucibles.* Wash the precipitate with a little water followed by a little ethanol and dry to constant weight.

From the weight of the dry silver iodide obtained, calculate the weight of iodine present (hence the amount of iodine in the original weight of compound) and calculate the percentage of iodine in your sample of Me_4NI_3. Compare your value with the theoretical percentage and comment on the result.

Using a similar procedure to that above, prepare and analyse a sample of tetramethylammonium pentaiodide.

2.23.2 Questions

1. What are the shapes of the I_3^- and I_5^- ions?
2. What would be the products of the thermal decomposition of $KICl_2$ and KBrICl? Explain your answer.

2.24
Interhalogen Compounds

Ivan P. Parkin

The halogens form many compounds amongst themselves in binary combinations that may be neutral or ionic, for example, BrCl, IF_5, Br_3^+, I_3^-. Tertiary combinations are possible but occur only in polyhalide ions such as, for example, $IBrCl^-$.

Neutral interhalogen compounds are of the type XY_n where n is always odd and Y is always the lighter halogen. The compounds are all diamagnetic with the valence electrons present either as bonding pairs or unshared pairs. In these complexes, the X atom can be considered to have a net oxidation state of n^+.

In this experiment, you will prepare the interhalogen ICl and react this with caesium bromide to form a polyhalide. You will determine the formula of the polyhalide by gravimetric, titrimetric and spectroscopic methods.

Special Safety Precautions

1. Chlorine gas is toxic. The whole cylinder should be securely clamped inside a fume cupboard. If in any doubt whatsoever about safe operation of the cylinder, consult a demonstrator. Conduct all experiments with Cl_2 in a fume cupboard.
2. Iodine is toxic, grind the crystals in a fume cupboard.
3. Wear rubber gloves (Marigold) at all times. Iodine monochloride (ICl) is corrosive. If any is split, douse it immediately with thiosulfate solution (preferably) or water. If any ICl(l) gets onto your hands, wash them immediately in dilute thiosulfate solution first and then with water.
4. Chloroform is toxic by inhalation and contact.
5. All apparatus should be dry (oven dried) prior to use otherwise the ICl(l) will decompose.
6. All reactions must be carried out in a fume cupboard.

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2.24.1 Experimental

a) Iodine Monochloride, ICl

In this experiment, as described below, you will prepare iodine monochloride, ICl, by passing dry chlorine through a known mass of iodine until it increases in mass by an appropriate amount.

$$I_2(s) + Cl_2(g) = 2ICl(l)$$

Grind up some iodine using a dry pestle and mortar. Then transfer 8 g into your internal-seal trap (Fig. 2.24-1). The easiest method of transfer is to lay the trap on its side and attach a small glass funnel (with a very short piece of vinyl tubing) to the side-arm. Then stand the trap containing the iodine upright in a beaker as shown in Figure 2.24-1.

Weigh the supported trap on the rough balance in the fume cupboard, and hence work out the mass of the trap when all the iodine has been converted to iodine monochloride.

Pass dry chlorine into the trap slowly (so as not to blow out your product) and shake or swirl the trap gently. After a couple of minutes, weigh the flask on the balance in the fume cupboard to see how near you are to the required mass. Continue passing in chlorine until this mass is reached, *but no longer.* (With excess chlorine, the reaction will continue to give iodine trichloride, ICl_3, so you must be careful not to overshoot.)

Using great care, pour your product through the side-arm of the trap into a dry 25 cm^3 conical flask with a glass stopper. **Stopper it** and label it with your name and the mass. *This must be kept and used in a fume cupboard.*

Run the electronic spectrum of your product in a solution of dry $CHCl_3$. Using a dropping pipette, take only one drop (that is, a minimal amount) of ICl in 10 ml of

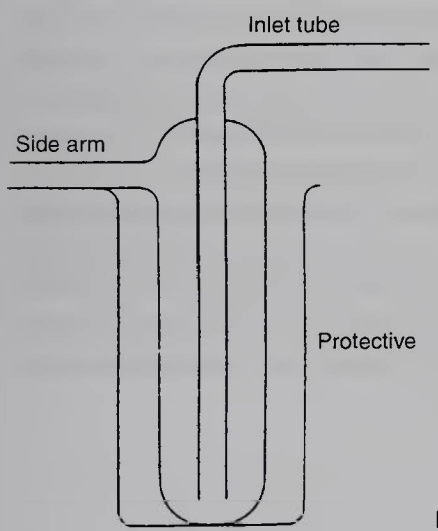

Fig. 2.24-1 The internal-seal trap.

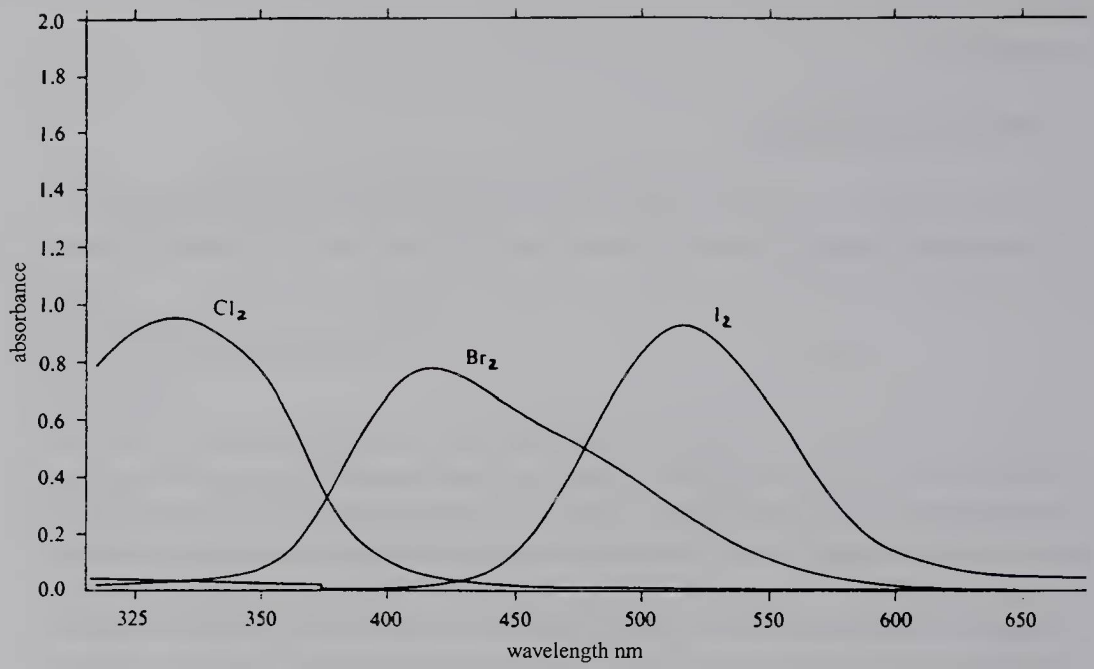

Fig. 2.24-2 Electronic spectra of chlorine (0.013 3 M in CCl_4), bromine (0.004 4 M in CCl_4) and iodine (0.000 9 M in CCl_4). For all three spectra the path length was 10 mm.

solvent. If the solution is too concentrated, dilute it as necessary. Don't forget to keep the solutions, and the iodine monochloride, stoppered. Use a 1 cm silica cell, and obtain the spectrum from 700–325 nm. Compare your spectrum with the electronic spectra of the halogens (Fig. 2.24-2). Which halogen spectrum does the spectrum of your product resemble? Why?

b) A Polyhalide

To investigate this reaction, take 2 g of finely powdered CsBr (use a pestle and mortar) and pour it into your iodine monochloride in the conical flask in the fume cupboard. Stir the mixture very thoroughly with a glass rod for two minutes, ensuring that the CsBr has dissolved completely. Then add 20 cm^3 of chloroform to the mixture, stir well, stopper and leave to stand for ten minutes with occasional shaking. Stir thoroughly again to try to disperse any brown lumps in the product.

To purify your product, transfer it to a small beaker and wash it thoroughly with several small (~5 ml) aliquots of chlorofom (in the fume cupboard), decanting off and discarding the washings, until the final chloroform wash is almost colourless. Filter using a clean dry Büchner funnel. When the residual chloroform has evaporated, transfer your product to a dry sample tube. Stopper it and reweigh. Keep the tube stoppered to prevent damp air from entering.

c) Thermal Decomposition of the Polyhalide

Before you go on to identify the halogen(s) in your product from (b), first heat with a Bunsen burner a *small* portion in a test-tube in the fume cupboard, gently, then strongly, watching to see what happens. Try to devise a method of collecting and identifying the gas given off. Heat until there is no further change, and then identify the residue by heating a small amount on Nichrome wire (what colour is produced?) and by dissolving the solid in water (2 ml) and adding dilute $AgNO_3$ (aq). Discuss your results.

d) Quantitative Analysis of the Polyhalides

Caesium Analysis

It is possible to determine the percentage of caesium in the polyhalide complex quantitatively using *gravimetric analysis*. The method is to take a known amount of the complex in solution, react it with a suitable reagent to form an insoluble caesium compound, filter this off quantitatively, dry it and weigh it. Caesium is determined gravimetrically as caesium tetraphenylborate, $CsB(C_6H_5)_4$, using a solution of sodium tetraphenylborate as precipitant.

Take two no. 4 sintered glass crucibles, label them clearly A and B and with your initials using a soft pencil. Then put them in the oven to dry at 100–120 °C. Weigh accurately about 0.5 g *(but not more than 0.6 g)* of the polyhalide and dissolve it in 40 cm^3 of 1 M HCl. Carefully transfer the solution to a 100 ml volumetric flask and make up to the mark with distilled water. Shake well and pipette 25 ml of the solution into each of two clean 250 ml beakers. To *each beaker* add $\approx$0.1 g of NaI (the amount on the round end of a standard spatula), stir until it dissolves and then add 20 ml of 0.05 M $Na_2S_2O_3$ (sodium thiosulfate or 'hypo'). If the solution does not clear completely, add more thiosulfate solution until it does.

Add 35 ml of distilled water and then place the beaker in an ice-water bath for about 10 minutes. *Slowly* add 40 ml of sodium tetraphenylboron solution with stirring. Stand for 10–15 minutes (but not more than an hour) in the ice-water bath. While the beakers are cooling, take your two crucibles from the oven and put them in a dessicator to cool, then weigh them on an accurate balance. Filter each precipitate through a weighed sintered glass crucible, making sure that *all* the precipitate is transferred. Wash the precipitate several times with small amounts of distilled water. Dry the precipitate at 100–120 °C for 1 hour. Cool in a desiccator and reweigh.

Calculation: Caesium tetraphenylboron contains 29.39 per cent of caesium.

$$\text{percentage Cs in complex} = \frac{\text{mass of precipitate (g)} \times 29.39}{\text{mass of sample (g)}}$$

Iodine Analysis

As a confirmation of the formula of the polyhalide, it is possible to determine quantitatively the amount of iodine in a weighed sample using a volumetric method.

Dissolve an accurately weighed sample of the polyhalide ($\approx$0.5 g) and acidify with a few ml of dilute HCl. (This releases the iodine from the complex.) Titrate the released iodine *immediately* with standard 0.05 M sodium thiosulfate using starch indicator.

The procedure for this titration is to run the sodium thiosulfate into the brown solution until it becomes straw coloured. At this stage, add a few drops of starch indicator. Continue titrating until the blue colouration disappears and the solution becomes colourless.

Only freshly prepared or properly preserved starch indicator should be used, and the *same volume* of starch solution should be added to each titration.

The starch must not be added until just before the end-point is reached, because at high iodine concentration some iodine may remain adsorbed even at the end-point.

The equations for the above reactions are:

$$I^+(aq) + I^-(aq) = 1_2(s)$$

$$2\,S_2O_3^{2-}(aq) + I_2(s) = S_4O_6^{2-}(aq) + 2\,I^-(aq)$$

Calculate the percentage of iodine in your polyhalide.

2.24.2 Exercises

1. From your observations in part c), what elements are present in the polyhalide?
2. From your calculations in part d), together with your observations in part c), suggest a molecular formula for the polyhalide.
3. Based on the VSEPR rules, predict the shape of the polyhalide anion.

2.25
Preparation of $K[ICl_4]$

Iain Smellie

Interhalogens are a family of compounds whose members are comprised of different combinations of halogen atoms in a variety of oxidation states (representative examples include ICl, BrF_3 and IF_7). In this experiment, a potassium salt of the ICl_4^- anion will be prepared and series of tests to investigate the reactivity the product will be conducted.

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

$$6H^+ + IO_3(V) + 2e^- \rightarrow I(III) + 3H_2O$$

$$I(III) + 4Cl^- \rightarrow [ICl_4]^-$$

$$K^+ + [ICl_4]^- \rightarrow K[ICl_4]$$

Special Safety Precautions

Interhalogens and polyhalide salts are toxic, irritating and bleaching materials. The reaction involves the use of concentrated HCl, which is corrosive. The reaction also involves release of toxic and irritating chlorine gas. You should take particular care NOT to get these materials on your skin or clothing and DO NOT breathe any resultant vapours! You should handle all the materials in this experiment in a fume cupboard and be clean and tidy. It is recommended that you remove any jewellery prior to carrying out this experiment, as it may become tarnished. Silver nitrate solution is toxic and is an oxidising agent.

2.25.1
Experimental

Place 3 g of potassium iodate in a 50 cm^3 conical flask. Add in 1 cm^3 portions, from a dry measuring cylinder, 10 cm^3 of concentrated HCl. Warm the mixture *gently* using a hotplate until a yellow solution forms (*DO NOT overheat*! The solution

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should become deep orange–yellow. Use tongs to handle the hot flask!) Allow the solution to cool slowly to room temperature (it may be necessary to scratch the cooled solution with a glass rod to initiate crystallisation). Filter off the crystals using a Buchner funnel *Do not* use a metal spatula to scrape crystals out of the flask! Use the filtrate to wash out any residue in the conical flask. Weigh the dried crystals.

Note: Prolonged storage of $KICl_4$ is not recommended; this material should be treated with 1 M NaOH solution to destroy it.

2.25.2 Exercises

To investigate the chemical properties of your product, you should perform the following tests, note down your observations and provide explanations.

1. Place four microspatula tips of the interhalogen compound in a boiling tube. Heat the sample in a Bunsen burner flame and note the colour of the gas evolved and its effect on contact with moist litmus paper. *Heat the tube until any coloured vapours have been driven off and only a white solid remains* – the residue should be retained for use in exercise 4.
2. Transfer 1 cm^3 0.1 M KCl solution into a test-tube and add five or six drops of 2 M nitric acid. Add 10–15 drops of 0.1 M silver nitrate solution and note the colour of the precipitate. Add 1 cm^3 of 5 M aqueous ammonia to the tube and note down any effects on the solubility of the precipitate.
3. Transfer 1 cm^3 0.1 M KI solution into a test-tube and add five or six drops of 2 M nitric acid. Add 10–15 drops of 0.1 M silver nitrate solution and note the colour of the precipitate. Add 1 cm^3 of 5 M aqueous ammonia to the tube and note down any effects on the solubility of the precipitate.
4. Dissolve the residue from exercise 1 in 1 cm^3 of water and add five or six drops of 2 M nitric acid. Add 10–15 drops of 0.1 M silver nitrate solution and note the colour of the precipitate. Add 1 cm^3 of 5 M aqueous ammonia to the tube and note down any effects on the solubility of the precipitate.
5. Place two microspatula tips of the interhalogen compound in a test-tube and add 2 cm^3 of 0.1 M KI solution dropwise. As you slowly add the solution, note your observations.

Note: If the sample in exercise 1 is not heated until all coloured vapour has been driven off, exercise 4 may result in the formation of a black precipitate of $NI_3 \cdot NH_3$. Concentrated solutions or dry samples of this material can be *explosive*! Any black precipitate from exercise 4 should be treated with 1 M NaOH solution.

2.26
Synthesis and Infrared Spectroscopic Characterisation of Boranes and Germanes

Ivan P. Parkin

This experiment is concerned with the study of certain aspects of boron-hydrogen and boron-oxygen chemistry. Boron has an extensive chemistry. In the first part of the experiment, the ability of sodium borohydride, $NaBH_4$, to reduce GeO_2 to GeH_4 will be investigated by gas phase infrared spectroscopy. Since in the gas phase molecules are generally free to rotate as well as vibrate, the spectrum will show complex vibrational-rotational absorption bands rather than purely vibrational bands. Since rotational quanta are smaller than vibrational quanta (it takes less energy to rotate a molecule in the gas phase than to vibrate a bond), the vibrational-rotational interactions cause a splitting of single vibrational bands into a closely spaced series of bands with a characteristic pattern of intensities.

In the second part of the experiment the strength of boric acid, $B(OH)_3$ will be determined by titrimetric techniques. Finally the preparation of boron hydrides from magnesium borides, using gas phase infrared spectroscopy as a "fingerprinting" technique will be studied.

Special Safety Precautions

1. All preparations must be conducted in a fume cupboard. Wear gloves, safety glasses and a lab coat at all times.
2. Magnesium boride reacts with water evolving highly toxic boranes which can be severe irritants of the mucous membranes.
3. The boranes and germanes released in this experiment are toxic and flammable.
4. Orthophosphoric acid, sodium hydroxide and glacial acetic acid are corrosive and toxic.

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2.16.1 Experimental

a) The Preparation of Monogermane, GeH_4, Using $NaBH_4$

In a **fumehood**, assemble the apparatus as shown in Figure 2.26-1. Begin by putting about 3 g sodalime [$Ca(OH)_2$/NaOH mixture] between cotton wool plugs in the wide side-arm of the infrared cell. The sodalime is necessary to absorb any CO_2 liberated from carbonate impurities in NaOH or $NaBH_4$ on reaction with acetic acid. Then cover each end of the cell with a single layer of cling-film, stretched to give a clear, wrinkle-free window that forms a crudely gas-tight seal to the glass. Put 10 cm^3 of glacial acid in the side-arm test-tube provided, clamp the test-tube in a vertical position at bench level and attach it to the infrared cell via the rubber tubing provided. The narrow side-arm tube from the cell should be vertical to allow escape of hydrogen but not the denser GeH_4.

Procedure

Weigh out about 150 mg of NaOH. Add the NaOH together with the provided preweighed GeO_2 (20 mg) into a 5 cm^3 sample vial, and add 1 cm^3 of water. Stir the mixture until it is a slightly cloudy solution, then cool it in ice. While this is cooling, weigh out about 100 mg of $NaBH_4$ and dissolve it in the cooled sodium germanate (Na_2GeO_3) solution. Insert a dry teat pipette into the hole in the rubber stopper that fits the top of your side-arm test-tube. Suck the Na_2GeO_3/$NaBH_4$ solution into the pipette (try to have the liquid as a single, unbroken column) and put the rubber stop-

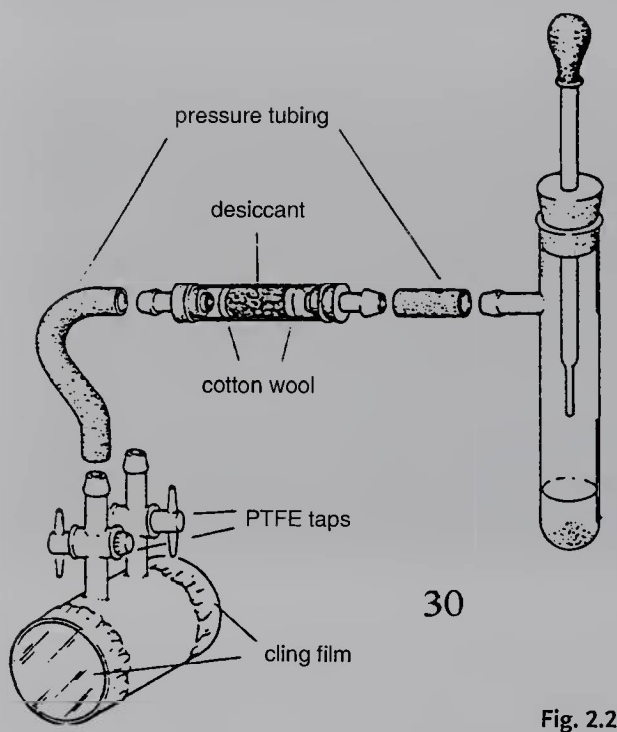


Fig. 2.26-1

per plus loaded pipette into the side arm test-tube. Make sure that the apparatus is set-up in a fume-cupboard like that in Figure 2.26-1. Then squeeze the pipette bulb carefully to add the solution dropwise to the acetic acid over a five-minute period. With each drop, there will be evolution of gas (H_2 + GeH_4) and a yellow-white cloudiness will appear in the acetic acid. When all the solution has been added, allow the apparatus to stand for two or three minutes, then detach the infrared cell from the side-arm test-tube and quickly close up the two PTFE side-arm taps of the cell. The GeH_4 trapped in the cell will remain for several hours if the windows are properly fitted [CARE: GeH_4 is a toxic gas, dangerous at concentrations >0.5 ppm in air].

$$GeO_3^{2-} + 2\,BH_4^- + 4\,H^+ + 3\,H_2O \rightarrow GeH_4 + 2\,B(OH)_3 + 4\,H_2$$

Record the infrared spectrum of your sample of GeH_4 over the range 2400–1900 cm^{-1}. When a satisfactory spectrum is obtained, dismantle your cell and remove the clingfilm windows in a fume cupboard. Push out the soda-lime and wash and dry the cell and side-arm test-tube for use in part c).

Determine the position of the central peak and measure to see if the spacing between other bands is constant or variable.

Note: Clingfilm has no IR absorptions in the range **2700–1900** cm^{-1}.

b) The Strength of Boric Acid

It is possible to convert most boron compounds to the very stable boric acid, $B(OH)_3$, and this is often used in volumetric analysis of boron compounds. However, boric acid is a very weak monobasic acid in aqueous solution and it ionises by abstracting OH^- from water according to the equation.

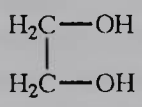
$$B(OH)_3 + 2\,H_2O \rightarrow B(OH)_4^- + H_3O^+$$

There is a very gradual change in pH when alkali is added to boric acid so that it is impossible to titrate $B(OH)_3$ and NaOH to ge a sharp end-point. However, the $B(OH)_4^-$ ion reacts with some *cis*-diols to eliminate water and form complex ions of the type shown (4). This reaction pulls the above equilibrium to the right and makes boric acid appear as a much stronger acid in the presence of suitable *cis*-diols and hence capable of being titrated against NaOH.

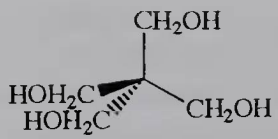
Procedure

Check the validity of the above statements by the following experiments. Titrate 10 cm^3 of the 0.1 M boric acid solution provided against 0.1000 M NaOH (the latter in the burette) using two drops of phenolphthalein as indicator. Note the titre when the solution becomes just pink.

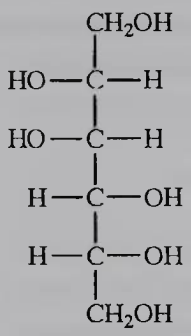
Repeat the titration with fresh 10 cm^3 portions of boric acid in which you have dissolved respectively (1) about 0.5 cm^3 ethylene glycol, (2) about 500 mg mannitol and (3) about 500 mg pentaerythritol (see structures above). Note the titre at the end-



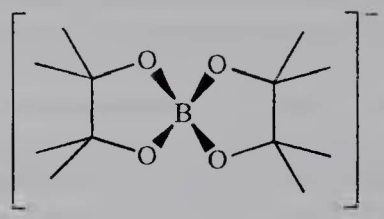
(1) Ethylene glycol



(2) Pentaerythritol



(3) Mannitol



(4) Complex ion

point in each case and using the most appropriate system (either (1), (2), or (3)) obtain consistent titres. Use your results to confirm that boric acid is monobasic.

c) Preparation of Boron Hydrides from Magnesium Borides

Hydrides of non-metals can often be made by hydrolysis of magnesium compounds of the non-metals, e.g. Mg_3N_2 gives NH_3; Mg_3P_2 gives PH_3; Mg_2C_3 gives C_3H_4 (propyne), and Mg_2Si gives SiH_4 and higher silanes, Si_nH_{2n+2}. In this experiment, you will hydrolyse MgB_2 (made by heating magnesium and boron to 900 °C in an inert atmosphere) with orthophosphoric acid. You will pass the liberated hydrogen and boranes directly into your infrared gas cell and then record their spectrum. Boranes sometimes ignite spontaneously in air and they are smelly and very toxic. It is very important that you wear safety glasses and work in a **fume cupboard**.

Procedure

The gas cell and associated side-arm test-tube must be clean and dry. Place about 2 g of anhydrous calcium sulfate between cotton wool plugs in the side arm of the cell (see Fig. 2.26-1). Spread clingfilm over each window of the cell as described for the germane experiment. Clamp the side-arm test-tube in a vertical position at bench level and attach the gas cell. Carefully transfer the solid magnesium boride (200 mg) to the bottom of the side-arm test-tube. Fit a teat pipette through the hole in the rubber bung which fits the side-arm test-tube and then suck about 1 cm^3 water into the pipette. Pour about 3 cm^3 of concentrated orthophosphoric acid on to the magnesium boride and *immediately* stopper the side-arm test-tube with the bung and teat pipette. The orthophosphoric acid reacts slowly with the magnesium boride but on addition of the water from the pipette a vigorous evolution of hydrogen and boranes occurs. The gas mixture is dried as it passes through the anhydrous calcium sulfate

into the cell. When the rapid evolution of gas has ceased, detach the gas cell from the side-arm test tube and immediately close up the PTFE side-arm taps. As quickly as possible after filling the cell record the infrared spectrum of the gases over the range **2700–2000** cm^{-1}, following the instructions on the spectrometer. The bands observed will be broader with less rotational fine structure than seen in the GeH_4 spectrum. Some CO_2 may be produced with the boranes and this will give a broad band around 2350 cm^{-1}.

Remove the clingfilm and the drying agent and clean out the cell and side-arm test-tube in a fume cupboard. Leave these items in a fume cupboard for as long as possible on the day so that all of the germane can dissipate.

2.26.2 Exercises

1. Unlike borane (BH_3) which readily dimerises, boron halides are stable monomers. Why is this?
2. Can you account for the complex nature of the infrared spectrum of germane in the region 2400–1900 cm^{-1}?
3. Comment on why ethylene glycol is less effective than pentaerythritol or mannitol in competing with the borate ion.
4. Use the boranes spectrum to try to determine which boranes were present in the cell by comparison with the band positions listed below for the more common, volatile boranes.

B-H stretching frequencies for boranes (cm^{-1}):

Diborane	B_2H_6	2590 (s)	Pentaborane (9)	B_5H_9	
		2601 (s)			
		2550 (s)			2598 (s)
Tetraborane	B_4H_{11}	2600 (s)	Pentaborane (11)	B_5H_{11}	2600 (s)
		2510 (s)			2500 (s)
		2160 (s)			2050 (m)

Further Reading

Huheey, Keiter and Keiter, *Inorganic Chemistry*, pp. 789–800.
Shriver, Atkins and Langford, *Inorganic Chemistry*, pp. 283–286 and pp. 334–339.

3
Intermediate Experiments

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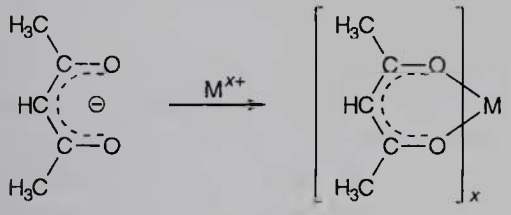
3.1
Metal Acetylacetonate Complexes: Preparation and Characterisation

Christopher Glidewell

Acetylacetone (2,4-pentanedione), $CH_3COCH_2COCH_3$, is a typical β-diketone which can ionise in aqueous solution as a weak acid (Eq. 1).

$$CH_3COCH_2COCH_3 \rightleftharpoons H^+ + CH_3COCHCOCH_3^- \quad (1)$$

The resulting anion can act as a ligand towards metal ions, forming complexes in which the ligand is usually bonded to the metal through both oxygen atoms, hence forming a six-membered ring (Eq. 2).



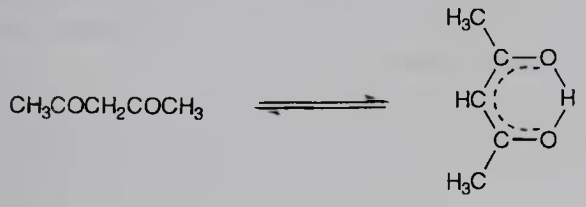
(2)

In general, the complexes isolated as crystalline solids are neutral so that a metal ion M^{x+} forms a complex having the stoichiometry $M(CH_3COCHCOCH_3)_x$ (Eq. 3).

$$xCH_3COCH_2COCH_3 + M^{x+} \rightleftharpoons xH^+ + M(CH_3COCHCOCH_3)_x \quad (3)$$

In the complexes, since the MO_2C_3 six-membered rings are planar and contain 6 π-electrons, they may be regarded as weakly aromatic. In $M(CH_3COCHCOCH_3)_3$ complexes the MO_6 array is octahedral, in $Cu(CH_3COCHCOCH_3)_2$ the CuO_4 group is square planar and in $VO(CH_3COCHCOCH_3)_2$, the VO_5 group is square pyramidal.

In pure acetylacetone, or in its solution in non polar organic solvents, the diketo form is in equilibrium with a cyclic enol-like form (Eq. 4).



(4)

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This second tautomer may be regarded as a complex in which the proton H^+ takes the role of the metal ion M^{x+}.

In this experiment, you will prepare and purify one metal complex (consult a demonstrator about this), and identify the components in a mixture of complexes using thin-layer chromatography. You will also interpret ^1H and ^{13}C NMR spectra and mass spectra of representative examples.

Special Safety Precautions

1. Vanadium pentoxide, V_2O_5, is toxic.
2. Cyclohexane is flammable.
3. All organic liquid waste from recrystallisations must be placed in the waste bottles provided.

3.1.1 Experimental

a) Metal Acetylacetonates

Al^{3+} Complex

Weigh into a 100 cm^3 conical flask 3 g (3 cm^3; ca. 0.03 mol) of acetylacetone, using a dropping pipette to transfer the liquid into the flask. Add 40 cm^3 of distilled water followed by 8 cm^3 of 5 mol dm^{-3} ammonia solution (dil. NH_4OH). Dissolve 3 g (ca. 0.005 mol) of aluminium sulfate $[Al_2(SO_4)_3 \cdot 16H_2O]$ in 30 cm^3 cold distilled water. To the almost clear solution add the ammoniacal acetylacetone solution in portions with shaking. After complete addition of the acetylacetone, check the pH using blue litmus paper (or pH paper) and, if the solution is still acidic, add further small portions of 5 mol dm^{-3} ammonia solution until it is neutral to litmus. Allow to stand for 15 minutes. Filter off the cream coloured product at the water pump, wash with 100 cm^3 of cold distilled water and suck dry for 10 minutes.

Transfer the dry product to a weighed sample tube and dry in a vacuum desiccator over anhydrous $CaCl_2$. Weigh the dry product and calculate the percentage yield (Eq. 5).

$$Al^{3+} + 3CH_3COCH_2COCH_3 \rightarrow 3H^+ + Al(CH_3COCHCOCH_3)_3 \qquad (5)$$

Recrystallise a small sample (ca. 0.5 g) from cyclohexane. The reslulting needles should be filtered at the water pump, washed with a little cold cyclohexane, and sucked dry for 15 minutes. Record the melting point.

$(VO)^{2+}$ Complex

Place 5 cm^3 distilled water in a 50 cm^3 "Quickfit" round-bottomed flask and slowly add to it an equal volume of concentrated H_2SO_4. Then add 12 cm^3 of ethanol followed by 2.5 g (ca. 0.014 mol) vanadium pentoxide, V_2O_5. Add a water cooled vertical condenser and reflux this mixture for about 1.5 hours over a small bunsen flame. The solution will turn a dark blue-green colour. Cool the mixture under the tap and filter using cotton wool, discarding any solid residue. Add 6 cm^3 of acetylacetone dropwise to the filtrate with shaking. Neutralise the mixture by adding it carefully to a solution of 20 g of anhydrous Na_2CO_3 in 150 cm^3 distilled water, contained in a 500 cm^3 conical flask, while stirring the mixture using a magnetic stirrer. The resulting mixture should then be cooled in ice water for 15 minutes before filtering at the pump. Wash the dark green product with cold distilled water (2 × 15 cm^3). Suck dry at the pump for 15 minutes, then dry in a vacuum desiccator over anhydrous $CaCl_2$. Weigh the dried product and calculate the percentage yield (Eqs. 6 and 7).

$$V_2O_5 + 4H^+ \rightarrow 2(VO)^{2+} + 2H_2O + 1/2\,O_2 \qquad (6)$$

$$(VO)^{2+} + 2CH_3COCH_2COCH_3 \rightarrow 2H^+ + VO(CH_3COCHCOCH_3)_2 \qquad (7)$$

Dissolve a small portion (ca. 0.5 g) of the crude, dry product in 6 cm^3 dichloromethane; carefully decant from any residue. Add 20 cm^3 of light petroleum (b.p. 40/60 °C), swirl the mixture and allow to stand for 10 minutes. Filter off the product at the water pump and wash with cold petroleum (2 × 20 cm^3). Suck dry and record the melting point.

Cr^{3+} Complex

Weigh directly into a 100 cm^3 conical flask 1.4 g (ca. 0.005 mol) of chromium(III) chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) and dissolve it in 50 cm^3 distilled water. Weigh out 10 g urea and add it in 3 or 4 portions to the deep green chromium solution, shaking well after each addition. Then add 3 g (ca. 0.03 mol) of acetylacetone, using a dropping pipette. Shake the resulting mixture, cover it with a watch glass and heat rapidly to 80–90 °C on a hot plate. Monitor the temperature with a short stem thermometer. The solution is initially very dark and almost black in appearance, but as the reaction proceeds, deep maroon plate-like crystals form. After 1.5 hours heating, cool the reaction mixture and filter off the product at the water pump. Do not wash the product: dry it in air. Record the percentage yield (Eqs. 8 and 9).

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2 \qquad (8)$$

$$Cr^{3+} + 3CH_3COCH_2COCH_3 + 3NH_3 \rightarrow 3NH_4^+ + Cr(CH_3COCHCOCH_3)_3 \qquad (9)$$

The urea undergoes slow hydrolysis, liberating ammonia, which then controls the pH of the reaction mixture.

Dissolve a small sample (ca. 0.4 g) in approx. 70 cm^3 of boiling cyclohexane, decant the solution, reduce the volume to about half, and then allow to cool. Filter off the deep red needles at the water pump. Suck dry, then determine the melting point.

Mn^{3+} Complex

Dissolve 2.6 g (ca. 0.013 mol) of manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$) and 6.8 g (ca. 0.05 mol) of sodium acetate in 100 cm^3 of distilled water. Add 10 g (ca. 0.1 mol) of acetylacetone and shake the mixture before adding, portionwise with magnetic stirring, a solution of 0.52 g (ca. 0.003 mol) of potassium permanganate in 25 cm^3 of distilled water (ensure that the $KMnO_4$ is completely dissolved and use a dropping pipette for this addition, which should take 10–15 minutes).

Stir for a further 10 minutes and then add, in a similar manner, a solution of 6.3 g (ca. 0.046 mol) of sodium acetate in 25 cm^3 distilled water. While still stirring, heat the resulting dark mixture on a hot plate to between 60° and 70 °C for 15 minutes (monitor the temperature using a short stem thermometer) and then cool to room temperature. Filter off, at the water pump, the very dark, almost black product and wash it with 60 cm^3 of cold distilled water. Suck dry for 15 minutes and dry it in a vacuum desiccator over anhydrous $CaCl_2$. Weigh the dry product and record the percentage yield.

The stoichiometry of this preparation is complicated. First the Mn(II) complex is formed according to Eq. (10). The manganese(II) then reacts with the manganese(VII) of the permanganate to give manganese(III) (Eq. 11) and, in outline, the overall stoichiometry is in Eq. (12).

$$Mn^{2+} + 2CH_2COCH_2COCH_3 \rightarrow 2H^+ + Mn(CH_3COCHCOCH_3)_2 \quad (10)$$

$$Mn(VII) + 4Mn(II) \rightarrow 5Mn(III) \quad (11)$$

$$5Mn^{2+} + MnO_4^- + 15CH_3COCH_2COCH_3 \rightarrow 4H_2O + 7H^+ + 5Mn(CH_3COCHCOCH_3)_3 \quad (12)$$

The purpose of the sodium acetate is to neutralise the acid released, since acetic acid is a *weak* acid (Eq. 13).

$$7H^+ + 7CH_3COO^- \rightarrow 7CH_3COOH \quad (13)$$

In this preparation, the potassium permanganate is the limiting component on which percentage yields should be based, i.e. 1 mol $KMnO_4$ gives 5 mol product.

To about 0.2 g of the dry crude product contained in a 25 cm^3 conical flask, add 12 cm^3 of cyclohexane and boil on a steam bath for 1 minute. Place a small filter funnel in the neck of the flask to act as a reflux condenser. Allow the mixture to settle for 30 seconds before **carefully decanting** from any solid residue into a clean 100 cm^3 conical flask. Reheat for 1 minute to ensure complete solution before adding 40 cm^3 of light petroleum (b.p. 40–60 °C). Cool slowly to room temperature and, when cool,

further in an ice water bath for 15 minutes. Filter off at the water pump the black lustrous needles, wash with 10 cm^3 of cold light petroleum and suck dry for 15 minutes. Record the melting point.

Fe^{3+} Complex

Dissolve 3.3 g (ca. 0.012 mol) of finely-ground iron(II) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in 25 cm^3 of distilled water. Add, over a period of 15 minutes, a solution of 3.8 g (ca. 0.038 mol) of acetylacetone in 10 cm^3 methanol: stir throughout the addition using a **large** magnetic stirrer. Add to the resulting blood red mixture, over a period of 5 minutes, a solution of 5.1 g of sodium acetate in 15 cm^3 of distilled water, maintaining the stirring throughout. At this point, a red crystalline solid should precipitate. Heat the whole rapidly to about 80 °C using a hot plate (monitor the temperature with a short stem thermometer) and keep at this temperature for 15 minutes, still maintaining rapid stirring. Cool to room temperature under the tap, and then in an ice water bath. Filter off the product at the water pump, wash with 100 cm^3 of cold distilled water and suck dry for 15 minutes. Then dry in a vacuum desiccator over anhydrous $CaCl_2$. Weigh the dry product and calculate the percentage yield (Eq. 14).

The sodium acatate is added to neutralise the acid released: acetic acid is a *weak* acid (Eq. 15).

$$Fe^{3+} + 3CH_3COCH_2COCH_3 \rightarrow 3H^+ + Fe(CH_3COCHCOCH_3)_3 \quad (14)$$

$$3H^+ + 3CH_3COO^- \rightarrow 3CH_3COOH \quad (15)$$

Weigh ca. 0.2 g of the dried crude product into a 25 cm^3 conical flask and add 3 cm^3 distilled water. Warm on a steam bath and add methanol dropwise, maintaining gentle heating, until the crude product *just* dissolves. Cool in an ice water bath for 15–30 minutes. Filter at the water pump, suck dry for 15 minutes and finally dry in a vacuum desiccator over anhydrous $CaCl_2$. Record the melting point.

Co^{3+} Complex

Weigh into a 100 cm^3 conical flask 2.5 g (ca. 0.021 mol) of cobalt carbonate and add 20 cm^3 (ca. 0.20 mol) of acetylacetone. Heat the mixture to about 90 °C on a hotplate with continuous stirring. Monitor the temperature with a short stem thermometer. While maintaining the temperature around 90°C, add dropwise 30 cm^3 of a 10% hydrogen peroxide solution using a dropping pipette. Cover the flask with a watch glass between H_2O_2 additions. The whole addition of the H_2O_2 solution should occupy about half an hour. Stirring should be maintained throughout the addition, and then for a further 15 minutes. Cool in an ice-water/salt bath for 30 minutes. Filter the dark green product at the water pump, suck dry for 15 minutes and then dry in the oven at 110 °C. Weigh the dry product and record the percentage yield (Eqs. 16 to 18).

In this preparation, the Co(II) complex is formed first according to Eq. (16). This Co(II) complex is then oxidised by the hydrogen peroxede (Eq. 17) and the overall stoichiometry may be written as in Eq. (18).

$$CoCO_3 + 2CH_3COCH_2COCH_3 \rightarrow CO_2 + H_2O + Co(CH_3COCHCOCH_3)_2 \quad (16)$$

$$2Co^{2+} + H_2O_2 \rightarrow 2Co^{3+} + 2OH^- \quad (17)$$

$$2CoCO_3 + 6CH_3COCH_2COCH_3 + H_2O_2 \rightarrow 2Co(CH_3COCHCOCH_3)_3 + 2CO_2 + 4H_2O \quad (18)$$

Add ca. 0.3 g of the dried product to 10 cm^3 of toluene and heat for about 5 minutes on a steam bath. Allow to settle for about a minute and carefully decant the very dark solution into a 100 cm^3 flask through a small plug of cotton wool contained in a filter funnel. Reheat the solution and then add 20 cm^3 of boiling light petroleum (b.p. 40/60 °C). Cool to room temperature, and then in an ice water bath for 15 minutes. Filter at the water pump and wash the crystals with 50 cm^3 cold light petroleum. Suck dry and record the melting point.

Cu^{2+} Complex

To a solution of 4 g (ca. 0.025 mol) copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) in 25 cm^3 of distilled water, contained in a 250 cm^3 conical flask, add dropwise over a period of 20 minutes a solution of 5 cm^3 (ca. 0.05 mol) of acetylacetone in 10 cm^3 methanol, while maintaining constant stirring. Add to the resulting mixture 6.8 g of sodium acetate in 15 cm^3 distilled water over a period of 5 minutes. Heat the mixture to ca. 80 °C on a hot plate for 15 minutes, still maintaining rapid stirring. (Monitor the temperature with a short stem thermometer). Cool to room temperature and then in an ice water bath. Filter off the blue-grey product at the water pump, wash with 100 cm^3 of cold distilled water and suck dry for 15 minutes before drying in an oven at 110 °C. Weigh the dry product and record the percentage yield (Eq. 19).

$$Cu^{2+} + 2CH_3COCH_2COCH_3 \rightarrow 2H^+ + Cu(CH_3COCHCOCH_3)_2 \quad (19)$$

The sodium acetate is added to neutralise the H^+ liberated: acetic acid is a *weak* acid (Eq. 20).

$$H^+ + CH_3COO^- \rightarrow CH_3COOH \quad (20)$$

To about 0.2 g of the dried crude product contained in a 100 cm^3 conical flask, add 25 cm^3 of methanol and 2 anti-bumping granules. Place a small filter funnel in the neck of the flask to act as a reflux condenser and boil on a steam bath for 5 minutes. Carefully decant from any solid residue the blue solution into a clean 100 cm^3 flask containing about 5 cm^3 of hot methanol. Cool to room temperature before filtering

off the fine blue-grey needles at the water pump. Wash with a little ice-cold methanol and suck dry at the pump.

Submit labelled samples of your crude and purified products for inspection

b) Thin-Layer Chromatography (TLC) of Metal Acetylacetonate Complexes

TLC is a useful technique for establishing either the number of components in a mixture or, alternatively, that a given substance is pure. For mixtures, it is also possible, by comparison with known substances, to establish the identity of the individual components. The stationary phase is usually silica (SiO_2) or alumina (Al_2O_3) spread in a thin layer of uniform thickness on a glass plate or an aluminium backed sheet. The sheet can incorporate a fluorescent dye for identification of colourless compounds by exposure to ultraviolet light. The mobile phase can be any suitable solvent. The unknown is introduced as a solution in the form of a very small spot, usually applied using a drawn-out melting-point tube. In this experiment, a mixture of metal ions already converted to the acetylacetonate complexes is subjected to TLC and identified by comparison with samples of the pure metal acetylacetonates. It is the neutral character of these complexes, and their solubility in organic solvents, which enables TLC to be done: the chromatography of the uncomplexed ions would be much less easy.

You are provided with seven solutions. One contains a mixture of three metal acetylacetonate complexes, selected from $(VO)^{2+}$, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+} and Cu^{2+} complexes dissolved in dichloromethane. Each of the other six solutions contains one of the pure complexes, also dissolved in dichloromethane. Draw out 7 melting-point tubes for use in spotting the t.l.c. plates (consult a demonstrator here).

Spot the unknown mixture and the pure substances onto the plate, using very small spots (less than 2 mm in diameter). The spots should be in a line about 1 cm from the short edge of the plate. Each solution should be spotted, dried in air and respotted several times: the $(VO)^{2+}$, Cr^{3+} and Cu^{2+} can be respotted up to six times.

Carefully place the plate in the jar containing ca. 0.5 cm depth of a 1% solution of methanol in CH_2Cl_2 (provided in a Winchester bottle) ensuring that the top of the solvent is below the line of spots. Allow to run for ca. 30 minutes, after which time the solvent front should be at least 3/4 of the way up the plate. Measure the R_f values for each spot and tabulate these with the spot colours. Deduce the composition of the unknown mixture.

c) Nuclear Magnetic Resonance Spectra of Acetylacetonates

In this section, the ^1H and ^{13}C NMR spectra of one diamagnetic metal acetylacetonate, $Al(CH_3COCHCOCH_3)_3$, and of acetylacetone itself are examined and assigned.

For the ^{13}C spectra, several different versions of the spectrum were obtained using different pulse sequences. Note that in all the ^{13}C spectra, however, the H–C coupling is suppressed and not displayed. In the normal spectrum, all types of carbon environment (CH_3, CH_3, CH, and quaternary C) are displayed. In the DEPT spectrum, the resonances due to quaternary C are suppressed and those due to CH_2

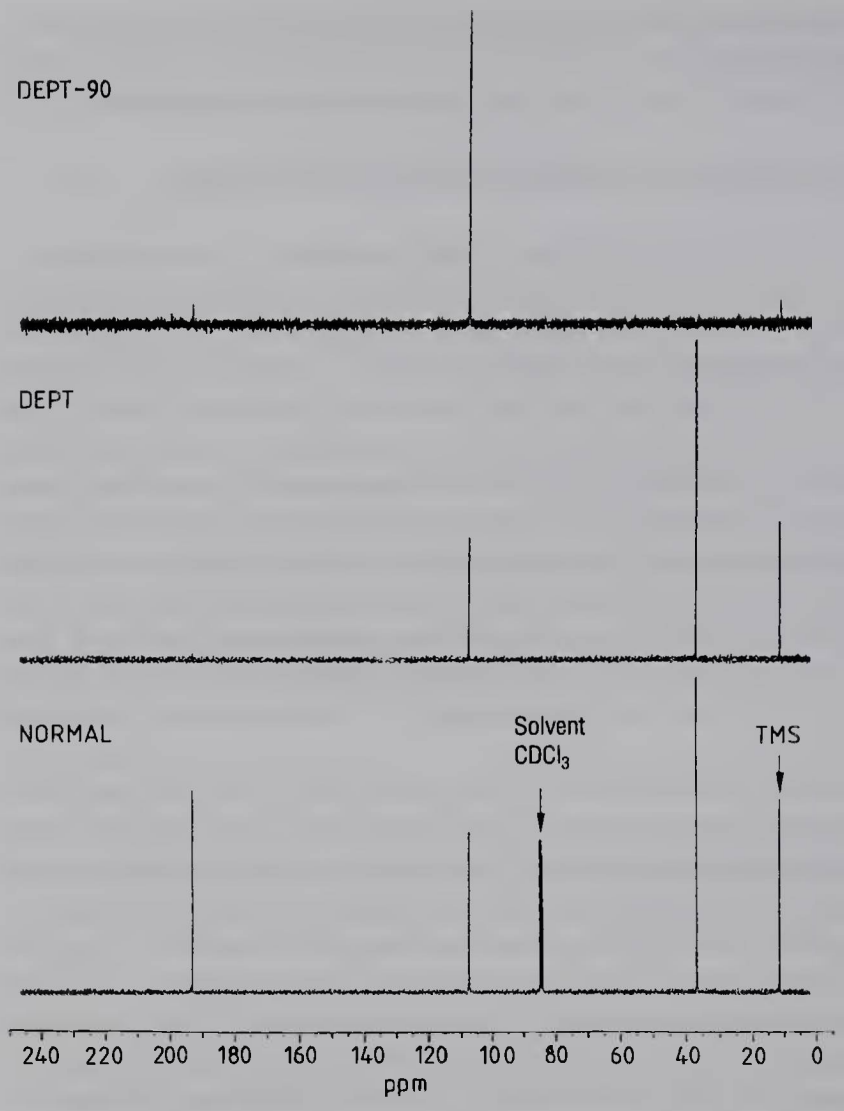

Fig. 3.1-1 The ^{13}C NMR spectrum of $Al(CH_3COCHCOCH_3)_3$.

are inverted, while in the DEPT-90 spectrum, only the resonances due to CH appear. Hence all four types of carbon environment can be readily identified.

Examine first the ^{13}C spectrum of $Al(CH_3COCHCOCH_3)_3$ (Fig. 3.1-1) and, bearing in mind that the three ligands are all symmetrical and equivalent (D_3 molecular symmetry), assign the resonances. Next assign the ^1H spectrum of this complex (Fig. 3.1-2).

In acetylacetone itself, both keto and enol forms are present (Eq. 4). Since the enol form can be regarded as a complex of H^+, its ^1H and ^{13}C NMR spectra may be expected to show similarities with those of the aluminium complex. Examine first the ^{13}C spectrum (Fig. 3.1-3) and assign the resonances due to the enol tautomer by comparison with Figure 3.1-1; then assign the keto resonances. Finally, assign the ^1H spectrum (Fig. 3.1-4), again by comparison with Figure 3.1-2, and calculate the keto : enol ratio.

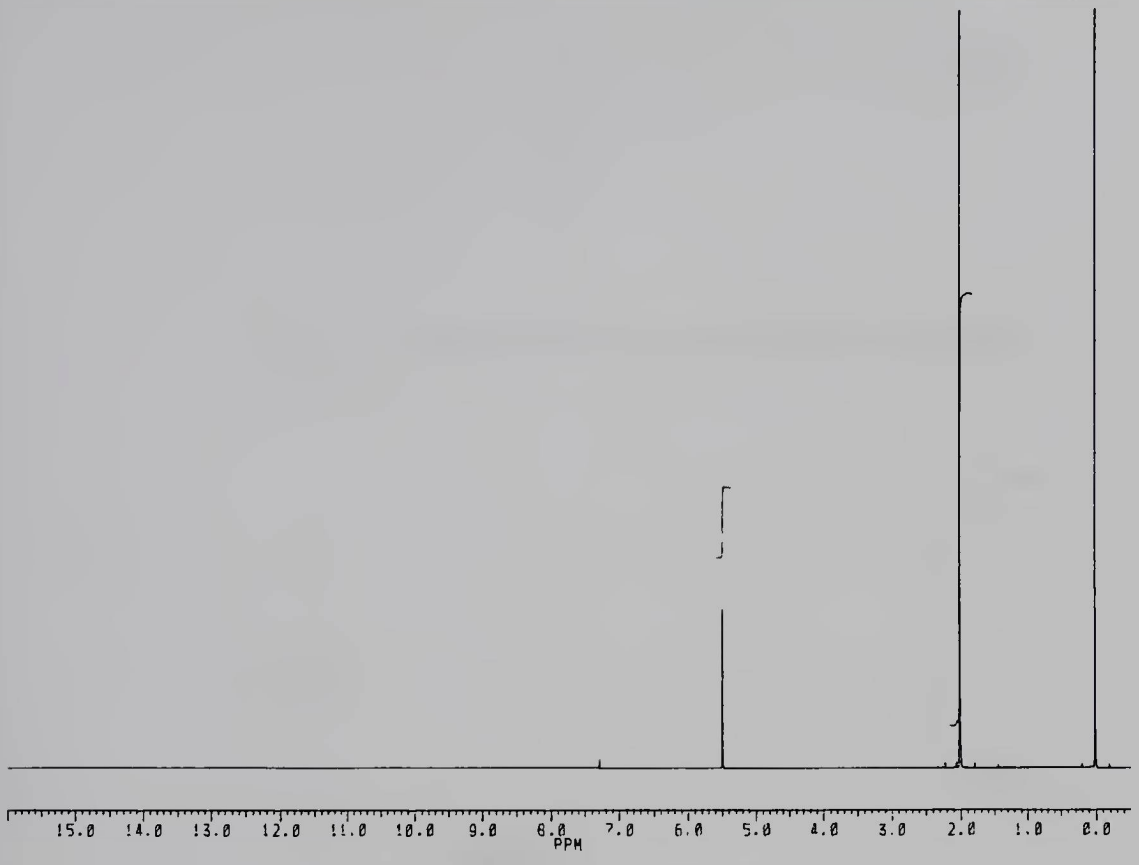

Fig. 3.1-2 The ^{1}H NMR spectrum of Al$(CH_3COCHCOCH_3)_3$.

d) Mass Spectra of Acetylacetone and its Aluminium Complex

The mass spectrum of acetylacetone contains the following peaks (with relative abundances scaled to the most intense as 100%):

m/z	RI (%)
100	67
85	89
72	8
59	8
43	100

Identify the composition of the ions at $m/z = 100$, 85, 72 and 43, and suggest structures for these ions. Suggest also how they might arise. Speculate on the structure of the ion having $m/z = 59$.

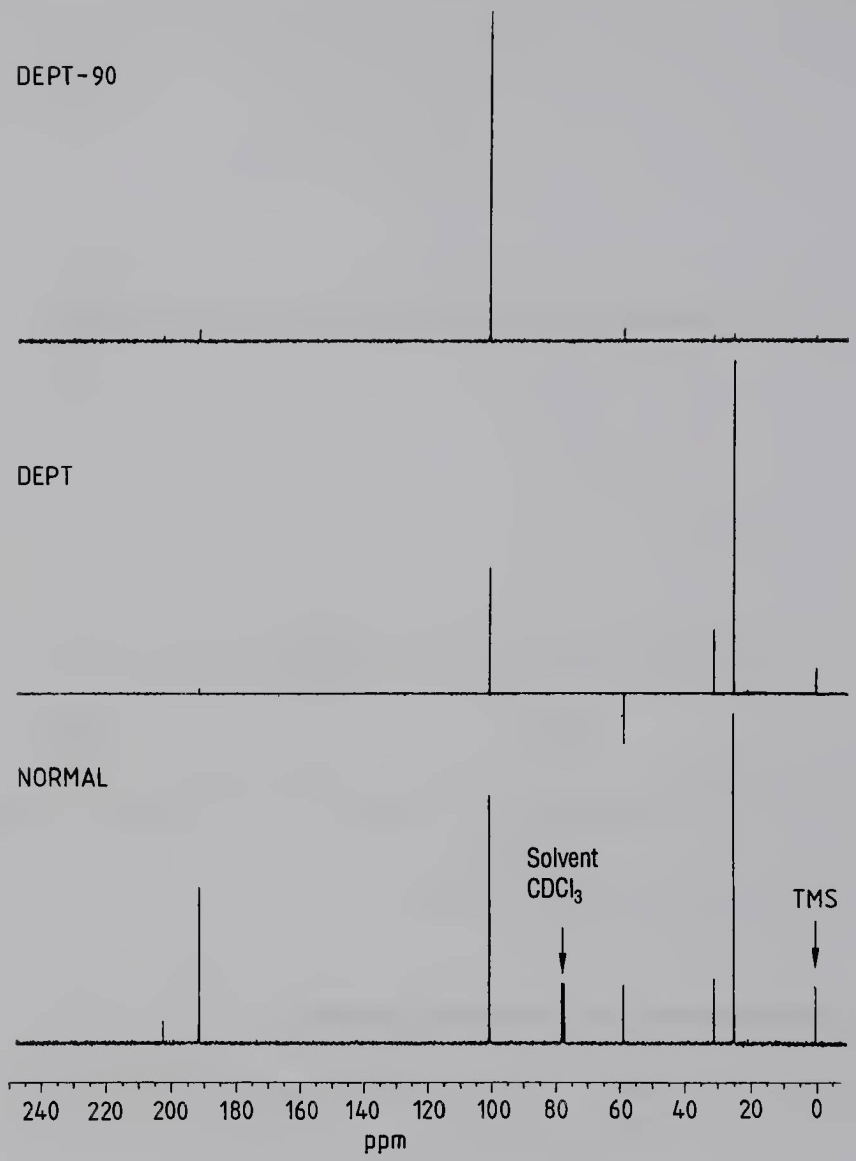

Fig. 3.1-3 The ^{13}C NMR spectrum of $CH_3COCH_2COCH_3$ containing both keto and enol forms.

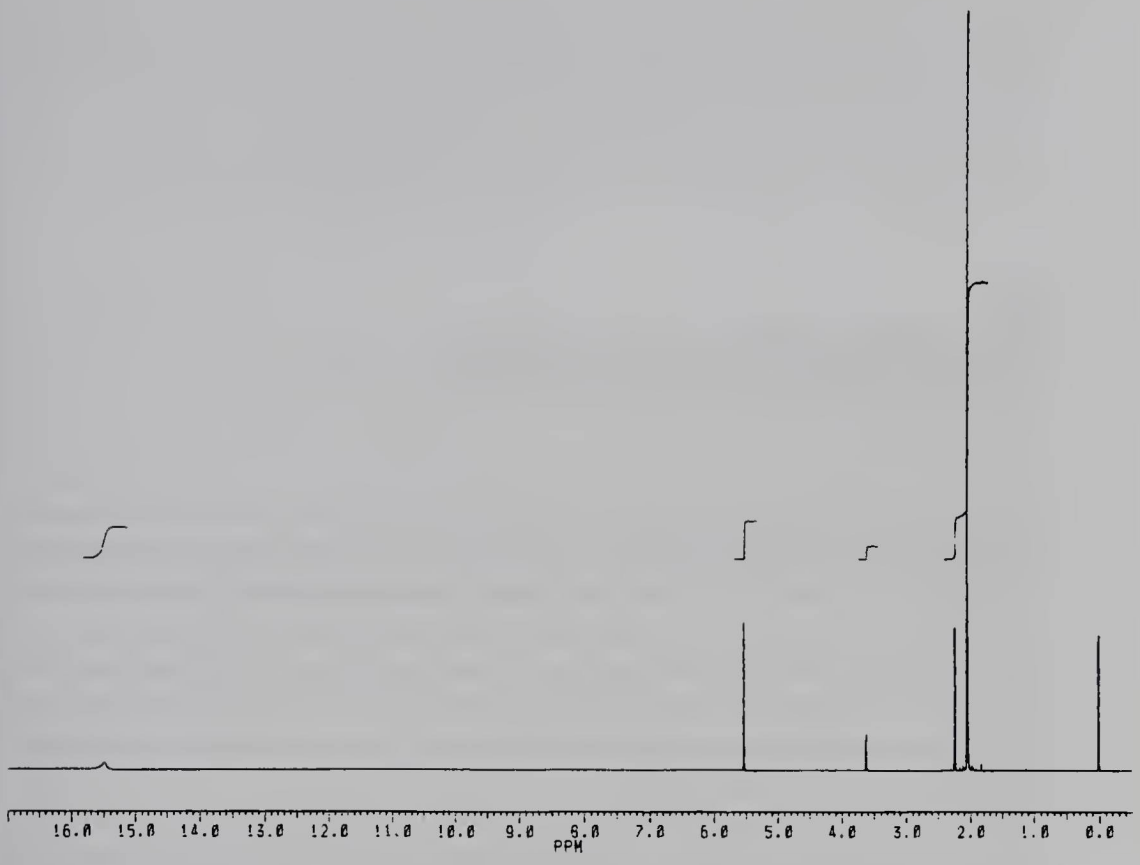

Fig. 3.1-4 The ^{13}C NMR spectrum of $CH_3COCH_2COCH_3$ containing both keto and enol forms.

The mass spectrum of the aluminium complex $Al(acac)_3$ contains the following peaks:

m/z	RI (%)
324	4
226	17
225	100
143	10
141	17
127	5
126	6
43	18

Identify the ions having $m/z = 324$, 225, 126 and 43. Suggest compositions for the ions having $m/z = 226$, 141 and 127. Suggest a structure for the ion having $m/z = 143$, whose composition is $(C_5H_8AlO_3)^+$.

3.2
Nickel Dihalide Phosphine Complexes

Ivan P. Parkin

The physical and chemical properties of a coordination complex are dependent on its geometry. This distinction becomes important when different geometric isomers are possible. For example, *cis* and *trans* isomers and square planar or tetrahedral isomers can have different IR spectra, magnetic moment values and UV spectra.

In this experiment, you will synthesise three nickel halide bis-phosphine complexes and determine their geometry using spectroscopic methods. From this data, you will be in a position to predict the geometry of the complexes and suggest reasons for a specific geometric isomer.

Special Safety Precautions

1. Nickel salts are toxic. They are also irritants. Wear gloves to handle all nickel salts.
2. The carbon disulfide generated in the experimental is highly toxic and flammable. This preparation must be carried out in a fume cupboard.
3. Phosphines are irritants and toxic.
4. Carry out all reactions in a fume cupboard.

3.2.1
Experimental

a) $NiCl_2(PPh_3)_2$

Triphenylphosphine (2.8 g), propan-2-ol (30 cm^3, dried) and two antibumping granules are placed in a dry 100 ml B24 neck round-bottomed flask. The flask is fitted with a B24 reflux condenser and the mixture brought to reflux.

Nickel dichloride (1.2 g $NiCl_2 \cdot 6H_2O$) is dissolved in ethanol (15 ml) in a 50 ml conical flask and the solution warmed to approximately 40 °C. The warm solution of nickel dichloride is added with care down the condenser to the refluxing triphenyl-

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phosphine solution. Normally, the precipitate of $NiCl_2(PPh_3)_2$ will form immediately upon addition. The reaction mixture is allowed to cool to room temperature and the product filtered off using a sintered glass filter and Büchner funnel. Wash the precipitate on the filter with cold ethanol (15 ml) and cold dry ether (15 ml). Dry by suction.

Record the yield, melting point, IR spectrum (4000–200 cm^{-1}), UV spectrum (in toluene or dry $CHCl_3$) and magnetic moment.

b) $[Ni(NCS)_2(PPh_3)_2]$

Charge a B24 100 ml Quickfit round-bottomed flask with nickel nitrate, 1.5 g $Ni(NO_3) \cdot 6H_2O$, ethanol (25 ml) and two antibumping granules or glass beads. Stir or swirl to dissolve, heating gently if necessary. Then add the *finely ground* sodium thiocyanate (0.8 g), top the flask with a B24 reflux condenser and reflux for 20 minutes (during which time you should prepare a phosphine solution as described in the first paragraph of the $NiCl_2(PPh_3)_2$ preparation). Cool the thiocyanate solution in an ice bath, while scratching the inside of the flask with a glass rod to precipitate the sodium nitrate and any unreacted sodium thiocyanate.

Filter the nickel thiocyanate solution through a sintered glass funnel into a Büchner flask. Always remove the tubing from your Büchner flask *before* you turn off the water tap, so that water does not suck back. The thiocyanate solution should be transferred to a conical flask and heated on a hotplate with one or two (not more) antibumping granules. The hot nickel thiocyanate solution is than carefully added down the reflux condenser to the refluxing phosphine solution. The reaction mixture is allowed to cool to room temperature and the product filtered off using a sintered glass filter and Büchner funnel. Wash the precipitate on the filter with cold ethanol (15 ml) and cold dry ether (15 ml). Dry by suction.

Record the yield, melting point, IR spectrum (4000–200 cm^{-1}), UV spectrum (in toluene or dry $CHCl_3$) and magnetic moment.

c) $[NiCl_2(PCy_3)_2]$

A dinitrogen atmosphere is essential to avoid oxidation of the phosphine. Dinitrogen is bubbled through the solution of the adduct $PCy_3 \cdot CS_2$ to remove the carbon disulfide, which is highly flammable and toxic. *This preparation must therefore be carried out in a fume cupboard.*

Assemble the reflux apparatus as shown in Figure 3.2-1. There should be a small amount of liquid paraffin in the dinitrogen trap to prevent air entering the apparatus, and to allow dinitrogen to escape from the apparatus.

Flush the system with dinitrogen by passing a fairly rapid stream of dinitrogen through the apparatus for a few minutes. The pressure should not exceed 25 kPa, which gives a flow rate of about 4 bubbles per second.

Weigh 1.9 g of the tricyclohexylphosphine-carbon disulfide adduct into the flask and add dry propan-2-ol (20 ml) together with antibumping granules. Attach the condenser and pass dinitrogen through the solution for five minutes. Make sure that the dinitrogen inlet is well below the liquid surface.

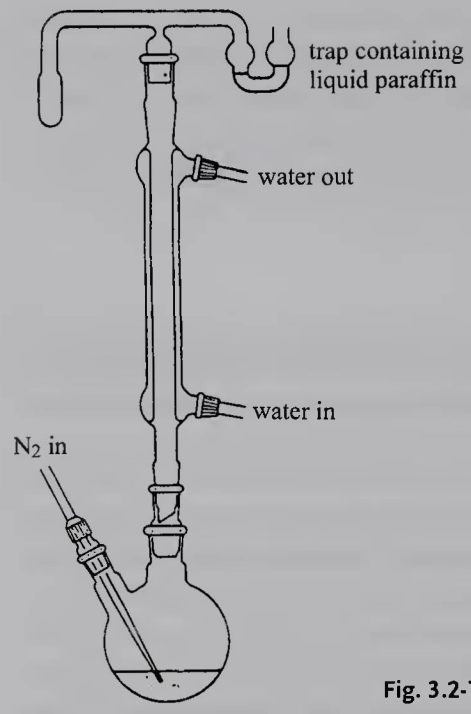


Fig. 3.2-1 Reflux apparatus for the preparation of $[NiX_2(PR_3)_2]$.

Maintain the dinitrogen supply and heat the flask to reflux. If the flow is sufficient, the CS_2 will be driven off within fifteen minutes. The solution will then be clear and colourless (or a very pale straw colour), but you should continue until you are certain that there is no further colour change, and until you are ready to add the warm nickel salt. (You may have to top up with degassed solvent, since this evaporates during the reflux.)

Nickel dichloride (0.6 g $NiCl_2 \cdot 6H_2O$) is dissolved in dried ethanol (15 ml) in a 50 ml conical flask and the solution warmed to 40 °C. The warm nickel dihalide solution is added to the refluxing phosphine carefully down the condenser and the product obtained as previously described for $NiCl_2(PPh_3)_2$,

Record the yield, melting point, IR spectrum (4000–200 cm^{-1}), UV spectrum (in toluene or dry $CHCl_3$) and magnetic moment.

3.2.2 Exercises

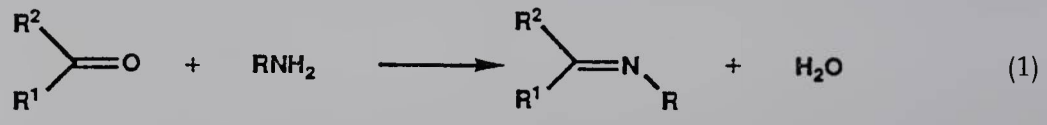
1. Four coordinate nickel complexes can be either square planar or tetrahedral. Draw three diagrams for $NiCl_2(PPh_3)_2$ showing the possible geometric isomers.
2. Metal chloride stretches occur in the infrared between 400–250 cm^{-1}. How many Ni-Cl stretches are seen for $NiCl_2(PPh_3)_2$ and $NiCl_2(PCy_3)_2$? Does this suggest a particular geometric isomer for each complex?
3. Calculate the extinction coefficient ε for the bands in the UV spectra of the three nickel complexes. Does this value suggest tetrahedral or square planar coordination?

4. Draw a simplified splitting diagram for the *d*-orbitals in a tetrahedral and square planar crystal field. Fill in the appropriate number of electrons for Ni^{2+} in both cases. Compare the number of unpaired electrons with the magnetic moments you measured. Does this predict a certain geometry?
5. Compare the ligand field properties of the thiocyanate and chloride ions and use this to explain the differences in the experimental results for $NiCl_2(PPh_3)_2$ and $Ni(NCS)_2(PPh_3)_2$. What are the steric and electronic differences between PPh_3 and PCy_3 which account for your findings?
6. Can you suggest any further methods we could use to differentiate between square planar and tetrahedral geometries?

3.3
Nickel(II) Complexes of Some Schiff Base Ligands

Christopher J. Jones

The condensation of an aldehyde or ketone with a primary amine leads to the formation of an imine linkage with the liberation of one molecule of water as shown in Eq. (1) where R, R^1 and R^2 are hydrocarbyl substituents. The nitrogen atom in the product carries a lone pair of electrons and can function as a Lewis base, forming complexes with transition-metal ions. The first recorded example of such a complex was reported as early as 1840 by Ettling, who isolated a copper complex of the product formed in the reaction between salicylaldehyde and ammonia. However, it was Schiff who, in 1869, established the 1:2 metal:ligand stoichiometry of this complex and lent his name to the compounds containing the azomethine fragment.



(1)

Since these early discoveries, a wide range of complexes derived from Schiff base ligands have been isolated. These compounds have played a major role in the development of modern coordination chemistry, providing examples of macrocyclic ligand systems and the effects of steric interactions on coordination geometries. Schiff base complexes have also been used to model biological systems, such as the haem group and vitamin B_{12} coenzyme, which contain transition metals.

Two general methods may be used to prepare Schiff base complexes. The first entails the prior formation and isolation of the ligand system, followed by its reaction with the metal to form a complex. The second method does not entail prior isolation of the ligand but instead, the condensation and complexation reactions are performed together during a single synthetic process. In fact, there are some ligands which will only form in the presence of a metal ion in a so-called 'template' reaction. In some reactions of this type, it is thought that the metal ion complexes one or both of the ligand precursors before the condensation reaction occurs in what has been called a kinetic template effect. Thus, the metal ion can act as a template orienting the reacting species and controlling the product formed. One example of such a template reaction is provided by the reaction between 1,8-diaminonaphthalene and pyr-

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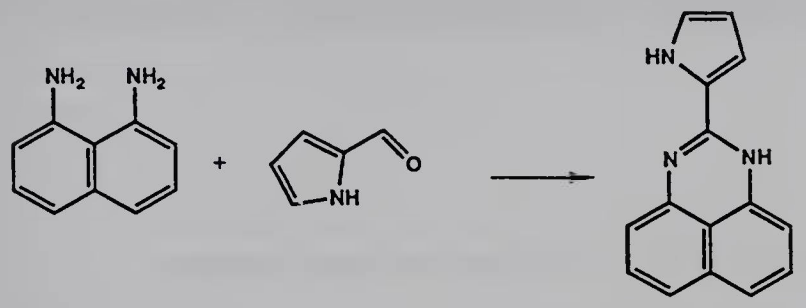
role-2-aldehyde. The normal product of this reaction in air is a heterocycle (Eq. 2). With pyrrole-2-aldehyde in the presence of nickel(II) ions, however, a different product can be obtained as its nickel complex (Eq. 3).



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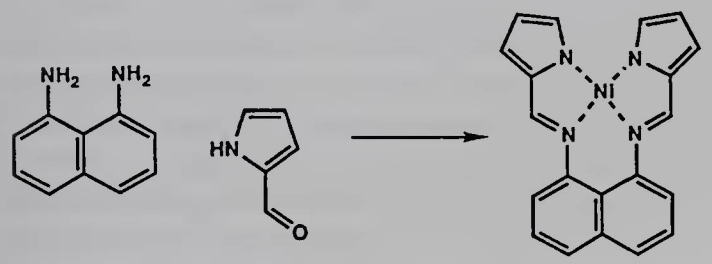

(3)

In the following experiments, nickel complexes of two isomeric ligands derived from diaminopropane and pyrrole-2-aldehyde are prepared using different methods.

^{1}H NMR, MS and IR spectral measurements can be used to investigate the structures of these compounds.

Special Safety Precautions

If any chemicals in this experiment should come in contact with your skin, wash them off immediately with copious amounts of water, then consult a demonstrator. In the event of spillage keep others away from the area of the spill and consult a demonstrator. Absorb the spillage on an inert absorbent (e.g. vermiculite) and remove it to a fume cupboard to be packaged for disposal. Skin contamination by, or inhalation of, these materials must be avoided.

Materials	*Hazards*
Nickel(II) ethanoate, $Ni(O_2CCH_3)_2 \cdot 6H_2O$	Toxic
1,2-Diaminopropane	Corrosive
1,3-Diaminopropane	Toxic, Corrosive
Ethanol	Harmful, Flammable
Dichloromethane	Harmful
Sodium carbonate	Irritant
Petroleum ether 40/60	Irritant, Flammable
Sodium hydroxide	Corrosive

Disposal of Wastes

Waste solvents must be disposed of into the containers provided.
For further information consult the suppliers data sheets.

3.3.1 Experimental

a) A Schiff Base Ligand from 1,3-Diaminopropane and Pyrrole-2-aldehyde

This reaction is to be carried out in a fume cupboard. Dissolve pyrrole-2-aldehyde (0.95 g) in ethanol (5 cm^3) in a round-bottomed flask (100 cm^3). Using a graduated pipette, add 1,3-diaminopropane (0.40 cm^3) to the solution and mix the liquids. Fit a reflux condenser and warm the flask and contents on a steam (or boiling water bath) to boiling for 3–4 minutes and then stand them in an ice bath for 2 hours. The mixture may solidify to a crystalline mass or remain liquid. If a solid has deposited on cooling, collect this by filtration and wash it with a few cm^3 of diethyl ether. The combined filtrate and washings may deposit more product, as crystalline needles, on standing. If the mixture remains liquid, reduce the volume on a rotary evaporatory, until solid starts to appear and then stand the flask in an ice bath to complete the crystallisation. Proceed to collect the product as described above. Allow the product to air dry and record your yield. Obtain the IR (KBr disc), ^1H NMR and mass spectra of your product.

b) A Ni(II) Complex from the Schiff Base Ligand

Dissolve a portion (0.5 g) of the ligand prepared above in a) in warm ethanol (10 cm^3). Slowly add a solution of nickel ethanoate (nickel acetate, $Ni(OCOCH_3)_2 \cdot 4H_2O$, 0.5 g) in water (10 cm^3) to produce a turbid, brick red mixture. Next add a solution of sodium carbonate (0.2 g) in water (5 cm^3) and stir the mixture for 20 minutes. After this time, collect the crude product by filtration and wash it with a little ethanol-water mixture (1 : 1, a few cm^3). Redissolve the red product in dichloromethane (ca. 40 cm^3) and dry the solution over a little magnesium sulfate. Remove the magnesium sulfate by filtration and wash it with a little dichloromethane. Add light-petroleum (80–100 °C, 40 cm^3) to the combined washings and filtrate, then remove the dichloromethane using a rotary evaporator (use a room temperature water bath, do not heat the flask). The red product will precipitate from the light-petroleum as the dichloromethane is removed. The product may be collected by filtration and air dried. Record your yield and obtain the IR (KBr disc), ^1H NMR and mass spectra of your product.

c) A Nickel(II) Complex with 1,2-Diaminopropane and Pyrrole-2-aldehyde

In a fume cupboard, set up a round-bottomed flask (100 cm^3) equipped with twin-necked adaptor, reflux condenser and dropping funnel. Place an ethanol-water mix-

ture (1:1 v/v, 50 cm^3) in the flask along with pyrrole-2-aldehyde (0.95 g), nickel ethanoate (nickel acetate, $Ni(OCOCH_3)_2 \cdot 4H_2O$, 1.25 g) and 3 or 4 anti-bumping granules. Heat the flask to dissolve the nickel ethanoate (a turbid rather than clear solution will form) and then add an aqueous solution of NaOH (10% w/v, 4 cm^3). Dissolve 1,2-diaminopropane (0.4 cm^3) in water (20 cm^3) in the dropping funnel. Add this diamine solution dropwise, over a period of about 20 minutes, to the refluxing suspension of nickel hydroxide and aldehyde. Next add water (10 cm^3) and allow the mixture to cool. Collect the crude orange product by filtration and wash it with a little ethanol-water (1:1). Redissolve the product in dichloromethane (ca. 40 cm^3) while still in the filter funnel and allow the orange dichloromethane solution to filter into a clean conical flask (100 cm^3). Dry this solution with a little magnesium sulfate, remove the magnesium sulfate by filtration and wash the magnesium sulfate with a little dichloromethane. Add light-petroleum (80–100 °C) to the combined filtrate and washings and remove the dichloromethane using a rotary evaporator. (Use a room temperature water bath and do not heat the flask). The orange product will precipitate from the light-petroleum as the dichloromethane is removed and may then be collected by filtration and allowed to dry in air. Record your yield and obtain the IR (KBr disc), ^1H NMR and mass spectra of your product.

3.3.2 Exercises

1. Consult the IR spectra obtained. Given that >N–H bonds give rise to IR bands (νNH) in the region 3000 to 3400 cm^{-1} and that >C=N$^-$ bonds give rise to IR bands (νC=N) in the region 1550 to 1600 cm^{-1}, what evidence do the spectra provide for the formation of a nickel complex from the ligand in parts a) and b).
2. Consult the mass spectra and list the major ions observed. Comment on the appearance of the molecular ion peaks in the nickel complexes and explain why prominent ions are observed at $m/z = 284$ and 286 in each case? How do the spectra of the two isomers differ.
3. Draw the structures of the complexes prepared in parts b) and c). Consult the ^1H NMR spectra and list the shifts and, where appropriate, coupling constants of the signals in these spectra. Show how these spectra are consistent with the structures of the compounds prepared and how the spectra of the two isomeric nickel complexes differ. Explain the appearance of the signals in the region δ_{TMS} 3 to 4 in the NMR spectrum of the compound derived from 1,2-diaminopropane.
4. Square planar complexes of nickel(II) are diamagnetic and exhibit NMR spectra. Use a crystal field splitting diagram to explain why this should be so when octahedral nickel(II) complexes are paramagnetic with 2 unpaired electrons.

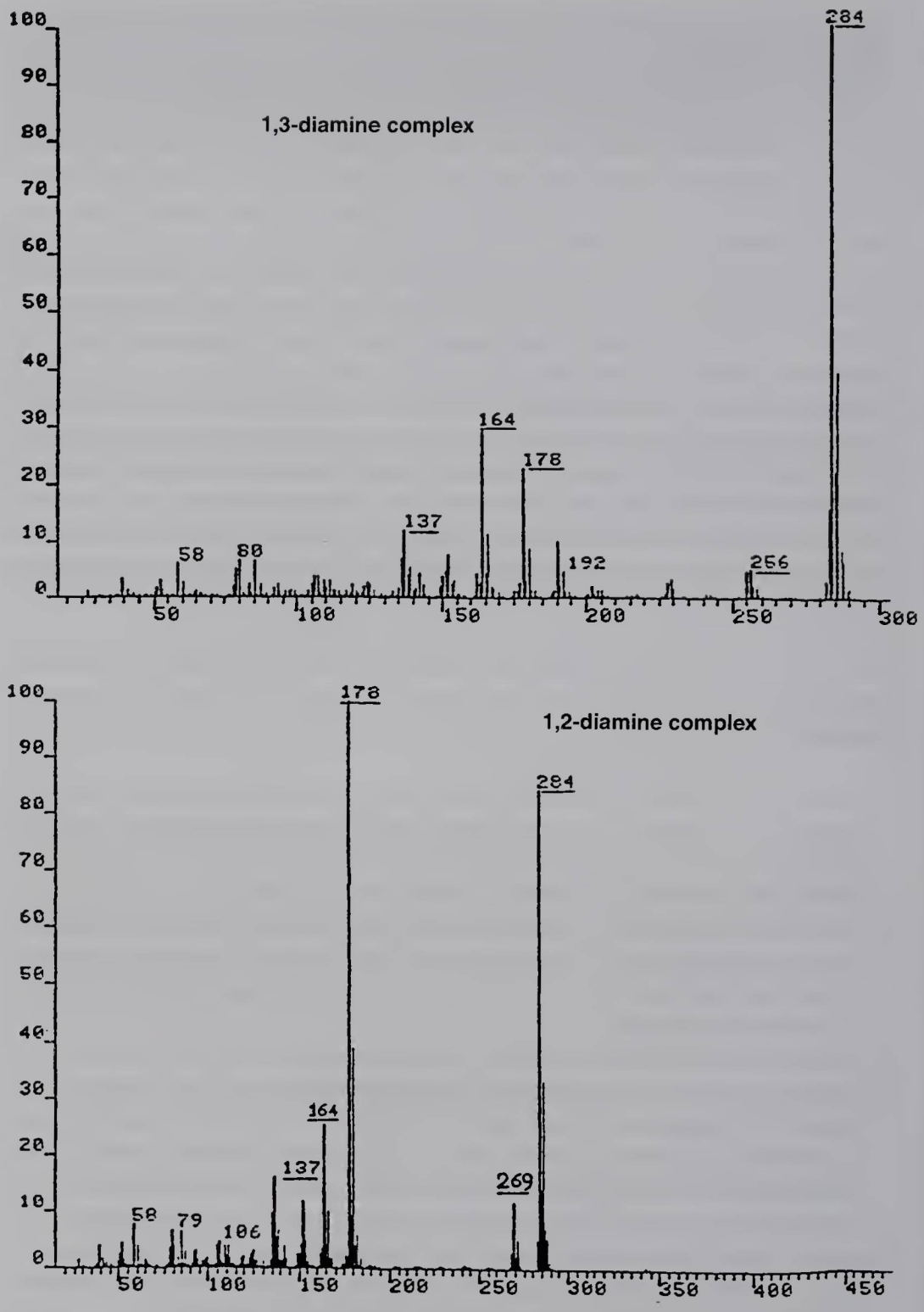

Fig. 3.3-1 Mass spectra of the nickel Schiff base complexes.

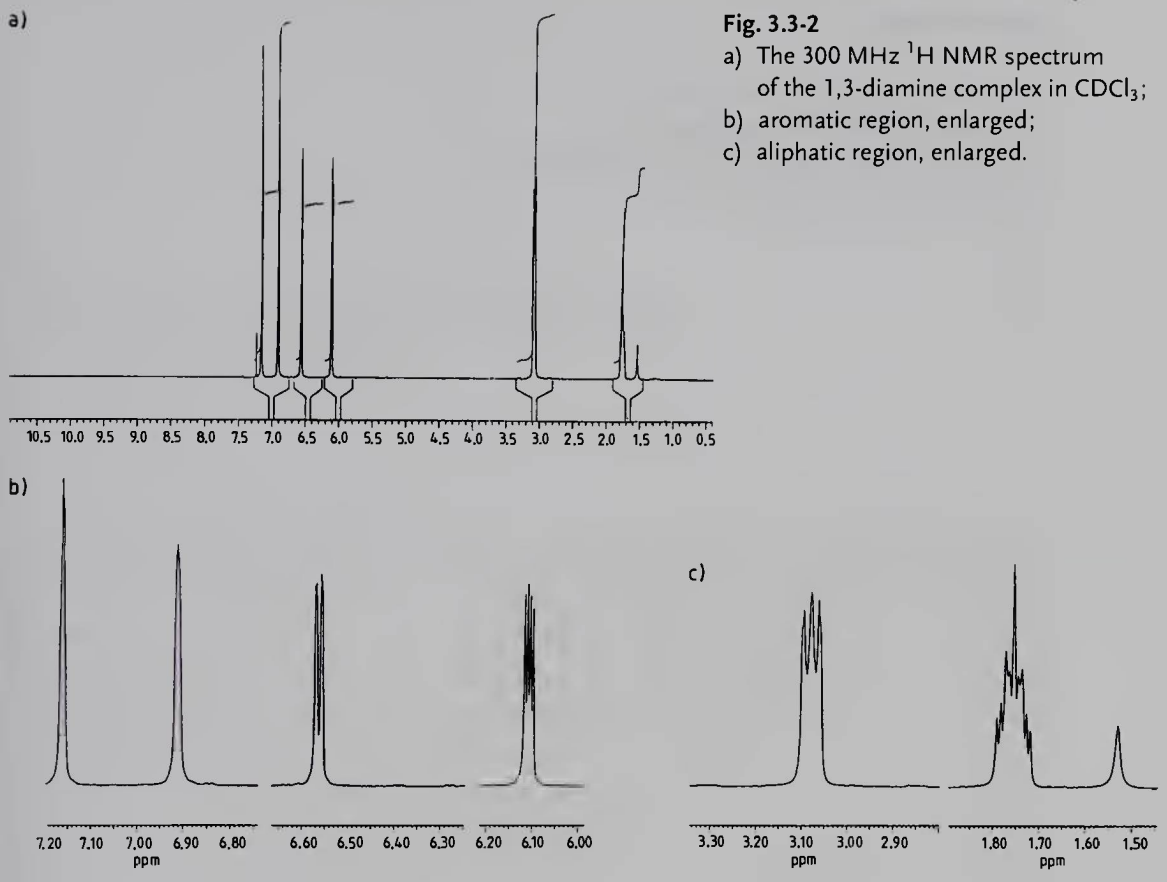

Fig. 3.3-2
a) The 300 MHz ^{1}H NMR spectrum of the 1,3-diamine complex in $CDCl_3$;
b) aromatic region, enlarged;
c) aliphatic region, enlarged.

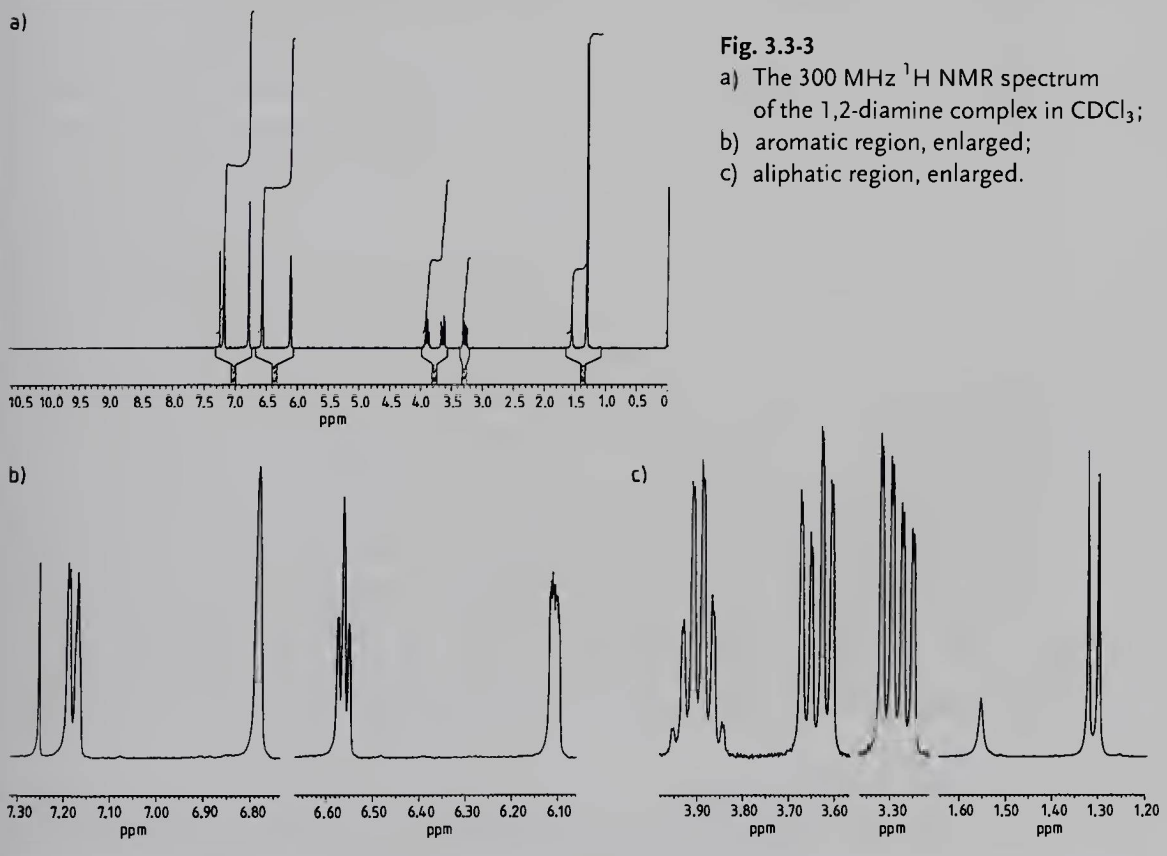

Fig. 3.3-3
a) The 300 MHz ^{1}H NMR spectrum of the 1,2-diamine complex in $CDCl_3$;
b) aromatic region, enlarged;
c) aliphatic region, enlarged.

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3.4
The Synthesis and Coordination Chemistry of Macrocyclic Complexes

Martin Schröder

Macrocyclic ligands are ligands in which the donor atoms are contained within the same ring. Common examples of macrocyclic ligands include porphyrins, which are present at the active site of *haem* proteins, and phthalocyanins. The beginnings of current interest in synthetic macrocyclic ligands and their complexes can be traced to the synthesis of the nickel(II) complex of the tetraaza macrocycle, L^1 (Fig. 3.4-1).[1)] The original paper by Curtis describes the synthesis of $[Ni(L^1)]^{2+}$ by the condensation of *tris*(ethylenediamine)nickel(II) perchlorate, $[Ni(en)_3](ClO_4)_2$, with acetone. The synthesis of $[Ni(L^1)]^{2+}$ represents a common method of macrocyclic ligand preparation, namely, Schiff-base template condensation of an amine with a ketone around a metal ion. However, this synthesis is not suitable as an undergraduate experiment because the condensation reaction occurs rather slowly over several days and affords a mixture of nickel(II) complexes of L^1 and L^2 [2)] (Fig. 3.4-1), which are related by the position of the imino C=N bonds within the ring. Complexes of L^1 can, however, be conveniently prepared by metal insertion into the preformed macrocyclic ligand. Curtis and Hay first reported the preparation of the metal-free ligand as its diprotonated salt, and this synthetic procedure was subsequently adapted by Tait and Busch. The preparation of the metal-free ligand and its corresponding copper(II), nickel(II) and cobalt(III) complexes via metal insertion reactions provides an excellent introduction to macrocyclic chemistry for undergraduate students.

As a result of the restricted inversion of the chiral secondary amine centres, metal complexes of L^1 can exist as the N-*meso* (**I**) or the N-*racemic* (**II**) diastereoisomers as shown in Figure 3.4-1. These can be interconverted in basic solution. The N-*meso* diastereoisomers can be distinguished in the case of the diamagnetic nickel(II) complexes by ^1H NMR studies. The N-*racemic* diastereoisomer (thiocyanate salt) displays three equally intense resonances at δ 2.67, 2.52 and 1.75, while the N-*meso* diastereoisomer (thiocyanate salt) shows these signals at δ 2.69, 2.21 and 1.75 in D_2O. These methyl signals are assigned to the imine methyls (equatorial) and to the axial and equatorial geminal methyl groups respectively. The infrared bands near 3200 and 1650 cm^{-1} are assignable to the ν(N–H) and ν(C=N) vibrations respectively. Ionic

1) The full name for L^1 is: 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene.
2) The full name for L^2 is: 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,14-diene.

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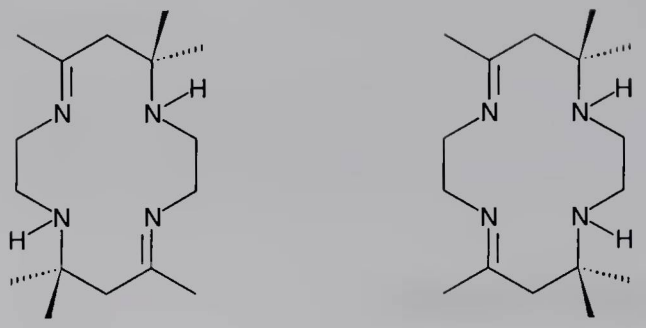
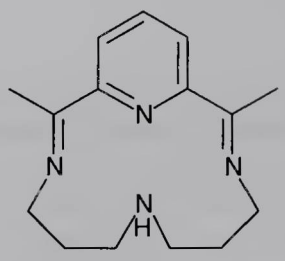
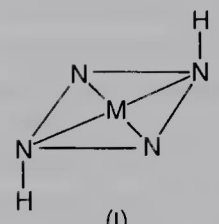


L^1

L^2

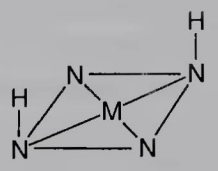


L^3



(I)

N - *meso*



(II)

N - *racemic*

Fig. 3.4-1

perchlorate (T_d symmetry) leads to a broad band at 1100 cm^{-1} and a sharp band at 625 cm^{-1}. The ligand field strength of L^1 has been calculated to be 15690 cm^{-1}, making the ligand one of the most strongly coordinating synthetic macrocyclic quadridentates on nickel(II). The NCS^-, PF_6^- and BF_4^- salts have been prepared and characterised.

A further set of experiments can be undertaken based upon a convenient *direct* Schiff-base condensation of 2,6-diacetylpyridine with an appropriate diamine, in this case, 4-azaheptane-1,7-diamine, in the presence of nickel(II) to form $[Ni(L^3)]^{2+}$.[3] In the absence of nickel(II) ion, the Schiff-base condensation reaction affords intractable polymeric materials.

The complex $[Ni(L^3)]^{2+}$ is particularly suitable for electrochemical investigation by cyclic voltammetry and coulometry. The complex shows one one-electron oxidation to afford a stable nickel(III) species, and two one-electron reductions, the first corre-

3) The full name for L^3 is: 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]septadec-1(17),2,11–13,15-pentaene.

sponding to the formation of a nickel(II)-ligand radical species. Both one-electron redox products can be detected by ESR spectroscopy.

Special Safety Precautions

1. All perchlorate (ClO_4^-) salts are potentially explosive, particularly when heated to dryness, and must be handled with care at all time. Perchlorates should not be heated. In all the experiment below, $NaClO_4$ may be replaced by $NaBF_4$ or NH_4PF_6, although the resultant metal complex BF_4^- and PF_6^- salts are often more difficult to isolate from solution than their corresponding ClO_4^- salts.
2. Nickel salts are potential carcinogens. Avoid skin contact.
3. Hydrogen peroxide is highly oxidising and corrosive. Spills should be cleaned and washed off immediately.

3.4.1 Experimental

a) 1,2-Diaminoethane Dihydrobromide

Dissolve 1,2-diaminoethane (30 g, 33.5 cm^3, 0.5 mol) in methanol (100 cm^3). Cool the solution in an ice bath and carefully add concentrated (49%) hydrobromic acid (175 cm^3) dropwise with stirring. Collect the colourless dihydrobromide salt by filtration on a glass sinter, wash the product with diethyl ether and dry *in vacuo*. A further crop of dihydrobromide salt can be obtained by reducing the volume of the filrate or by adding ether to the filtrate.

b) $L^1 \cdot HBr \cdot 2H_2O$

To 1,2-diaminoethane dihydrobromide (11.1 g, 0.05 mol) prepared above, add acetone (100 cm^3) and 1,2-diaminoethane (3.0 g, 0.05 mol). Heat the mixture on a water bath using a reflux condenser for ca. 30 minutes, during which time a copious white precipitate of the crystalline macrocycle dihydrobromide forms. Cool the solution, collect the product by filtration and wash the precipitate with ice-cold acetone, then diethyl ether and dry *in vacuo*. The yield is ca. 15.5 g (80% based on ethylenediamine). Measure the melting point of the sample [m.p.: 107–108 (dec.)], and run an IR spectrum as a KBr disk to identify the C=N stretching vibration [ν_{max}: 1670 cm^{-1}]. The dihydrobromide salt can be stored for 2–3 months without appreciable decomposition.

c) N-meso and N-racemic Nickel(II) Complexes of L^1, $[Ni(L^1)]^{2+}$

Dissolve $L^1 \cdot 2HBr \cdot 2H_2O$ (5 g, 0.01 mol) in the minimum volume of water (ca. 30 cm^3) and add an excess of nickel(II) carbonate. Heat the resultant slurry on a

water bath for ca. 30 minutes. Remove any unreacted nickel(II) carbonate by filtration and add a saturated aqueous solution of sodium perchlorate, $NaClO_4$ (3 cm^3).[4] Cooling in an ice bath affords yellow crystals of the perchlorate salt of $[Ni(L^1)]^{2+}$. The sample obtained is a mixture of N-*meso* (I) and N-*racemic* (II) diastereoisomers. These diastereoisomers can be distinguished by IR and ^1H NMR spectroscopy. The pure N-*meso* diastereoisomer can be obtained by rapid recrystallisation of the sample from hot methanol.

d) N-meso and N-racemic Copper(II) Complexes of L^1, $[Cu(L^1)]^{2+}$

A mixture of N-*meso* and N-*racemic* diastereoisomers of $[Cu(L^1)]^{2+}$ can be prepared using the same procedure as for the nickel(II) complex, but replacing nickel(II) carbonate with copper(II) carbonate. Addition of a saturated aqueous solution of sodium perchlorate, $NaClO_4$ (3 cm^3) leads to rapid crystallisation of the perchlorate salt. The N-*meso* diastereoisomer is orange and the N-*racemic* diastereoisomer red. The N-*meso* diastereoisomer can be obtained by recrystallisation from water-ethanol, and the N-*racemic* diastereoisomer by extraction into boiling dioxane.

e) Cobalt(III) Complexes

The N-*racemic* cobalt(III) complex of L^1 can be prepared by reacting the ligand dihydrobromide salt with $Na_3[CO_3)_3 \cdot 3]H_2O$ in the presence of hydrochloric acid.

Sodium tris(carbonata)cobalt(III)trihydrate, $Na_3[Co(CO_3)_3] \cdot 3H_2O$

This complex can be readily prepared by the method of Bauer and Drinkard. Dissolve $[Co(NO_3)_2] \cdot 6H_2O$ (29.1 g, 0.10 mol) in water (40 cm^3) and slowly add hydrogen peroxide (30%) (10 cm^3). Add this solution dropwise with stirring to a cold slurry of sodium hydrogen carbonate, $NaHCO_3$, (42.0 g, 0.50 mol) in water (50 cm^3). Allow the mixture to stand at 0 °C for 1 hour with continuous stirring. Collect the olive green product by filtration, wash the precipitate with 3 × 10 cm^3 portions of cold water, then thoroughly wash with absolute alcohol and diethyl ether and dry *in vacuo*.

trans-$[CoCl_2(L^1)]ClO_4$

Heat a slurry of $Na_3[Co(CO_3)_3] \cdot 3H_2O$ (7.24 g, 0.02 mol) and the ligand dihydrobromide (12 g, 0.025 mol) in methanol-water (1 : 1 v/v, 100 cm^3) on a water bath until effervescence ceases (ca. 20 min). Filter the resultant red solution hot and add concentrated hydrochloric acid (20 cm^3) to the filtrate, which is then heated on a water bath and the volume reduced to ca. 20 cm^3. Allow the solution to cool and add a concentrated aqueous solution of sodium perchlorate, $NaClO_4$ (ca. 5 cm^3). Green crystals of the required complex crystallise on cooling.

4) $NaClO_4$ may be replaced by $NaBF_4$ or NH_4PF_6 in the preparation although the resultant BF_4^- and PF_6^- salts are often more difficult to isolate from solution than the corresponding ClO_4^-.

f) Template Schiff-base Condensation to Form $[Ni(L^3)]^{2+}$

Dissolve $[Ni(H_2O)_6]Cl_2$ (2.4 g, 0.1 mol) and 2,6-diacetylpyridine (1.6 g, 0.1 mol) in 50% aqueous ethanol (200 cm^3) and bring the solution to reflux. Add 4-aza-heptane-1,7-diamine (1.3 g, 0.1 mol) dropwise with stirring to the solution and reflux the resultant solution for 12 hours. Allow the reaction solution to cool and add a concentrated solution of sodium perchlorate,

$NaClO_4$. Cool the solution to 0 °C to allow full precipitation of the product, which should be collected by filtration and dried *in vacuo*.

Discussion

Measure the electronic spectra of the complexes and obtain the energy and intensities (extinction coefficients) of the *d-d* transitions. Measure the molar conductivities of the complexes. Measure the IR, NMR and ESR spectra of the products as appropriate.

The metal complexes of L^1 display many interesting features not normally seen with classical polyamine complexes. The copper(II) complex is quite stable to strong mineral acids and dissociates only slowly ($t_{1/2} \approx 9.6$ min in 6.1 M HCl at 25 °C). The slow dissociation can be readily monitored spectrophotometrically at 500 nm in 6.1 M HCl at 25 °C. A plot of log $(A_t - A_\infty)$ versus time is linear and the observed first order rate constant (k_{obs}) can be readily derived from such plots.

Molecular models can be constructed to illustrate the detailed stereochemistry of these complexes. Discuss the formation of L^1 from the condensation of diamine with acetone.

Further Reading

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3.5
[Co(dinosar)]Cl_3: An Encapsulation Complex Prepared by a Template Reaction

David J. Otway

The reactions of coordinated ligands is an extremely important area. In template reactions the metal coordination sphere acts as a shape former, bringing appropriate parts of ligands into close contact to allow subsequent reaction with each other or an external agent and thus minimising unfavourable entropy contributions to reaction energies. The natural syntheses of many metalloproteins and metalloenzymes are based on template reactions. In some cases the new molecule will decoordinate from the metal. In this instance, though, the resulting macrobicyclic species, dinosar (1,8-dinitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]-eicosane) – formed from a template "capping" on three 1,2-diaminoethane (ethylenediamine, en) ligands – completely encapsulates the cobalt.

Special Safety Precautions

Hydrogen peroxide is a powerful oxidant and its aqueous solutions cause skin damage rapidly. Avoid any contact. Formaldehyde is toxic and carcinogenic and any solutions containing it *must* be handled in a fume cupboard. All other reagents and products – cobalt complexes, 1,2-diaminoethane, nitromethane – should be regarded as toxic. Avoid ingestion by nose, skin (or mouth). Wear gloves. Hot acetic acid and concentrated, hydrochloric acid are corrosive and noxious. Wear rubber gloves and operate in a fume cupboard. Ethanol, acetic acid and nitromethane are flammable.

3.5.1
Experimental

a) Preparation of [Co(en)$_3$]Cl_3

Dissolve $CoCl_2 \cdot 6H_2O$ (6.0 g) in water (17.5 cm^3). Whilst dissolution is in progress, add anhydrous 1,2-diaminoethane (4.5 cm^3) to water (12.5 cm^3) in a conical flask, cool the mixture in ice and then cautiously introduce 6 M aqueous HCl (4.5 cm^3;

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concentrated hydrochloric acid is approximately 12 M). With continuous stirring, add the $CoCl_2$ solution to the diaminoethane solution, followed by 30% aqueous H_2O_2 (5.0 cm^3). Continue stirring for several minutes until effervescence has ceased then place the flask on a hot plate (in a fume cupboard) and boil gently. When the solution has evaporated to a volume of approximately 30 cm^3 (but no less, otherwise a green byproduct may be recovered) add an equal volume of concentrated hydrochloric acid, followed by ethanol (60 cm^3). Cool in ice and filter off the precipitate under suction. Wash with ethanol (2 × 20 cm^3) and diethyl ether (2 × 20 cm^3) and air-dry the product. Record the yield and measure the electronic spectrum (300–600 nm) of an aqueous solution of your product. (NB: You should use a known concentration since you must report extinction coefficients).

b) Preparation of [Co(dinosar)]Cl_3

Dissolve $[Co(en)_3]Cl_3$ (2.45 g) and Na_2CO_3 (1.2 g) in water (25 cm^3) in a conical flask. With continuous stirring, add 40% aqueous formaldehyde (18 cm^3 CAUTION) followed by nitromethane (2.85 g). Then, either (a) maintain the mixture at 30–40 °C (water bath on hotplate) for 60–90 minutes or (b) allow to stand at ambient temperature for (at least) 5 hours. If no precipitate appears, addition of a small quantity of ethanol (5 cm^3) should encourage it. The resulting solid is filtered under suction and cautiously dissolved in the minimum volume (ca. 7 cm^3) of hot 3 M hydrochloric acid. Cool this solution in ice/water and add ethanol (20–25 cm^3). Filter the recrystallised product under suction, air dry and place in a vacuum desiccator.

Record the electronic spectrum of a known concentration (300–600 nm) of an aqueous solution and the infrared spectrum of a Nujol mull. High field NMR spectra are available from the demonstrator.

3.5.2 Report

1. Briefly indicate the aims of the experiment.
2. Do not reproduce the experimental procedure unless your experiment differed.
3. Give balanced equations for both stages together with yields of the products.
4. Report the electronic spectra of both complexes.
5. Tabulate the NMR data for [Co(dinosar)]Cl_3 and assign the spectra.
6. Assign the characteristic vibrations in the IR spectrum.
7. What is the point group symmetry at cobalt?
8. Briefly suggest a plausible mechanism for the capping reaction.
9. Write a short conclusion.

Hand in with the report:

Samples of $[Co(en)_3]Cl_3$ and $[Co(dinosar)]Cl_3$
Electronic spectra for both samples
Fully assigned NMR spectrum of $[Co(dinosar)]Cl_3$
Fully assigned infrared spectrum of $[Co(dinosar)]Cl_3$

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3.6
Identification of Stereochemical (Geometrical) Isomers of $[Mo(CO)_4(L)_2]$ by Infrared Spectroscopy

Michael A. Beckett

Physical techniques are widely used to obtain structural information at a molecular level in both organic and inorganic chemistry. A quick and convenient laboratory bench-top spectroscopic analysis of a sample will often allow chemists insight into a structural problem without recourse to single crystal X-ray diffraction study. Vibrational spectroscopy is one such spectroscopic technique. Functional groups within a molecule vibrate at characteristic frequencies (group frequencies) and in doing so absorb radiation in the infrared (IR) region of the electromagnetic spectrum, 4000–200 cm^{-1}. Mononuclear metal carbonyl complexes are well suited to study by IR spectroscopy since intense absorptions due to the CO oscillations usually occur in the range 2100–1750 cm^{-1}. Furthermore, this region is also generally free from interference from absorptions due to other functional groups.[1)]

Separable geometrical isomers of complexes are common in ligand substituted mononuclear metal carbonyl chemistry. Group theory can be used to predict the number of IR active CO absorption bands to be expected for any particular isomer and so if the structural formula of a metal carbonyl complex is known, it is often possible to correctly identify which particular isomer is present by examining the CO stretching region of its IR spectrum. Thus, four carbonyl absorption bands are to be expected from a *cis*-$[M(CO)_4(L)_2]$ complex whereas only one band is expected from the *trans* isomer.

In this experiment, you will prepare, according to convenient literature methods, one isomer of the molybdenum carbonyl complex $[Mo(CO)_4(pip)_2]$ and both possible isomers of $[Mo(CO)_4(PPh_3)_2]$. These isomers will be identified by examining the CO stretching region of their IR spectra.

1) The N–N and N–O stretches in $M-N_2$ and M–NO complexes and M–H stretches also occur in this region. The method used for the preparation of the compounds should give some indication as to whether such functional groups might be present.

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Special Safety Precautions

Molybdenum hexacarbonyl and its derivatives are highly toxic, volatile materials. Chlorinated hydrocarbons, including CH_2Cl_2 and tetrachloroethene, are toxic and may be carcinogenic. Piperidene is a highly toxic, flammable liquid. Toluene, methanol and 60–80 °C petroleum ether are toxic and flammable. Triphenylphosphine is an irritant. The reactions given in the experimental are on a small scale and should present no special hazards provided reactions and manipulations (e.g. weighing, making up Nujol mulls, etc.) are carried out in a fume cupboard. Eye protection and rubber gloves should be worn at all times. Time allowed for the experiment should be ca. 6 h.

3.6.1 Experimental

a) An Isomer of $[Mo(CO)_4(pip)_2]$ (1) (pip = piperidine, HNC_5H_{10})

$[Mo(CO)_6]$ (1.0 g) is suspended in dry toluene (40 cm^3) under N_2 and piperidene (10 cm^3) is added. The mixture is heated at reflux for 2 hours and the $[Mo(CO)_6]$ should fully dissolve to give a yellow-orange solution. This solution should slowly become opaque as a yellow precipitate of the product (**1**) is produced. The reaction mixture is filtered *hot* using a Büchner flask/pump set up and the bright yellow product, remaining on the filter paper, is washed with cold 60–80 °C petroleum ether (2 × 10 cm^3 portions, previously cooled in an ice bath for 15 minutes). The product is conveniently dried at the pump. Record the weight of the product and calculate the percentage yield. Obtain the melting point of the complex and its IR spectrum as a Nujol mull.

b) An Isomer of $[Mo(CO)_4(PPh_3)_2]$ (2)

$[Mo(CO)_4(pip)_2]$ (**1**) (0.5 g, 1.32 mmol) is partially dissolved in dry CH_2Cl_2 (20 cm^3) under N_2 and PPh_3 (0.75 g, 2.86 mmol) is added as a solid. The reaction mixture is heated to reflux (whereupon **1** should fully dissolve) and reflux is maintained for 15 minutes. The reaction solution is allowed to cool to room temperature and the orange solution is filtered. The filtrate is reduced in volume to ca. 8 cm^3 (rotary evaporator or vacuum pump) and methanol (15 cm^3) is added. The solution is cooled in a freezer (<0°C) for 15 minutes and the pale yellow product should crystallise out. The product is collected by filtration using a Büchner flask/pump set up and dried at the pump. Record the weight of the product and calculate the percentage yield. Obtain the melting point of the complex and its IR spectrum in tetrachloroethene solution and as a Nujol mull.

c) Thermal Isomerisation of 2 to Give 3

$[Mo(CO)_4(PPh_3)_2]$ (2) (0.5 g, 0.68 mmol) is dissolved in dry toluene (10 cm^3) under N_2 to give a pale yellow solution. This solution is heated at reflux for 30 min and then allowed to cool to room temperature. The solution may darken upon heating. The toluene is removed on a rotary evaporator (or vacuum pump) to yield the product as a brownish off-white residue (3). The product may be purified by 'dissolving' in CH_2Cl_2 (15 cm^3). The coloured insoluble material can be removed by filtration and the pure product can be obtained from the filtrate by removal of the solvent. Record the weight of the residue and calculate the percentage yield. Obtain the melting point of the complex and its IR spectrum in tetrachloroethene solution and as a Nujol mull.

3.6.2 Exercises

1. Decide, by inspection of the CO stretching region of your IR spectra, the stereochemistry (*cis* or *trans* geometrical isomers) of your products.
2. Draw a reaction scheme which clearly shows the stereochemistry of **1**, **2**, and **3**, and conditions for conversions.
3. Compare the melting point of your complexes with those quoted in the literature.
4. Do these metal carbonyl substitution reactions go *via* a dissociative or an associative mechanism?
5. Explain why the mechanisms for the isomerization of $[Mo(CO)_4(L)_2]$ with $L = P^nBu_3$ and $L = PPh_3$ are different.
6. Are the *cis* or the *trans* isomers of $[Mo(CO)_4(PR_3)_2]$ thermodynamically more stable?

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3.7
Five Coordinate Complexes: $[VO(acac)_2]$ and $[Cr(NH_3)_6][CuCl_5]$

Christopher P. Morley

Five coordinate complexes are rare when compared to the abundance of four and six coordinate species. They commonly exhibit either square pyramidal or trigonal bipyramidal geometry. In this experiment, you will prepare and analyse an example of each type: vanadyl acetylacetonate, $[VO(acac)_2]$, and the pentachlorocuprate(II) anion as its hexaamminechromium(III) salt, $[Cr(NH_3)_6][CuCl_5]$.

Special Safety Precautions

1. Anhydrous liquid ammonia has a boiling point of –33 °C, and is corrosive. All operations involving liquid ammonia should therefore be conducted in a fume cupboard, whilst wearing protective gloves.
2. Sodium reacts violently with water. Any waste sodium scraps should be destroyed by adding them to a small beaker of anhydrous ethanol. When reaction is complete, the solution may be washed cautiously down the drain.
3. Chloroform is toxic by inhalation or contact.
4. Sulfur dioxide is a severe respiratory irritant. All reactions which may result in its evolution should be carried out in a fume cupboard.

3.7.1
Experimental

a) $VO(acac)_2$

Water (50 cm^3) and concentrated hydrochloric acid (25 cm^3) are added to vanadium(V) oxide (3.3 g) in a 600 cm^3 beaker. The mixture is heated on a hotplate (in the fume cupboard) and sodium sulfite (5 g) is added in 1 g quantities. After a few minutes at the boiling point, all the V_2O_5 should be reduced. After cooling, the solution is filtered. Acetylacetone (10 cm^3) is added, followed by saturated sodium carbo-

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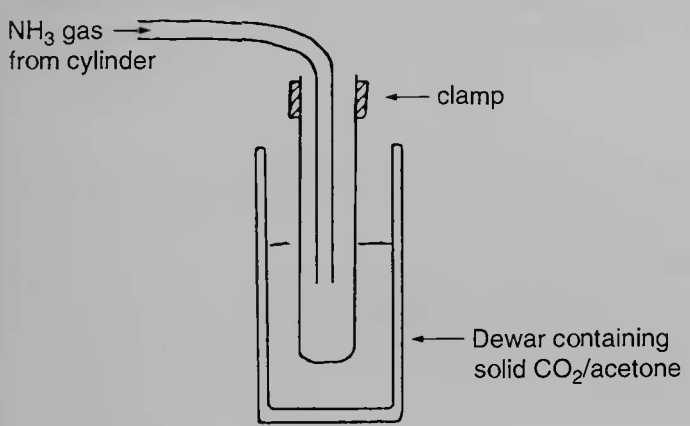
nate solution until no further effervescence occurs. The precipitate is collected by filtration on a Büchner funnel and dried thoroughly in a vacuum desiccator. The product is purified by dissolving it in a small volume of chloroform, filtering if necessary, and reprecipitating by slow addition of petroleum ether. Dry the product as before and record the yield.

Record the melting point, infrared spectrum (Nujol mull, NaCl plates), and visible spectrum ($CHCl_3$ solution, ca. 0.1 g in 20 cm^3) of your product. Rerun the visible spectrum using tetrahydrofuran as solvent and comment on any differences between the two spectra. Measure the magnetic susceptibility of your sample, and calculate the number of unpaired electrons using the spin-only formula.

Vanadium may be estimated by titration with permanganate. The acetylacetonate groups are, however, oxidised only relatively slowly by permanganate and must therefore first be destroyed. Add 25 cm^3 dilute sulfuric acid to a weighed sample of complex (ca. 0.25 g) and bring to the boiling point. From a burette, slowly add concentrated (approx. 0.2 M) $KMnO_4$ solution, reheating when necessary. Add a slight excess of permanganate and boil for a few minutes. Cool, reduce with an excess of sodium sulfite, and boil off the excess SO_2 (in a fume cupboard): this will take 10–15 minutes. A blue solution of V(IV) will be obtained. Allow this to cool to 50–70 °C and then titrate with standard (ca. 0.02 M) potassium permanganate until the first permanent pink colour is observed. After recording the endpoint, add a slight excess of $KMnO_4$ solution and boil. Repeat the reduction and titration to check that oxidation of the acetylacetonate groups was complete. Repeat if necessary until constant titres are achieved. Calculate the percentage vanadium in the complex, compare with the theoretical value and comment on the purity of your sample.

b) $[Cr(NH_3]_6]Cl_3$

A slush bath at –78 °C is prepared by slowly adding solid carbon dioxide to acetone in a Dewar vessel until the solid remains at the bottom of the vessel without vapourising. The reaction vessel is clamped so that about half of it is cooled in the slush bath (see figure), and ammonia is then passed into the reaction vessel from a cylinder. Allow about 40 cm^3 of NH_3 to condense. A small piece (<0.1 g) of freshly cut sodium is then added to the liquid ammonia, followed by a small crystal of ferric



nitrate (or other Fe(III) salt) to discharge the blue colour. The solution is stirred if necessary.

The dark solution of sodium amide thus produced, which also contains finely divided iron, is treated in small portions with anhydrous $CrCl_3$ (2.5 g in total), previously ground to a fine powder using a pestle and mortar. Only small portions of the relatively warm $CrCl_3$ are added, in order to avoid boiling the solution over the sides of the reaction vessel.

The contents of the reaction vessel are poured into an evaporating dish and allowed to dry. 1 g of the crude product thus obtained should be used in the preparation of the pentachlorocuprate(II) salt (see below). The remainder may be recrystallised as follows. Dissolve it in a small volume of 1 M hydrochloric acid at room temperature, filter to remove any unreacted $CrCl_3$ and iron containing impurities, and cool the solution to 0 °C in an ice bath. Add concentrated hydrochloric acid slowly until the initial volume is approximately doubled. The crystals obtained are collected by filtration, washed with ethanol, then dried.

Record the infrared (KBr disk) and visible spectra (aqueous solution, ca. 0.1 g in 20 cm^3) of your product and assign the absorptions observed. Measure the magnetic susceptibility of the sample and calculate the number of unpaired electrons using the spin-only formula.

c) $[Cr(NH_3)_6][CuCl_5]$

Hexaamminechromium(III) chloride (1 g, see above) is dissolved in water (15 cm^3). A solution of copper(II) chloride dihydrate (1 g) in water (15 cm^3) is added. The mixture is filtered if necessary, then heated to 60 °C. Concentrated hydrochloric acid (10 cm^3) is added: crystals form as the solution cools to room temperature. Filter off the product, wash with ethanol and dry in a desiccator. Calculate your yield.

Record the infrared spectrum (KBr disk) of your product and compare it with the spectrum of $[Cr(NH_3)_6]Cl_3$ obtained above.

The chromium and copper content of the sample should be determined using atomic absorption spectroscopy. The complex may be brought into solution using a small quantity of a mixture of concentrated nitric and sulfuric acids, followed by dilution with water to a known volume. Use sufficient complex to ensure that the final concentration of each metal is in the range 10–20 ppm. Calculate the percentage chromium and copper, compare with the theoretical value and comment on the purity of your sample.

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3.8
Preparation of *trans*-$PtHCl(PPh_3)_2$ and Measurement of its ^1H, ^{31}P and ^{195}Pt NMR Spectra

William P. Griffith

The development of Fourier transform techniques for NMR spectroscopy greatly stimulated the study of many nuclei including those with quite low magnetic moments and low sensitivities. In this experiment, you will make *cis*-$PtCl_2(PPh_3)_2$, convert it to *trans*-$PtHCl(PPh_3)_2$ and measure the ^1H resonance spectrum of the latter. The ^{31}P and ^{195}Pt NMR spectra are provided in Figures 3.8-1 and 3.8-2. From these and your ^1H spectrum you will be able to derive a number of chemical shifts and coupling constants for the hydrido complex.

Special Safety Precautions

1. Platinum salts can, in rare cases, cause skin disorders and asthma. Wash your hands after using them.
2. Hydrazine hydrate, potassium hydroxide solution and acetic acid are corrosive. If any is spilled on the skin wash it off with copious quantities of water.
3. Triphenylphosphine is toxic; avoid inhaling its dust.

3.8.1
Experimental

a) *cis*-$PtCl_2(PPh_3)_2$

Dissolve finely powdered $K_2[PtCl_4]$ (0.6 g) in 10 cm^3 of water with stirring. In a 100 cm^3 three-necked flask equipped with a reflux condenser, stirrer bar, N_2 inlet and dropping funnel, dissolve finely powdered triphenylphosphine (0.85 g) in degassed ethanol (10 cm^3), passing N_2 over the solution to avoid formation of Ph_3PO. Boil the solution gently and add the $K_2[PtCl_4]$ solution dropwise with continuous stirring. The solution should go pale yellow, followed by precipitation of the white complex.

Allow the solution to cool and continue stirring under a slow nitrogen stream. Centrifuge off the compound in air, wash with a little alcohol, then ether and allow

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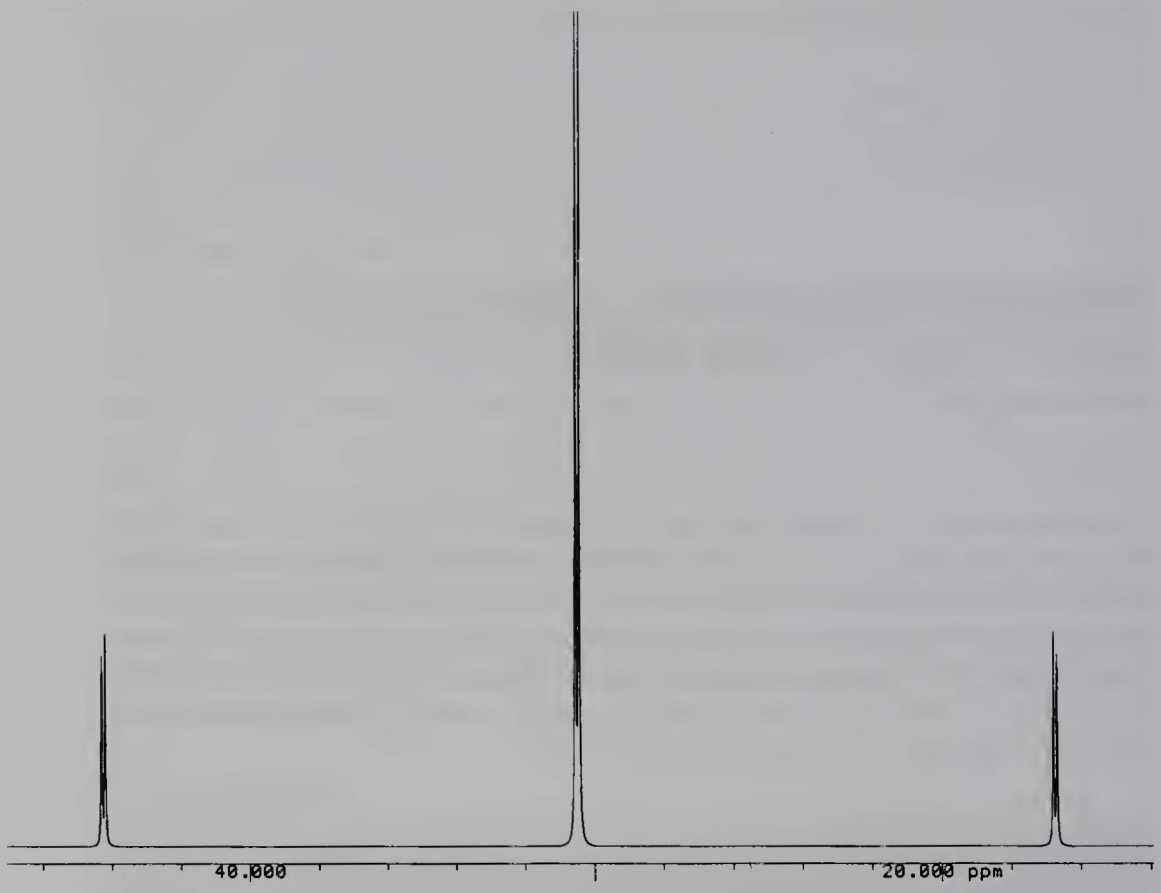

Fig. 3.13-1 109.3 MHz ^{31}P NMR Spektrum of *trans*-$PtHCl(PPh_3)_2$ ^{1}H decoupled at 7 ppm.

to dry. Take the melting point, record your yield, and run the infra-red spectrum (4000–200 cm^{-1}, pressed KBr disc). Compare your spectrum with that in the literature. Save a small (0.05 g) sample before proceeding to the preparation of *trans*-$PtHCl(PPh_3)_2$.

b) *trans*-$PtHCl(PPh_3)_2$

The quantities given here are based on the use of 1.0 g of *cis*-$PtCl_2(PPh_3)_2$. You should, however, use all of your product apart from the amount needed for the IR spectra, etc. in Part a) above, and adjust quantities according to the amount you have available. Make a suspension of *cis*-$PtCl_2(PPh_3)_2$ (1.0 g) in ethanol (30 cm^3) under N_2 using a three-necked flask equipped as before. With stirring, add 1 cm^3 from syringe of concentrated hydrazine hydrate (Corrosive!), and then quickly bring the mixture to reflux with a preheated heating mantle. Continue refluxing for five minutes, swirling the flask or stirring the contents. As clear pale-yellow solution should result.[1)]

1) If a yellow solid is formed, this is likely to be *trans*-$Pt(OH)Cl(PPh_3)_2$. In this event decant off the supernatant and convert it to the desired product (*trans*-$PtHCl(PPh_3)_2$) by dissolving the solid in the minimum quantity of 3M HCl (30 cm^3), refluxing under nitrogen for 15 minutes and filtering off the white hydride. Continue with the product as in c).

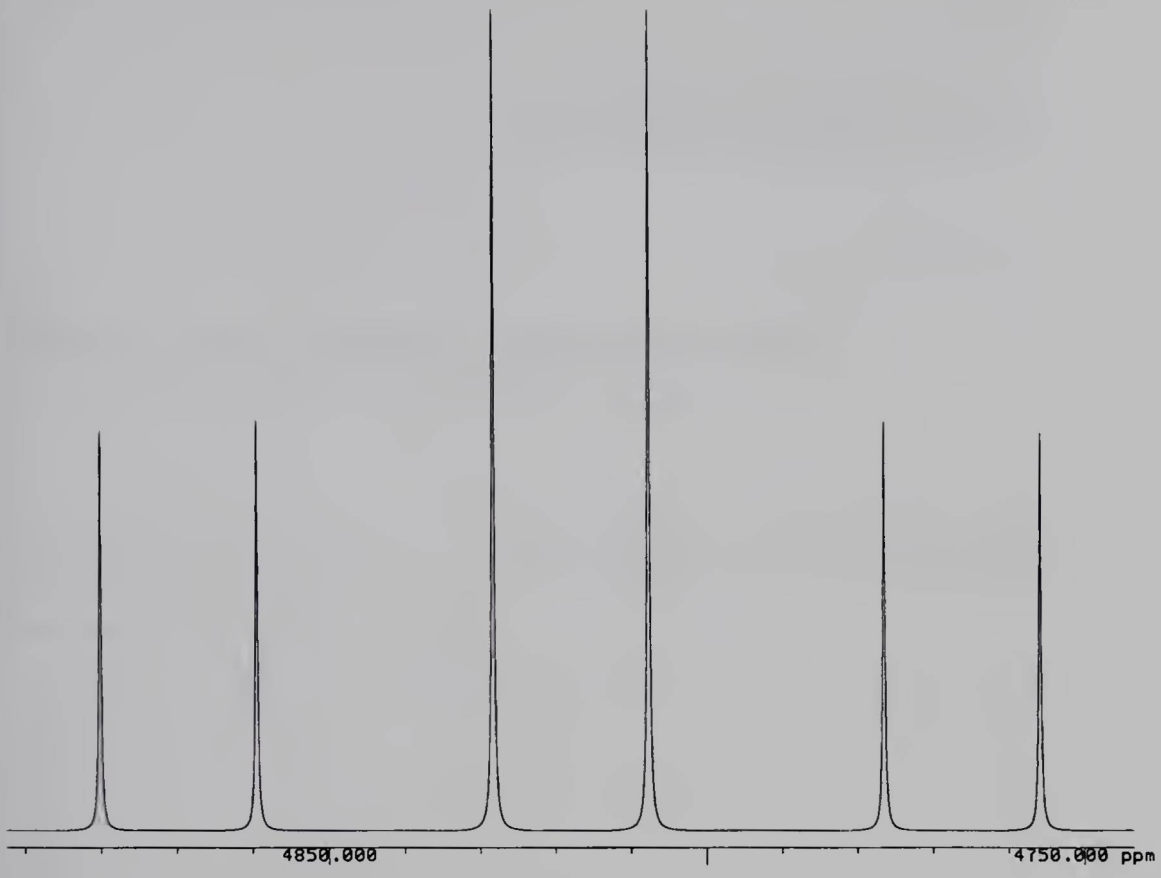

Fig. 3.8-2. 58.05 MHz ^{195}Pt NMR spectrum of *trans*-$PtHCl(PPh_3)_2$.

To the clear stirred solution or supernatant, still under nitrogen, add a mixture of 2 cm^3 of glacial acetic acid in 15 cm^3 of ethanol dropwise. Allow the solution to cool overnight. If little or no precipitate appears, evaporate off about half the solvent and leave the remainder in the refrigerator.

Centrifuge off the white crystals of the hydride, record the yield and melting point, and measure the infra-red spectrum (4000–200 cm^{-1}, pressed KBr disc). Compare your spectrum with that in the literature. Save a small (0.05 g) sample before running the ^1H NMR spectrum.

c) ^1H NMR Spectrum of trans-$PtHCl(PPh_3)_2$

Dissolve as much of your sample as necessary to make a saturated solution in the CH_2Cl_2 (1 cm^3); you may need to decant away from any undissolved solid. Measure the ^3H resonance spectrum. Since measurements will necessarily be made at high sensitivity levels, make sure that the phase trim is correct.

Interpret the proton resonance spectrum and calculate *chemical shifts* and *coupling constants* using your spectrum and using the ^{195}Pt and ^{31}P spectra given here.

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3.9
$[MoO_2Br_2(H_2O)_2] \cdot$ (diglyme) and $[MoO_2Br_2(DMF)_2]$

Francisco J. Arnáiz, María R. Pedrosa, and Rafael Aguado

Dioxomolybdenum halides are useful precursors for the synthesis of a number of species that mimic oxotransferases (1). Most of addition compounds of the halides are prepared by treating the hygroscopic, expensive MoO_2X_2 (X = Cl, Br) with the appropriate ligand in aprotic solvents (2).

However, the existence of $[MoO_2Br_2(H_2O)_2]$ in the solutions of alkali molybdates in concentrated hydrobromic acid was postulated in 1990 (3). More recently the species has been isolated and structurally characterised by X-ray diffraction as $[MoO_2Br_2(H_2O)_2] \cdot$ (15-crown-5) $\cdot H_2O$ (4). This suggests that the hydrate complex might be similarly stabilised with other common polyethers and a number of related compounds have been isolated.

Here we describe the preparation and characterisation of the outer-sphere hydrogen bonded addition compound $[MoO_2Br_2(H_2O)_2] \cdot$ (diglyme) and the dimethylformamide (DMF) adduct $[MoO_2Br_2(DMF)_2]$. The first synthesis illustrates how metals can be extracted from aqueous solutions with common solvents, and polyethers can stabilise hydrate complexes via hydrogen bonds. The latter shows that some strong coordinating ligands of low basicity toward the proton can displace water from the coordination sphere of metals without producing hydrolysis.

This experiment is appropriate for the advanced inorganic chemistry lab because of the chemical principles and techniques involved and to show how previous knowledge inspires chemical research.

Special Safety Precautions

Concentrated hydrobromic acid is corrosive, volatile (fumes in air) and toxic. Diethyl ether, diglyme and dimethylformamide are flammable and toxic. Use safety gloves and goggles, avoid inhalations of vapours and conduct all operations in a well-ventilated hood far from ignition sources.

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3.9.1 Experimental

a) $[MoO_2Br_2(H_2O)_2] \cdot$ (diglyme)

In a 15 × 150-ml test tube place: a stirring bar, ca. 1 g (4.13 mmol) of finely powdered $Na_2MoO_4 \cdot 2H_2O$ and ca. 5 g (29.04 mmol) of concentrated (ca. 47%) hydrobromic acid. Stir the mixture for 5 minutes. Add ca. 5 ml of diethyl ether and stir vigorously for 5 minutes. Stop the stirring and transfer the yellow upper ethereal layer (Pasteur pipette) to a 25-ml round-bottomed flask. Repeat similarly the extraction twice more and combine the ethereal extracts. Add ca. 1 g (7.45 mmol) of 2,5,8-trioxanonane (diglyme) to the solution. Concentrate the ethereal solution in vacuum at room temperature until a copious mass of yellow crystals is formed. Collect the solid by vacuum filtration (Hirsch funnel on 25 ml Schlenk tube), wash it with small portions (ca. 2 × 1 ml) of diethyl ether (add previously the ether to the flask to remove the remaining crystals and to get a saturated solution) and leave it to dry in air for 15 minutes. Weigh the yellow solid and calculate the yield (500–600 mg of product is easily obtained but note that the yield is quite dependent of the amount of mother liquor and washings, so be careful in the washing to avoid dissolving all the product). Wash the funnel with 5 ml of diethyl ether and conserve the mother liquor and washings in the Schlenk tube for the next preparation.

Use small portions of product to perform qualitative tests (e.g. $AgNO_3$ for bromide, warm $Pb(NO_3)_2$ solution to precipitate white $PbMoO_4$ while $PbBr_2$ remains dissolved, and NaI in acetone). Obtain the IR spectrum of the product as a dispersion in KBr. Obtain also that of a small drop of H_2O-diglyme between two KBr discs and compare the results. Note specially the two sharp stretching bands, at 912 and 950 cm^{-1}, characteristic of the *cis*-MoO_2 group.

Obtain the ^1H NMR spectrum of the product in acetone-d_6 (or in $DCCl_3$) and compare with that of a small drop of H_2O-diglyme in the same solvent.

b) $[MoO_2Br_2(DMF)_2]$

Add a stirring bar to the Schlenk tube containing the mother liquor and washings from the above preparation. Prepare in a test tube a solution of ca. 1 g of DMF in 10 ml of dry diethyl ether. Add the DMF solution by portions (1–2 ml, Pasteur pipette) to the molybdenum solution, with stirring, until precipitation ceases. Remove the liquid by decantation and wash similarly the solid in the tube with 2 × 10 ml of dry diethyl ether and vigorous stirring. Finally dry the solid in vacuum (water pump, room temperature). Remove the faintly yellow floury solid (avoid the use of a metallic spatula) from the tube and weigh it. Obtain the IR and ^1H NMR spectra of the product and DMF as above.

3.9.2 Exercises

a) $[MoO_2Br_2(H_2O)_2] \cdot$ Diglyme

1. Write a balanced equation for the reaction between Na_2MoO_4 and HBr. Explain why a large excess of concentrated hydrobromic acid is used for an effective extraction (note that the hard molybdenum centre has not a high affinity for the bromide ion).
2. Is the reaction of $MoO_2Br_2(H_2O)_2$ with NaI in acetone a simple metathesis? Try to find in the literature sources dioxomolybdenum(VI) iodides. Explain why heating is inadvisable in the preparation of the bromide solution.
3. Explain why in dioxomolybdenum(VI) compounds the oxo ligands show a strong preference for a *cis* placement (consider the pi-donor character of the oxo ligands, the number and symmetry of the Mo orbitals available for pi bonding, and optimisation of orbital overlapping).
4. From the IR and ^1H NMR spectra, do you find evidence for coordinated water? And for diglyme?

b) $[MoO_2Br_2(DMF)_2]$

1. From the amounts of $[MoO_2Br_2(H_2O)_2] \cdot$ (diglyme) and $[MoO_2Br_2(DMF)_2]$ obtained – assuming that all of the molybdenum extracted has been transformed in these compounds and that the volumes of the aqueous and ethereal phases are the same in each extraction process – calculate the distribution coefficient of molybdenum.
2. Compare the IR spectra of $[MoO_2Br_2(DMF)_2]$ and DMF. Do you find evidence of N- or O-coordination for DMF? Explain why amides show a strong preference to coordinate via the oxygen atom.
3. Compare the ^1H NMR spectra of the complex and DMF. Explain the presence of two signals for the methyl groups at room temperature. It has been found that the ^1H NMR spectrum of the product in DMSO-d_6 – is identical to that of DMF in this solvent. What does it suggest?
4. Perform a test on the capability of $[MoO_2Br_2(DMF)_2]$ to work as oxotransfer catalyst as follows: prepare in a test tube a solution formed by ca. 3 g of DMSO, 0.5 g of PPh_3 and 50 mg of the molybdenum complex. Heat it in a boiling water bath for 15 min and note the foul-smelling dimethyl sulfide produced (a well ventilated hood is imperative). Pour the resulting solution on 15 ml of 1 M NaOH. Collect the $OPPh_3$ precipitated and identify it (m.p. $157 \pm 1\,^\circ C$, strong $\nu(P{=}O)$ band at 1183 cm^{-1} in the IR spectrum). Note that to be sure on the role of the molybdenum complex it is advisable to conduct a blank experiment. Complementarily, a kinetic study of the oxo transfer process can be done in a simple manner by monitoring the intensity of the peaks for PPh_3 and $OPPh_3$ by ^{31}P NMR.

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3.10
Preparation of an Iron Dinitrogen Complex

Andrew W. G. Platt

Since the initial report on the synthesis of $[Ru(NH_3)_5N_2]X_2$ dinitrogen complexes, there has been considerable interest in coordination complexes of dinitrogen, partly due to the possible relationship between such complexes and the nitrogen fixation process. Whilst many dinitrogen complexes are sensitive to air and moisture, the compound synthesised here, $Na_2[Fe(EDTA)N_2] \cdot 2H_2O$, is stable to moisture and air over extended periods.

Special Safety Precautions

Sodium azide is toxic and liberates a harmful gas on treatment with acids. The compound must be handled with care and used only in the manner described. Concentrated ammonia solution is irritating to eyes and respiratory system and should only be used in the fume cupboard.

3.10.1
Experimental

a) $[Fe(HY)H_2O] \cdot H_2O(H_4Y = EDTA)$

Note that this experiment will take more than one laboratory session.

This complex is prepared by reacting freshly precipitated iron(III) hydroxide with EDTA. Dissolve 13.5 g of hydrated iron(III) chloride in 15 cm^3 of water with gentle warming. Allow to cool to room temperature and slowly add 20 cm^3 of SG 0.880 ammonia solution with constant stirring (carry out this operation in the fume cupboard). Heat the mixture on the steam bath for 15–20 minutes filter the iron(III) hydroxide by suction and wash well with water. Suspend 17.5 g of EDTA in 40 cm^3 water and add the moist iron(III) hydroxide. Make the volume up to about 100 cm^3 with water and heat on a steam bath for 2 hours. Allow the mixture to cool and filter the yellow solution from any unreacted EDTA.

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Reduce the volume to about 60 cm^3, cool and slowly add acetone to precipitate the product. The exact amount of acetone will depend on the yield of $[Fe(HY)H_2O] \cdot H_2O$, but 100 cm^3 is usually sufficient. If the product precipitates as an oil, decant the supernatant and stir the residue with small quantities of acetone to induce crystallisation. Filter and dry at the pump. Record the weight obtained and calculate the percentage yield. Record the infrared spectrum of the product.

b) The Dinitrogen Complex

Note the final product is reported to be thermally unstable. You should make sure that there is sufficient time to complete the preparation and the characterisation in one laboratory session.

Dissolve 0.5 g of the iron EDTA complex in 20 cm^3 nitrogen degassed water in a flask equipped with a magnetic stirrer bar and a nitrogen inlet. Add 0.5 g sodium azide and stir the solution at about 70 °C for 1 hour whilst maintaining a steady flow of nitrogen through the solution. Reduce the volume to about 10 cm^3. This can be done under reduced pressure or by evaporation under a flow of nitrogen. Cool to room temperature and add 50 cm^3 of ethanol. If the product precipitates as an oil, decant the supernatant and stir the residual oil with more ethanol to induce crystallisation. Record the weight obtained and calculate the percentage yield. Record the infra-red spectrum as either a KBr disc or as a Nujol mull and identify the bands due to coordinated N_2 and the CO groups of the EDTA.

3.10.2 Exercises

1. What is the structure of the $[Fe(HY)H_2O] \cdot H_2O$ complex?
2. Discuss the bonding of dinitrogen to metals.

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3.11
Preparation of Nitrosyl Complexes of Iron and Nickel

Andrew W. G. Platt

Nitric oxide is capable of forming many complexes with transition metals. There is some similarity between the NO molecule and carbon monoxide and nitric oxide does form a series of binary nitrosyls analogous to the binary carbonyls of the first row transition metals. Formally, nitric oxide can be considered as either a neutral three electron donor, a cationic two electron donor (isoelectronic with carbon monoxide) or even an anionic four electron donor.

Unlike carbon monoxide, nitric oxide is not stable in air as it is rapidly oxidised to NO_2. Nitric oxide can be used directly to generate complexes but only if atmospheric oxygen is excluded. This experiment illustrates two methods of forming nitrosyl complexes without the use of free nitric oxide. The first method generates NO in the presence of the metal, whilst the second method involves the reduction of nitrite ion already coordinated to the metal.

Special Safety Precautions

The toxicity of nitrosyl complexes is unknown. It is therefore prudent to assume that they are highly toxic. Avoid all contact with skin and wash throroughly in the event of contamination.

3.11.1
Experimental

a) Nitrosylbis(diethyldithiocarbamato)iron, $Fe(NO)(S_2CNEt_2)_2$

Carry out all manipulations in the fume cupboard. Weigh 2.5 g iron(II) sulfate, 0.75 g sodium nitrite and 5 g sodium diethyldithiocarbamate. Dissolve the iron sulfate and sodium nitrite in 15 cm^3 of dilute sulfuric acid and immediately add the sodium diethyldithiocarbamate. Stir vigorously for 5 minutes. Transfer the dark slurry to a separatory funnel and extract with small volumes of chloroform until the

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extracts are only lightly coloured. During the initial extractions, the boundary between the layers may be difficult to observe so proceed with care.

Combine the chloroform extracts, dry over anhydrous magnesium sulfate, filter and evaporate to about 10 cm^3. Slowly add about 50 cm^3 of petrol, filter the product and dry at the pump. If difficulty is experienced in crystallising the product in this way, decant the petrol from the dark oil and treat with fresh petrol. Record the weight obtained and calculate the percentage yield.

b) Bromonitrosylbis(triphenylphosphine)nickel, $NiBr(NO)(PPh_3)_2$

This preparation requires the use of $NiBr_2(PPh_3)_2$. Either use a provided sample or synthesise your own by adding the stoichiometric amount of nickel bromide in ethanol to a refluxing solution of triphenylphosphine in propan-2-ol.

Place 8 g of finely powdered, dry sodium nitrite in a flask with 5 g of $NiBr_2(PPh_3)_2$, 1.8 g triphenylphosphine and 50 cm^3 tetrahydrofuran. Stir under reflux for about 35 minutes. Cool and filter the solution and reduce the volume to about 25 cm^3 by evaporation on a steam bath (fume cupboard). Slowly add 25 cm^3 of petrol to the warm solution with stirring. Allow to cool to room temperature, filter the purple product and dry at the pump. Record the weight obtained and calculate the percentage yield.

Record the infrared spectra of both compounds.

3.11.2 Exercises

1. Assign the bands in your IR spectra which are due to the coordinated NO group. What can be deduced about the mode of bonding of the NO group from your spectra (free NO absorbs at 1878 cm^{-1})?
2. Discuss the possible oxidation states of the metal in the two complexes.
3. Electron spin resonance is a form of magnetic resonance in which an unpaired electron in a magnetic field is excited from one spin to another by a quantum of energy in the microwave region of the electromagnetic spectrum. It is entirely analogous to nuclear magnetic resonance but the appearance of the spectrum is usually rather different because it is normally presented as the first derivative of the absorption with respect to field, plotted against field. In practical terms, what this means is that a peak position is precisely measured by the field value at which the derivative *crosses* the baseline. The ESR spectrum of the iron complex is shown in Figure 3.11-1. The spectrum is characterised by two parameters, g and a.

The g value is analogous to the chemical shift in NMR. The free electron value is 2.0023; the value for a free radical in which the unpaired electron is centred on carbon is usually around 2.003; and if centred on nitrogen around 2.006. Metal ions can have very different g values (in general between about 1 and 8) but if there is only one unpaired electron the shift away from 2.0023 is often no more than about 0.2.

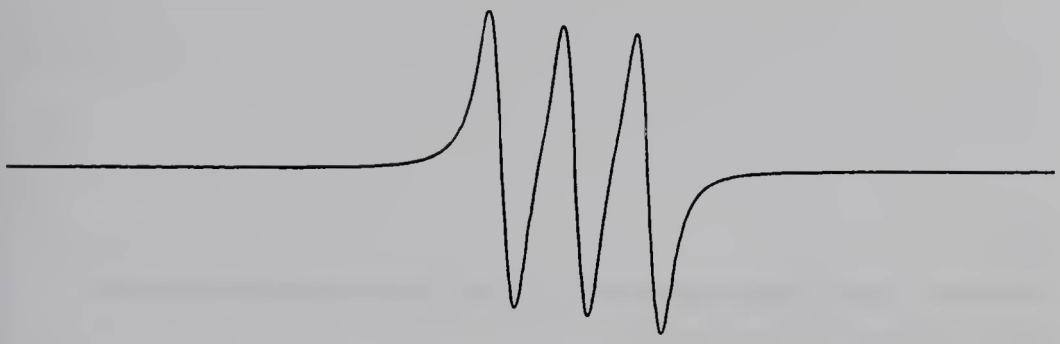

Fig. 3.11-1 Electron spin resonance spectrum of $Fe(NO)(dtc)_x$ in $CHCl_3$, frequency = 9.515 GHz, scale = 0.1 mT nm^{-1}, centre line = 0.333 T.

Calculate the g value from the field position of the central line using the formula $H\nu = g\beta \boldsymbol{B}$, which gives $g = 0.0714484\ \nu(\text{GHz})/\boldsymbol{B}(\text{tesla})$.

The a value is the symbol for the isotropic hyperfine coupling constant which arises when a nearby nucleus interacts with the electron; it is analogous to the spin-spin coupling constant in NMR. In your molecule, the unpaired electron clearly interacts with a nitrogen nucleus which has spin $I = 1$, having three projections along the magnetic field characterised by $M_I = +1, 0, -1$. The isotropic hyperfine coupling constant a_N may be measured in field units by measuring the separation between two adjacent lines. To convert to frequency units use $a\,(\text{MHz}) = g \times 13.99626 \times a(\text{mT})$.

What can you say about your molecule from its g value?

Given that an unpaired electron situated entirely on a free nitrogen atom has an isotropic hyperfine coupling constant a_0 of 1540 MHz, calculate by direct ratio of the coupling constants the percent probability of finding an unpaired electron on nitrogen in your molecule. What does this value tell you about the electronic structure?

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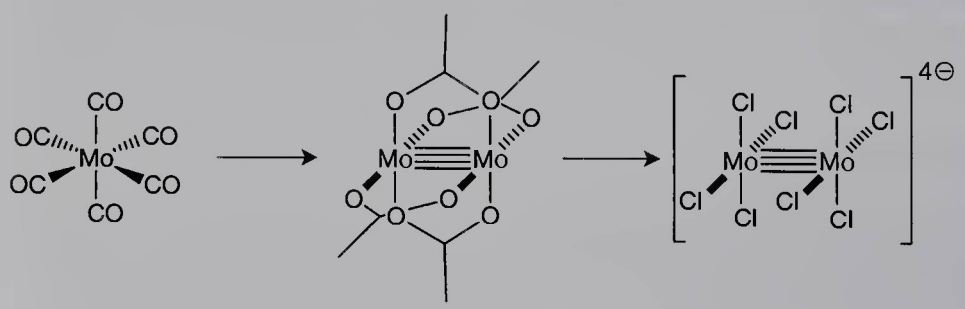
3.12
Synthesis and Characterisation of Two Metal–Metal Bonded Dimolybdenum Complexes

William Levason, Thomas A. Logothetis, and Gill Reid

Many metallic elements form complexes in which metal centres are directly bonded together. These range from dimers with two metal atoms, M–M, through to clusters with several hundred metal atoms (*Shriver and Atkins' Inorganic Chemistry*, 4th edn, pp. 452; see Further Reading). In this experiment, some complexes with Mo–Mo bonds will be studied. As you will find, interpretation of the spectroscopic properties requires consideration of the dimolybdenum unit, rather than of single molybdenum centres. The two compounds are dimolybdenum tetraacetate, $[Mo_2(O_2CMe)_4]$ (A), and the octachlorodimolybdate(II) anion in $K_4[Mo_2Cl_8] \cdot 2H_2O$ (B). In the former, there is an Mo–Mo bond and four bridging acetate groups; in the latter, only the (unsupported) Mo–Mo bond is present along with eight terminal chloride ligands. In this experiment, you will make two complexes containing Mo_2 units and determine some of their spectroscopic properties.



A B

Special Safety Precautions

It is the responsibility of the course organisers to carry out appropriate risk assessments for these experiments. The preparation of compound A should be conducted in a suitable fume cupboard.

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3.12.1 Experimental

3.12.1.1 Indicative Timeline

- **Session 1–3 hours:**
  Synthesis of A (requires overnight reflux)
- **Session 2– ~2 hours:**
  Isolation of A
  Analysis of A
- **Session 3– ~3 hours:**
  Synthesis of B
  Analysis of B

3.12.1.2 Synthesis of $[Mo_2(O_2CMe)_4]$ (A)

Set up a reflux apparatus consisting of a single-necked B24 250 ml round-bottomed flask, a reflux condenser and a nitrogen bubbler. Use grease to seal the ground-glass joints (they should be *clear* when connected and properly greased). To the flask add $Mo(CO)_6$ (2.64 g), glacial acetic acid (100 ml) and acetic anhydride (10 ml). Connect the nitrogen to the bubbler at the top of the condenser and heat the mixture to reflux. (The solution will become dark yellow or brown.)

The $Mo(CO)_6$ will sublime into the condenser and therefore has to be returned to the flask by *stopping the cooling water briefly*. Let the vapours move up to a maximum of 50% of the condenser height to dissolve the white substance, then switch on the cooling water. You will need to repeat this several times, roughly every 20 minutes for the first 3 hours. The refluxing time should be at least 10 hours (or gentle overnight reflux).

Allow the solution to cool to room temperature. Filter off the solid using a sintered-glass crucible and rinse the solid with 2×100 ml of ethanol and then 2×50 ml of diethyl ether and dry in a vacuum desiccator for 20 minutes. The product is air stable when pure, but may darken on the surface upon storage for several days.

- Record the yield and calculate percentage yield based upon $Mo(CO)_6$.

Retain some of the sample for spectroscopic study and use the rest to make the complex below.

3.12.1.3 Synthesis of $K_4[Mo_2Cl_8] \cdot 2H_2O$ (B)

In a 50 ml round-bottomed flask place a stirrer bar, add concentrated hydrochloric acid (20 ml) and then add sequentially A (0.50 g) and potassium chloride (0.69 g).

Stopper the flask and stir vigorously for 1.5 hours. The solution will become intensely red or purple during this process. Filter off the red crystalline product (take care to leave excess KCl behind; decant into the sinter) using a sintered-glass crucible and wash the product on the sinter with 2×50 ml of ethanol. Dry in a vacuum desiccator for 20 minutes. The crystals are air stable.

- Record the yield and calculate percentage yield based upon $[Mo_2(O_2CMe)_4]$.

3.12.2 Characterisation

The remaining part of the experiment is to obtain various spectroscopic data to identify the compounds.

3.12.2.1 IR Spectra

Record IR spectra (over the range 4000–600 cm^{-1}) for your two compounds and of anhydrous sodium acetate using pressed KBr discs.

Question 1:
The $Na(O_2CMe)$ contains acetate ions: deduce the point group of the acetate ion (treating the Me groups as a single point atom) and, using the appropriate character table, predict the number of C–O stretching vibrations. Identify these in your spectrum. Your spectrum should *not* show water vibrations [υ(OH) ≈ 3400 cm^{-1} and δ(HOH) 1610 cm^{-1}].

Question 2:
When acetate ions are coordinated to a metal, the ν (CO) vibrations will be at different frequencies and may split compared with the free ion, since the electron density in the unit has changed and the molecular unit is more complicated.

- From your spectrum of $[Mo_2(O_2CMe)_4]$, propose assignments for the acetate ligand C–O stretching vibrations.

The IR spectrum obtained from $K_4[Mo_2Cl_8] \cdot 2H_2O$ should be very simple in the normal range.

Question 3:
Does your spectrum show the presence of water (ensure you are using anhydrous KBr)? Is there any evidence of acetate in the spectrum?

3.12.2.2
Far-IR and Raman Spectra

Many inorganic compounds containing atoms heavier than those of the first row of the periodic table have important vibrations at lower frequencies than organic compounds. The bands in the far-IR and Raman spectra of the two molybdenum compounds are given below in cm^{-1}. In this region, you would expect the Mo–Mo stretch and Mo–O or Mo–Cl stretching vibrations to occur. The selection rules for IR and Raman activity are different and so the two techniques are complementary.

	$[Mo_2(O_2CMe)_4]$	$K_4[Mo_2Cl_8]\cdot 2H_2O$
Far-IR data:	368, 345, 337	305, 292, 275
Raman data:	402	340, 312, 273

Question 4:
Deduce the point group of the two compounds (ignore the Me hydrogen atoms in the acetate groups, i.e. treat the Me group as a single point). Do the molecules have a centre of symmetry? [Centrosymmetric molecules obey the *mutual exclusion rule*, which states that vibrations active in the IR are inactive in the Raman and *vice versa*.]

- Using the appropriate character table, convince yourself that the Mo–Mo stretching vibrations are of A_{1g} symmetry and Raman active only.
- By comparison of the IR and Raman spectra, suggest an assignment for the ν(Mo–Mo) stretch in each compound.

The other strong bands in the IR and Raman spectra are likely to be ν(Mo–O) and ν(Mo–Cl), respectively.

- List the main bands in each, remembering that due to the mutual exclusion rule the frequencies will not coincide (although they may be similar).

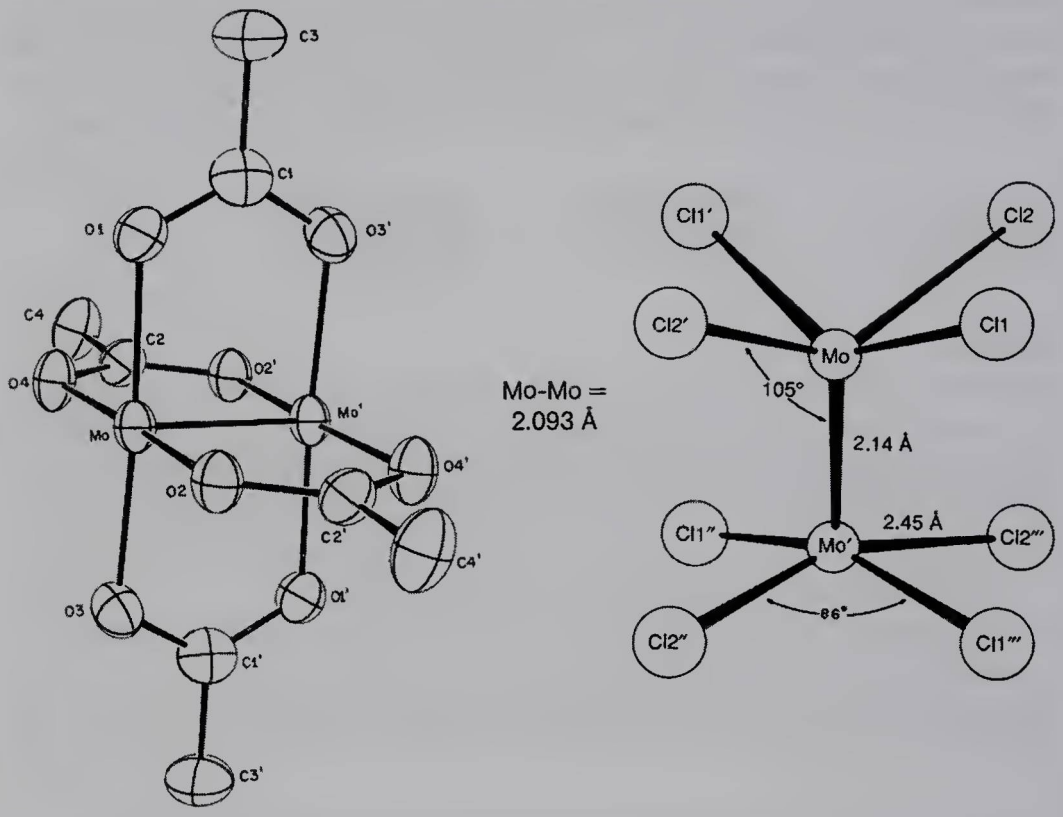
3.12.2.3
$^{13}C\{^1H\}$ NMR Spectrum

Question 5:
Using the $^{13}C\{^1H\}$ NMR spectrum of $Mo_2(O_2CMe)_4]$ provided in Figure 3.12-1, propose assignments for the resonances and explain briefly if the spectrum is consistent with the structure of the molecule.

3.12.2.4

Data Analysis and Bonding

X-ray crystallography shows that the complexes have the structures shown below:



The essential features are the short Mo–Mo bonds and the eclipsed geometry. In the bonding model proposed for these dimers (*Shriver and Atkins' Inorganic Chemistry*, 4th edn, p. 454; see Further Reading) each molybdenum atom has nine available atomic bonding orbitals, s, p_x, p_y, p_z, d_{xy}, $d_{x^2-y^2}$, d_{x^2}, d_{xz}, d_{yz}. Taking the Mo–Mo as the z-axis and the x- and y-axes along the Mo–O(Cl) bonds gives five orbitals available for σ-bonding to the ligands (s, p_x, p_y, p_z, $d_{x^2-y^2}$ – only four of which are used – in some dimers axial ligands *trans* to the M–M bond use the p_z orbital). That leaves four orbitals for the M–M bonding and by symmetry these are d_{x^2} (σ), d_{xz}, d_{yz} (π) and d_{xy} (δ), leading to a shorthand notation of the bonding system which contains four bonding and four corresponding antibonding orbitals as

$$\sigma^a\pi^b\delta^c\delta^{*d}\pi^{*e}\sigma^{*f}$$

where a, b, etc., are the number of electrons in each type of orbital. NB: there are two degenerate π-orbitals.

Depending on the number of electrons available for the M–M bond, it is possible to have bonds with anything from one electron (bond order) through to eight elec-

Fig. 3.12-1 $^{13}C\{^1H\}$ NMR spectrum (400 Hz, DMSO-d_6) of $[Mo_2(O_2CMe)_4]$.

trons (bond order 4): more than eight electrons enter the corresponding antibonding orbitals and reduce the bond order.

Question 6:
Deduce the Mo oxidation state in these two compounds and hence how many *d*-electrons are available for M–M bonding. Give the bonding description (in the form $\sigma^a\pi^b\delta^c$) and deduce the bond order. *Hint*: the compounds have no unpaired electrons (they are diamagnetic).

Question 7:
Based upon the bonding model, explain why the structures adopt an eclipsed configuration.

3.12.3
Demonstrators' Comments

Compound **A** is $[Mo_2(OAc)_4]$ which contains a quadruple bond between the Mo atoms and eclipsed, bridging O,O′-acetate ligands – as shown in the X-ray structure in the script. The preparation is straightforward and should give a reasonable yield (~40–70%)

Compound **B** is similarly very straightforward to make and should be $K_4[Mo_2Cl_8]\cdot 2H_2O$ with the structure shown in the script (yield ~90%). It is possible to obtain the anhydrous salt by using stronger HCl (concentrated HCl saturated with HCl gas), and it may be that under slightly different conditions this preparation could yield an anhydrous salt – the IR spectra will readily distinguish these. Again, the yield is very high. The filtrate is pink–purple and contains other Mo salts, including Mo(III) species.

IR and Raman Spectra

Check that the KBr is dry – if in doubt, run a blank disc and if strong water peaks at ~3400 and ~1620 cm^{-1} are present the KBr should be replaced with an anhydrous sample. The Raman and far-IR data are provided in the script.

Question 1:
Na(OAc) approximates to "free" acetate ions and should give a good KBr disc spectrum with strong bands at ~1410 and ~1580 cm^{-1}, which are the stretching vibrations of the OCO group. There are medium intensity features at ~1430 and ~1440 cm^{-1} (methyl group bending and rocking modes) and the bending mode of the OCO unit is at ~630 cm^{-1}.

Use the C_{2v} point group (it is conventional to ignore the Me hydrogen atoms) and hence two stretches are predicted, $A_1 + B_1$ (both IR active).

Question 2:
On coordination to the Mo, the OCO stretches shift and split – typical values are ~1512, ~1494, ~1480(sh) and ~1412 cm^{-1}. (The Mo–acetate unit is usually too complex for the students to treat by symmetry at this stage of their experience.)

The product should not contain significant absorption at ~3400 and ~1620 cm^{-1} (H_2O) or bands due to EtOH or diethyl ether (used in the synthesis). It is useful to point out that the absence of impurities, etc., can be shown by IR spectroscopy.

Note that some dimeric acetates do contain coordinated water *trans* to the M–M bond (Rh and Cr, for example).

Question 3:
The octachloro anion should contain strong water bands in the IR spectrum, but little else above 600 cm^{-1}, and should, of course, show no acetate.

Question 4:
The point group is D_{4h} in both cases and hence both have a centre of symmetry (the mid-point of the Mo–Mo bond).

The symmetric Mo–Mo stretch is A_{1g} symmetry and is Raman active but IR inactive.

For $[Mo_2(OAc)_4]$, there is a Raman band at 402 cm^{-1} with no corresponding feature in the IR spectrum – this is the Mo–Mo stretch. Hence the bands in the 300–400 cm^{-1} region must be Mo–O stretches.

For $K_4[Mo_2Cl_8]\cdot 2H_2O$, the Mo–Mo stretch is at 340 cm^{-1} and the features in the 270–320 cm^{-1} region in both the IR and Raman spectra are Mo–Cl stretches. A good student might wonder why the Mo–Mo stretch is so different in the two compounds – there are two factors: (a) in the acetate the bridging carboxylate unit also has to stretch and needs more energy and (b) the vibrations are coupled and not "pure" Mo–Mo in either case.

Question 5:
Standard "organic" $^{13}C\{^1H\}$ NMR spectrum: the multiplet is due to the C resonances in the DMSO-d_6 solvent (coupled to ^2H), the singlet at 23.5 ppm is the methyl-C and the carboxylate C is at 180.5 ppm. There is only one resonance of each type, hence the four carboxylates are equivalent, consistent with the structure in the solid state.

Question 6:
Both are Mo(II) – d^4. Hence there are eight electrons available for each dimer. The bonding model is explained on in the script and for eight electrons this leads to a description of the bonding as

$$\sigma^2\pi^4\delta^2\delta^{*0}\pi^{*0}\sigma^{*0}$$

hence a bond order of 4 (eight bonding electronss/2).

The diamagnetism confirms all electrons are paired and hence the description above is correct.

Question 7:

The eclipsed configuration is necessary for the δ-bond – if you rotate one end of the molecule, the "face to face" overlap of d_{xy}-orbitals is lost. The evidence for this is in the short Cl···Cl distance (shorter than the sum of the van der Waals radii for $2 \times$ Cl) and is presumably why the chlorines bend back from the other Mo centre (see structure). M–M bonded species with 6 or 10 electrons where δ-bonding does not matter are often staggered.

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3.13
Cobalt Complexes of Dioxygen

David T. Richens and Christopher Glidewell

Cobalt forms a large number of binuclear complexes of general type $[L_5CoXCoL_5]^{n+}$. This experiment investigates a pair of complexes having L = NH_3, X = O_2 and $n = 4$ or 5. When $n = 4$, the O_2 ligand is present as peroxide, O_2^{2-} thus, Co(III)(O_2^{2-})Co(III), having r(O–O) = 148 pm. When $n = 5$, the O_2 ligand is present as superoxide O_2^- thus, Co(III)(O_2^-)Co(III), having r(O–O) = 129 pm. (In ionic peroxides, r(O–O) = 149 pm; in ionic superoxides, r(O–O) = 128 pm). Some of these species have been of interest as models for biological oxygen containing metalloenzyme species.

In the experiment, you are asked to prepare samples of two compounds, one containing X = O_2^{2-} and other containing X = O_2^-, and then to identify them on chemical and physical grounds.

3.13.1
Experimental

3.13.1.1
Complex A

Dissolve 12 g of $Co(NO_3)_2 \cdot 6H_2O$ in 25 cm^3 water and filter the solution. Add 60 cm^3 of a slightly diluted concentrated aqueous ammonia solution (15 mol dm^{-3}; NB concentrated ammonia is 18 mol dm^{-3}), cool to below 10 °C and suck a current of air through the mixture for 3 hours by use of a water pump. Then add a solution of 5 g sodium nitrate in 10 cm^3 H_2O and suck air through for a further hour. Cool in ice and filter off the dark green crystals. Wash with concentrated ammonia solution and then with ethanol. This yields a dihydrate, which can be dehydrated by leaving overnight in a vacuum desiccator with silica gel. Record the yield of anhydrous product.

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3.13.1.2
Complex B

At intervals of **10 seconds***, add the following solutions to a 1 litre conical flask, stirring vigorously throughout: 50 cm^3 of 1 mol dm^{-3} $(NH_4)_2SO_4$, 100 cm^3 of conc. NH_3, 100 cm^3 H_2O, 50 cm^3 of 1 mol dm^{-3} $CoSO_4 \cdot 7H_2O$, 50 cm^3 of 3% hydrogen peroxide and finally 50 cm^3 of 1 mol dm^{-3} $(NH_4)_2S_2O_8$. Then stir for a further 15 minutes, after which a fine precipitate forms. Filter this off, wash with a dilute NH_3 solution and then with ethanol. Dry the dark green crystals in a desiccator over silica gel (preferably in the dark). Record the yield.

* **N.B.:** It is important to add the reagents **quickly** and in the **correct** order.

Dissolve ~5.0 g of the crude complex **B** (scale down if a low yield was obtained) in a minimum volume of 1.0 mol dm^{-3} sulfuric acid at 80 °C. Filter while still hot and then leave for several hours to crystallise (preferably overnight if time allows). Filter off the dark green lustrous crystals, and wash once with the mother liquor. Dry in a desiccator and record the yield of recrystallised product.

3.13.1.3
Atomic Absorption Analysis

Prepare samples of your two complexes (recrystallised form of **B**) for AAS analysis. Approximate concentrations of Co in the final solutions for analysis should be around 5 ppm for most instruments.

3.13.1.4
Magnetic Measurements

Complex **A** can be shown to be **diamagnetic. B** however is **paramagnetic.** Measure the molar magnetic susceptibility of **B**.

3.13.2 Exercises

1. Given that: **A** contains 34.5% of nitrogen
   and that: **B** contains 14.5% of sulfur, and 21.1% of nitrogen
   Calculate the atomic ratios, N : Co in **A** and S : N : Co in **B**. Use these atomic ratios, together with the magnetic data, to deduce the correct chemical identities of **A** and **B**. Note that sulfur may be present both as SO_4^{2-} and/or as HSO_4^-.
2. See what you can find out about the ESR spectra of transition metal complexes. Predict the number of lines and their relative intensities in the ESR spectrum of the superoxo complex (cobalt is monoisotopic and ^{59}Co has $I = 7/2$).

3. Observe the reaction of a sample of **A** with a dilute solution of sulfuric acid. What is the reaction occurring? Write a balanced equation. Compare with the behaviour of **B** which can be conveniently recrystallised from hot sulfuric acid as you have shown. Can you offer an explanation for the different chemical behaviour of **A** versus **B** here?
4. The Raman spectrum of **A** shows that it has an O–O stretching frequency at 851 cm^{-1} while that of **B** is at 1075 cm^{-1}. Explain this difference and why these bands are only very weak in the IR spectrum.
5. Consider the significance of the following observed magnetic moments (BM):

$K_3[Mn(C_2O_4)_3]$	= 4.81	$K_4[Mn(CN)_6]$	= 1.80
$K_3[Mn(CN)_6]$	= 3.18	$K_3[Fe(C_2O_4)_3]$	= 5.75
$K_3[Fe(CN)_6]$	= 2.40	$K_3[FeF_6]$	= 5.90
$K_3[CoF_6]$	= 4.70		

Further Reading

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3.14
Ferrocene, $(\eta^5\text{-}C_5H_5)_2Fe$, and its Derivatives

J. Derek Woollins

The discovery in 1951 of bis(pentahaptocyclopentadienyl)iron, commonly known as ferrocene, with its "sandwich" type structure and remarkable thermal inertness resulted in a vast amount of research into the synthesis and reactions of related organometallic compounds. A variety of organic reactions can be carried out on the cyclopentadienyl rings, which have aromatic character. In this experiment, ferrocene is prepared, acetylated and then the acetyl group is reduced. The various stages are studied by ^{1}H NMR spectroscopy.

Special Safety Precautions

Dicyclopentadiene, cyclopentadiene and dimethyl sulfoxide are poisonous. Avoid breathing vapour and skin contact. The KOH/ether mixture prepared in this experiment is very corrosive. Acetic anhydride is an irritant and should be used in a fume cupboard

3.14.1
Experimental

a) Ferrocene

Cyclopentadiene dimerises readily at room temperature to dicyclopentadiene by a Diels-Alder reaction. Accordingly, the commercial sample must be first 'cracked' on the day you plan to use it. The apparatus for doing this is set up in a fume cupboard and it may be convenient for you to carry out the cracking process in collaboration with other people doing this experiment. Check that the flask contains at least 60 ml of dicyclopentadiene (100 ml if more than one sample of cyclopentadiene is needed). Collect the distillate that condenses in the range 42–44 °C and keep it cooled with an ice bath around the receiving flask. (You will need about 8.5 ml).

While you are cracking the dicyclopentadiene, fit a three-necked 500 ml flask with a mechanical stirrer in the central neck, a 100 ml dropping funnel fitted to one side

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neck by means of a side-arm adaptor (connecting the side arm to a nitrogen supply), and a Liebig condenser in the other side neck, with the exit end of the condenser connected to a bubbler to prevent air entry and to monitor the nitrogen flow rate. Charge the flask with diethyl ether (100 ml) and *flake* potassium hydroxide (40 g), stir well and flush with nitrogen. Meanwhile, dissolve finely powdered iron(II) chloride tetrahydrate (10 g) in dimethylsulfoxide, degassed by bubbling nitrogen through it (40 ml, avoid skin contact; vigorous stirring for about an hour is usually required). Keep the iron(II) chloride solution in a sealed container to prevent oxidation.

With vigorous stirring and under a slow stream of nitrogen, add 8.5 ml cyclopentadiene to the KOH/ether mixture. After ca. 15 minutes, discontinue the nitrogen flow and add the iron(II) chloride solution dropwise. The reaction is exothermic and the ether may boil. When this subsides, restore a slow nitrogen flow. Replace any ether lost by evaporation. Continue stirring for a further 30 minutes. (**Care:** The KOH/solvent mixture is extremely corrosive). Decant the ether layer and wash the dark residue in the flask with 50 ml of ether. Combine the ethers and wash it with 2 M HCl (2 × 40 ml), to neutralise any hydroxide, and then with water (2 × 40 ml). Carefully evaporate off the ether to deposit orange crystals of ferrocene. Purify a small sample by sublimation using a Petri dish and lid on a warm hotplate *in a fume cupboard.* (Careful: too rapid heating or cooling of the dish may crack it). Remove the golden crystals of ferrocene periodically from the Petri dish lid. Record the m.p. and write equations for the reactions involved in the preparation.

Examine the solubility of ferrocene in a) water, b) dichloromethane, c) toluene and account for your observations in terms of the structure and bonding of the molecule. Add ferrocene (0.1 g) to water (5 ml) followed by concentrated nitric acid (5 ml) – *extreme* caution. Shake the tube gently for 2 minutes and record your observations.

b) Acetylation

Add crude ferrocene (3 g) to acetic anhydride (10 ml) in a 50 ml round-bottomed flask provided with a calcium chloride or silica gel guard tube. Carefully add orthophosphoric acid (2 ml) dropwise with shaking. Heat the mixture gently (e.g. on a steam bath) for 20 minutes, then pour the hot mixture onto crushed ice (80 g) with stirring. Wash your flask out with some additional ice and combine the aqueous materials. When all the ice has melted, neutralise the solution with solid sodium bicarbonate, cool the mixture in ice for 20 minutes and then filter off the brownish yellow solid. Dry it in a vacuum desiccator.

Recrystallise your product from cyclohexane or petroleum ether and check its purity by TLC (repeat the recrystallisation and TLC examination if necessary, and draw a representation TLC development in your report, including R_f values). Record the m.p.

c) Reduction of Acethylferrocene

Dissolve acethylferrocene (1 g) in ethanol (15 ml) and add water (5 ml). Dissolve sodium tetrahydroborate (0.8 g) in water (4 ml) and add this solution slowly to the stirred solution of acethylferrocene. After the solution has stood for 15 minutes, it may be

pale yellow, but often the colour does *not* become paler and stays brown. If necessary, add further portions of sodium tetrahydroborate to complete the reduction. Add water (100 ml) and extract the aqueous mixture with diethyl ether (2 × 20 ml). Dry the ether extracts over magnesium sulfate or calcium chloride, filter and then evaporate off the solvent on the rotary evaporator. Recrystallise the product, which is often an oil, from 40/60 petroleum ether and dry it in a vacuum desiccator. Record the m. p.

Study the ^{1}H-NMR spectra of acetylferrocene and its reduction product and interpret them. What is a plausible mechanism for the acetylation, given that ferrocene reacts some 3×10^{6} times faster than benzene?

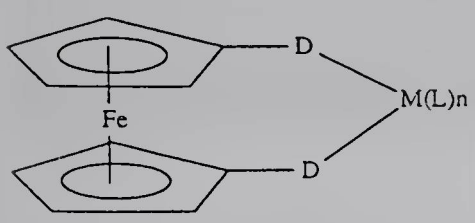
3.15
The Use of Organolithium Reagents in the Preparation of Ferrocene Derivatives

Ian R. Butler

The objective of this exercise is to gain an insight into some practical inorganic chemistry as you may find it in a research environment. The time spent waiting in the initial stages of the synthesis can be profitably used in the library. In this experiment, you will prepare some synthetically useful organometallic compounds and a metal complex of one of these. Your are required to work in pairs, although each person in a pair will prepare a different product. You will be able to practice working under an inert atomosphere (N_2), which will be extremely useful for your future research careers.

Although the general area of organometallic chemistry is over 100 years old, it was only in the early 1950's that major developments were made which turned it into one of the most intensely studied fields today. One of the milestones was the discovery of ferrocene, independently by Pauson and Keally and Miller, and the later realisation of its unusual bonding features by Wilkinson and Fischer. It was the first example of a sandwich compound in which the iron metal is bound to the 10 equivalent carbon atoms (in organometallic notation, $2 \times \eta^5$) in two aromatic cyclopentadienyl rings. The chemistry of ferrocene is dominated by its electrophilic aromatic substitution reactions. In essence, ferrocene can be treated as behaving like an aromatic organic compound with respect to electrophiles, the only difference being that ferrocene is typically about 100,000 times more reactive than benzene for example. Since the individual cyclopentadienyl rings in ferrocene are held apart at a constant distance, the ferrocene nucleus is a useful backbone for the design of ligands capable of chelating to a metal centre.

For example, disubstitution of ferrocene as shown below with two electron donating groups D will result in a compound which has the potential of binding to a metal centre



D = electron donor atom or group

M = metal (usually bound to some other ligands, L)

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The experimental details are intentionally non-exhaustive in that you may have to make slight modifications to solvent volumes, etc. as might happen in a research environment. In this way, you will learn to make necessary adjustments according to prevalent conditions. In this experiment, you will functionalise the ferrocene by generation of dilithioferrocene in the form of its TMEDA adduct. You will then prepare derivatives from this intermediate.

Special Safety Precautions

Before starting this experiment you must read the manufacturers safety data sheets on the chemicals you will be using. Rubber gloves and proper eye protection must be worn throughout the lab work.

1. *n*-Butyllithium Solutions in Hexane. This experiment deals with the use of *n*-butyllithium solutions which are extremely flammable. This reagent poses no danger when handled properly, but it is important that the correct handling procedure is adopted and that it is treated with respect. This is without doubt the most commonly used lithium based reagent in the organic and organometallic research laboratories. A typical reaction of *n*-butyllithium is shown below:

   R–H + *n*-BuLi → RLi + *n*-BuH

   where H is a relatively acidic proton.
   The reaction of *n*-butyllithium with water is a particularly violent one, therefore it is important that all apparatus that you will use is absolutely dry. In addition, all solvents must be predried. For details on how to work with air sensitive compounds see Aldrich Technical Information Bulletin Number AL-134, which is supplied with the reagent.

2. Other Reagents. *N,N,N′,N′*-Tetramethylethylenediamine (TMED), chlorodiphenylphosphine, chloro-tri-*n*-butyltin and dimethylformamide (DMF) are all highly toxic and all transfers should be carried out in a properly vented fume cupboard. Nickel chloride hydrate and ferrocene are toxic and should also be weighed out and handled in a fume cupboard.

3. Solvents. Hexane(s), toluene, diethyl ether and methylated spirits are all highly flammable and must be kept away from sources of ignition. Dichloromethane and deuterated chloroform are toxic by inhalation or contact and should be handled in a fume cupboard.

4. Alumina. Alumina (Al_2O_3) powder can be harmful if ingested — always use in a well vented fume cupboard.

5. Residues. All residues should be disposed of in an appropriate waste receptacle.

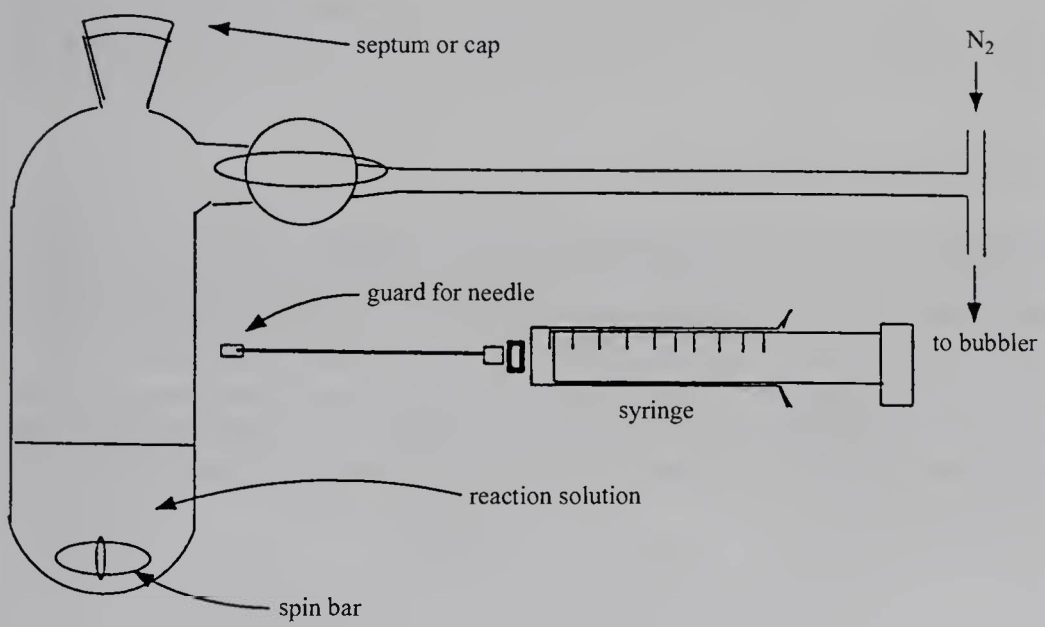
3.15.1 Experimental

3.15.1.1 Lithiation of Ferrocene

This part of the procedure must be carried out under a dry nitrogen atmosphere (work in pairs with each person carrying out one experiment).

Ferrocene (1.86 g, 10 mmol) is placed in a 250 ml Schlenk tube. The tube is then evacuated and refilled with nitrogen (or flushed with nitrogen for 2 minutes), then dry hexane (or hexanes) (30 ml) is added. A solution of *n*-butyllithium in hexane (1.6 M, 13 ml) is then added using a syringe. The correct method of using the syringe and the experimental set up is shown here.

When using a syringe, always guard against accidentally stabbing yourself by making sure the tip of the syringe has a cap on it except when actual transfers of reagent are being performed. Firstly, fill the syringe with nitrogen by placing the tip of the needle into the neck of your Schlenk tube and slowly pulling back the plunger to the desired volume. Next, withdraw the syringe and expel the nitrogen and repeat the procedure, this time filling the syringe with a slightly larger volume of nitrogen than the volume of the solution you will require (approx. 16 ml) – do not expel the nitrogen this time. One person then holds the bottle of *n*-butyllithium steady, while the other carefully inserts the needle through the septum on the top of the bottle. Keeping the tip of the needle above the headspace, inject the nitrogen in the syringe into the bottle, then allow the tip of the syringe to go below the surface of the liquid and withdraw 13 ml of the *n*-butyllithium solution. Slowly extract the needle and immediately transfer the *n*-butyllithium into the Schlenk tube. The person holding the bottle should recap it as soon as the syringe has been removed. The syringe should now



be washed by removing the plunger and rinsing both parts under running water – a slight hiss may be heard due to the reaction of water with traces of residual *n*-butyllithium.

Now add *dry* tetramethylethylenediamine (1.2 g, approx. 30 mmol) to the well stirred solution (using a Pasteur pipette). Cap the Schlenk tube and allow the reaction mixture to stir overnight, making sure the butane produced in the reaction is vented through the bubbler.

Repeat the experiment reversing roles with your partner.

After the solution has been stirred overnight, you will observe the formation of a pale orange precipitate of 1,1-dilithioferrocene · TMEDA. This is a pyrophoric solid, therefore you will continue directly without its isolation. Outlined below are three different experimental procedures. Each pair of workers will carry out reaction a) and either b) or c). Cool the Schlenk tube in an ice bath, then using a Pasteur pipette add either

a) chlorodiphenylphosphine (4.6 g, 21 mmol) or
b) chloro-tri-*n*-butyltin (6.67 g, 21 mmol) or
c) dry diethyl ether (60 ml) then dimethylformamide (1.6 g, excess) dropwise. After the addition, allow the mixture to warm up to room temperature and stir for a further 2–3 hours then hydrolyse carefully by the slow addition of water (50 ml).

a) The Chlorophosphine Procedure: Bis-diphenylphosphinoferrocene

An orange-brown precipitate will form. Decant the supernatant hexane layer or remove the supernatant hexane layer by syringe and wash the solid with methylated spirtits (2 × 10 ml) and hexane (3 × 30 ml). Finally redissolve the residue in approx 20 ml hot toluene (ca. 80°C). Add hot hexane until the solution becomes turbid. The solution is then cooled to room temperature to give fine orange crystals of the product, which should be isolated by filtration. Record the melting point and submit your sample for ^{1}H NMR analysis using $CDCl_3$ as the solvent (a few mg of your product are required). Interpret the spectrum as far as possible. Record the weight and % yield of your product.

Preparation of a Nickel Complex

A solution of the bis(diphenylphosphino)ferrocene (dppf) (0.55 g, 1×10^{-3} mol) in methanol (20–30 cm^3) is placed in a round-bottomed 2-necked flask equipped with a reflux condenser, a nitrogen inlet (placed on top of the condenser), and a magnetic stirrer. The solution is then brought to a gentle reflux and $NiCl_2 \cdot 6H_2O$ (0.20 g, 8.5×10^{-4} mol), dissolved in hot methanol (15 ml), is added. A fine green precipitate will form immediately. This can be separated by filtration while the solution is still warm and washed with cold methanol, then air dried. Record the weight and % yield of the product.

b) The Stannyl Reaction: Bis(tri-n-butylstannyl)ferrocene

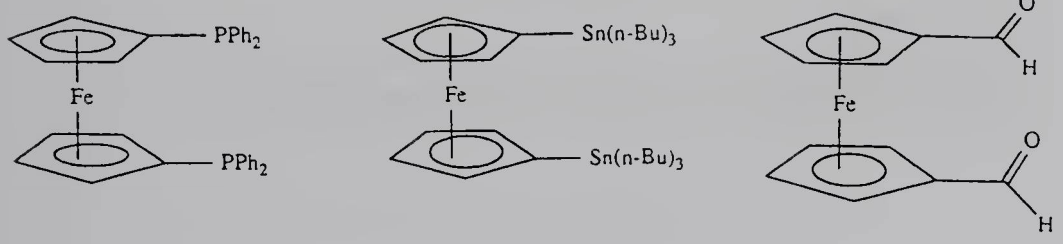
Add 30 ml dichloromethane, then separate the organic layer and discard the aqueous fraction. Dry the organic fraction over anhydrous $MgSO_4$ (~5 g) for 20 minutes, or overnight if necessary. Filter off the $MgSO_4$ and wash with 10 ml dichloromethane to ensure the product is fully removed from it (you should observe the leaching of the yellow colour). Concentrate the organic fraction to a few ml using the rotary evaporator. Record the crude yield of product which is an oil.

Make up a column packed with neutral alumina (approx. 100 g) by making a slurry of the alumina in hexane or hexanes in a beaker and fill the column slowly with this. (Some workers may try a dry packed column – ask the demonstrator which you should use.)

Allow the solvent volume to run down to just above the top of the alumina, then apply a little (1.0 g) of the crude product in a small quantity of hexane. (If you use a dry packed column, the reaction mixture (in a little hexane) can be applied directly to the top of the column.) Let this run into the column, then add a few ml more of hexane. Again allow this to run into the column, then fill the column with the eluting solvent (hexane). Collect the product bis(tri-*n*-butylstannyl)ferrocene as the first pale-yellow/orange fraction to elute from the column. Obtain the ^1H NMR spectrum of this and any subsequent products and access their purity. Store the product sample(s) in a dark bottle(s) under nitrogen. If your product is not pure, you will observe peaks in the spectrum attributable to ferrocene and mono(tri-*n*-butylstannyl)ferrocene. Assign all the peaks in the ferrocenyl region of the spectrum (3.5–5 ppm) and estimate the product purity.

c) Reaction with Dimethylformamide: Ferrocene-bis-carboxaldehyde

Add a further 30 cm^3 of water to the dichloromethane reaction mixture (60 cm^3). The dark red organic layer should then be separated (separatory funnel) and flash chromatographed through a plug of alumina in a Büchner funnel, the alumina being washed with more dichloromethane to ensure your product is fully extracted. Dry the organic layer over anhydrous magnesium sulfate (30 min minimum time), filter and reduce the volume until a precipitate is observed. [If an oil is observed add a small quantity of diethyl ether to the oil and place the solution in a freezer in a sealed container to crystallise.] Cool the solution by placing the product in a stoppered flask in the refrigerator or freezer. This should give dark red-brown crystals which can be filtered off, washed with ether and dried under vacuum. Obtain a ^1H NMR spectrum of your product (in $CDCl_3$) and interpret the data. Record your product yield.



In addition to the ^{1}H NMR spectra of the products, decide which other spectroscopic or physical techniques would be useful to carry out on your product(s), e.g. IR for the ferrocene-bis-carboxaldehyde, magnetic susceptibility for the nickel complex of the bis(diphenylphosphino)ferrocene, mass spectrometry, etc. If the appropriate resources are available, carry out the respective analyses or obtain the data if the technique you choose is not "hands on".

2
Exercises

1. What is the easiest method of assessing the purity of your samples by ^{1}H NMR?
2. In the experiment, you have used *n*-butyllithium solutions. It would have been possible to use a *t*-butyllithium solution equally well from a chemical standpoint. Explain why this particular reagent would not be a good choice from a safety point of view and give reasons to support your argument.
3. In each of the three preparations, both of the cyclopentadienyl rings have been substituted. Why does disubstitution of one ring not occur?
4. What are the possible coordination geometries of the nickel complex that you have prepared? Of these, which is most likely? How could you determine the correct geometry?
5. From a commercial point of view, the compounds which you have prepared are a very saleable commodity. If you had to sell your product, how much would be a reasonable charge for the compound you have made? (Base your answer on a discussion with several others in the class taking into account the cost of reagents, solvents, labour, etc.).
6. Can you draw a reaction mechanism to account for the formation of the bis-aldehyde product?

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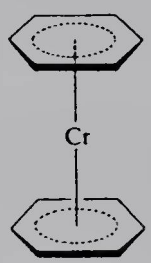
3.16
Complexes of π-Bonding Arene Ligands

Andrew W. G. Platt

The first complexes of neutral aromatic hydrocarbons were synthesised in 1919 by the reaction of phenyl magnesium bromide with anhydrous chromium chloride. At the time, it was assumed that the product was a polyphenyl chromium compound, and it was only in 1954 that the true nature of the complex as bis-benzene chromium(0), **1**, was deduced.

$(\eta^6\text{-}C_6H_6)_2Cr$
Bis-benzene chromium(0)



A more general synthesis for this type of compound was then devised as outlined in Eq. (1).

$$3\,CrCl_3 + Al + AlCl_3 + 6\,C_6H_6 \rightarrow [Cr(\eta^6\text{-}C_6H_6)_2]^+\,AlCl_4^- \qquad (1)$$

The reduction of the cation gives the neutral chromium(0) complex.

This general method can be extended to other metals and to other aromatic hydrocarbons. For example, $(\eta^6\text{-arene})_2M$ complexes are known for M=Ti, V, Nb, Cr, Mo and W. Cationic derivatives such as $Fe(arene)_2^{2+}$ and $Mn(arene)_2^{+}$ are common and isoelectronic with the zero valent chromium systems.

Special Safety Precautions

Compounds such as $FeCl_3$ and $AlCl_3$ are extremely corrosive. Avoid all contact with the skin and wash any spillages immediately with cold water. Both mesitylene and cyclohexane are flammable materials, do not carry out the reflux using a naked flame.

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3.16.1 Experimental

3.16.1.1 Bis-mesitylene Iron(II) Hexafluorophosphate, $[\eta^6\text{-}C_6H_3(CH_3)_3)_2Fe^{2+}][PF_6^-]_2$

The reaction of mesitylene (1,3,5-trimethylbenzene) with anhydrous iron(II) chloride and aluminium chloride produces the bis-mesitylene cation as the $AlCl_4^-$ salt which is then readily converted into the hexafluorophosphate. However, it is more convenient to prepare the complex according to Eq. (2). This is then converted into the PF_6^- salt which is easier to handle.

In this preparation, several of the reagents are sensitive to moisture. The reaction can be left at any of the points indicated with a* until the next laboratory session as long as the flask is stoppered to exclude atmospheric moisture.

$$3\,FeCl_3 + Al + 5\,AlCl_3 + 6\,\text{mesitylene} \rightarrow 3[Fe(\text{mesitylene})_2][AlCl_4]_2 \qquad (2)$$

Note that as both $FeCl_3$ and $AlCl_3$ are hygroscopic, the time that these reagents are exposed to the air is best kept to a minimum. Plan your work accordingly and make sure that the lids are replaced on the reagent bottles immediately. The aluminum chloride should be yellow in colour. If the sample contains grey or white material, it is likely that some hydrolysis has occured.

Weigh out about 2.5 g of anhydrous $FeCl_3$ (the exact amount is not important so long as the weight taken is known). Place in a round-bottomed flask equipped with a magnetic stirrer bar, and cover with about 30 cm^3 of cyclohexane. Add the required amount of $AlCl_3$ and Al powder and a slight excess of mesitylene, use Eq. (2) to calculate the amounts. (Note that it is best to finely powder the $AlCl_3$ in a dry mortar and pestle before addition to the reaction flask).*

Stir the mixture vigorously whilst heating to reflux for about 2 hours. Cool the mixture to room temperature* and carefully decant the solvent from the solid product. To the remaining solid add a slurry of KPF_6 in water. Stir the mixture vigorously, making sure that all the dark coloured material is dislodged from the sides of the reaction flask. (You may need to scrape off any obstinate pieces with a spatula). Filter the mixture and wash with water and then a little ethanol and dry at the pump to leave a pale orange-tan coloured solid. Record the weight obtained and calculate the percentage yield. Record the infrared spectrum of the product (as a KBr disc), and of mesitylene for comparison.

3.16.2
Exercises

1. Briefly describe the function of the reagents used in the preparation.
2. Discuss the bonding of mesitylene to the iron and show how the infrared spectrum of the product supports this theory.
3. In what way would the bonding in this compound be likely to differ from that in the isoelectronic chromium(0) compounds.
4. Bearing the answer to 3 in mind, arrange the following in the order of expected metal to ligand bond strengths for iron(II): benzene, 1,3,5-trimethoxybenzene and hexacyanobenzene (think of the electronic properties of the substituents).

3.17
Organotin Chemistry

Kieran C. Molloy and Timothy T. Paget

Organotin compounds have been widely used as PVC stabilisers, agrochemicals, wood preservatives, anti-fouling paints and precursors for the chemical vapour deposition (CVD) of electrically conducting films of SnO_2. Recent work has shown that certain di-organotin compounds show anti-tumour activities in excess of that of *cis*-platinum. Our understanding of organotin compounds is aided by the wide variety of physical methods which can be applied to their study. ^{119}Sn (8.6% abundance) has I = 1/2, and has an NMR chemical shift range of ca. 1000 ppm. In addition, couplings to both this nucleus and the less abundant ^{117}Sn (7.6%, I = 1/2) can be seen in the corresponding ^{1}H and ^{13}C NMR spectra, and provide valuable information about the coordination sphere about the metal. ^{119}Sn is Mössbauer active, and is the most widely studied Mössbauer nucleus after ^{57}Fe. Finally, with ten stable isotopes, the largest number for any element in the Periodic Table, mass spectral fragments show characteristic isotopic distribution patterns making assignments relatively facile.

In this experiment, you will first prepare a tetra-organotin, [Ph_3MeSn], using a Grignard reagent and then convert this compound to an organotin halide (either $Ph(Me)SnCl_2$ or $Ph(Me)SnBr_2$), the usual starting materials for the synthesis of functionalised organotins, by the selective electrophilic cleavage of Sn-C (phenyl) bonds, and finally use this latter derivative as a precursor for the synthesis of an organotin heterocycle, Ph(Me)SnS.

$$Ph_3SnCl + MeMgBr \rightarrow Ph_3MeSn + MgBrCl$$
$$Ph_3MeSn + 2Br_2 \rightarrow Ph(Me)SnBr_2 + 2PhBr$$
$$Ph_3MeSn + 2HgCl_2 \rightarrow Ph(Me)SnCl_2 + 2PhHgCl$$
$$Ph(Me)SnX_2 + Na_2S \rightarrow Ph(Me)SnS + 2NaX$$
$$X = Cl, Br$$

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Special Safety Precautions

1. Diethyl ether is highly flammable. Keep away from flames.
2. Carbon tetrachloride is toxic by inhalation and contact.
3. Bromine is toxic by inhalation and causes severe burns to eyes and skin. Use only in a fume cupboard. Wear rubber gloves at all times.
4. All mercury compounds are potentially poisonous, particularly Hg(II). Solid residues should be collected and stored in a designated waste container. Avoid inhalation of powder.
5. Vacuum distillations should be carried out in a fume cupboard and behind a safety screen. The distillation flask should be allowed to cool before air is admitted to the apparatus.

3.17.1 Experimental

a) Methyltriphenylstannane, $CH_3(C_6H_5)_3Sn$

A 3-necked 250 ml oven-dried round-bottomed flask, fitted with reflux condenser and $CaCl_2$ guard tube, and a 150 ml pressure-equalising dropping funnel, is charged with 0.51 g (21 mmol) of magnesium. The metal is just covered with dry diethyl ether and then a few drops of methyl iodide are added. The formation of the Grignard reagent can be initiated by the addition of a crystal of iodine if necessary. When Grignard formation has commenced, a further 25 ml of solvent is added to the reaction mixture, and a solution of methyl iodide (3.00 g, 21 mmol) added dropwise from the funnel at a rate which maintains solvent reflux. When Grignard formation is complete (ca. 1 hour), a solution of chlorotriphenylstannane (5.79 g, 15 mmol) in 100 ml ether is added dropwise from the funnel. When the addition is complete, the mixture is refluxed for 1 h. After allowing the solution to cool, water is added slowly to decompose the remaining Grignard reagent.

The reaction mixture is then transferred to a separatory funnel, the organic layer isolated and dried over anhydrous magnesium sulfate. After filtering the inorganic salts, the ether is removed on a rotary evaporator, and the residue recrystallised from ethanol. Record the yield, melting point and ^1H NMR spectrum of your product. Interpret the Mössbauer spectrum of the product, shown in Figure 3.17-1.

b) Methylphenyldibromostannane, $CH_3(C_6H_5)SnBr_2$

To a stirred solution of Ph_3MeSn (2.00 g, 5.5 mmol) in 25 ml carbon tetrachloride (100 ml round-bottomed flask) add dropwise a solution of bromine (1.75 g, 11 mmol) in the same solvent (25 ml) over a 30 min period. Continue stirring for at least

1 hour (preferrably overnight), during which time the colouration due to the halogen will have largely disappeared. The solvent and bromobenzene are removed on a rotary evaporator, leaving the product as a yellow oil which can be purified by vacuum distillation. Record the yield and ^{1}H NMR spectrum of the product. Interpret the mass spectrum of the product shown in Figure 3.17-2, using the isotope distribution patterns shown in Figure 3.17-5. Account for the appearance of the Mössbauer spectrum of $Me(Ph)SnCl_2$ shown in Figure 3.17-4.

c) Methylphenyldichlorostannane, $CH_3(C_6H_5)SnCl_2$

To a solution of Ph_3MeSn (3.1 g, 8.4 mmol) in acetone (30 ml), cooled in an ice bath, add 4.62 g (17.0 mmol) of mercury(II) chloride in small portions. After addition of the solid, remove the ice bath and allow the suspension to continue stirring for at least 1 hour (preferably overnight). The solvent is then distilled on a rotary evaporator, and the residue stirred for 10 minutes with 40 ml petroleum ether (60/80). Phenylmercuric chloride is separated by filtration. Solvent removal from the filtrate as before yields the product as a light yellow oil. A white solid is obtained after purification of this material by vacuum distillation. Record the yield, melting point and ^{1}H NMR spectrum of the product. Interpret the mass spectrum of the product shown in Figure 3.4-3 using the isotope distribution patterns shown in Figure 3.17-5. Account for the Mössbauer spectrum of the product shown in Figure 3.17-4.

d) Methylphenyltin Sulfide, $CH_3(C_6H_5)SnS$

A solution of **either** $Me(Ph)SnBr_2$ (0.93 g, 2.5 mmol) **or** $Me(Ph)SnCl_2$ (0.71 g, 2.5 mmol) in ethanol (15 ml) is added dropwise to a suspension of $Na_2S \cdot 9H_2O$ (0.90 g, 3.7 mmol) in the same solvent (15 ml). After refluxing the mixture for 2 hours, the solution should be cooled and evaporated to dryness on a rotary evaporator. Ether (30 ml) and water (30 ml) are added to the solids, and the mixture shaken in a separatory funnel. The ether layer is separated, dried over anhydrous $MgSO_4$, filtered and the solvent evaporated *in vacuo* to yield the product as a pale-yellow oil. Record the ^{1}H NMR of the product and identify the products formed by analysis of the Sn–Me signals.

Further Reading

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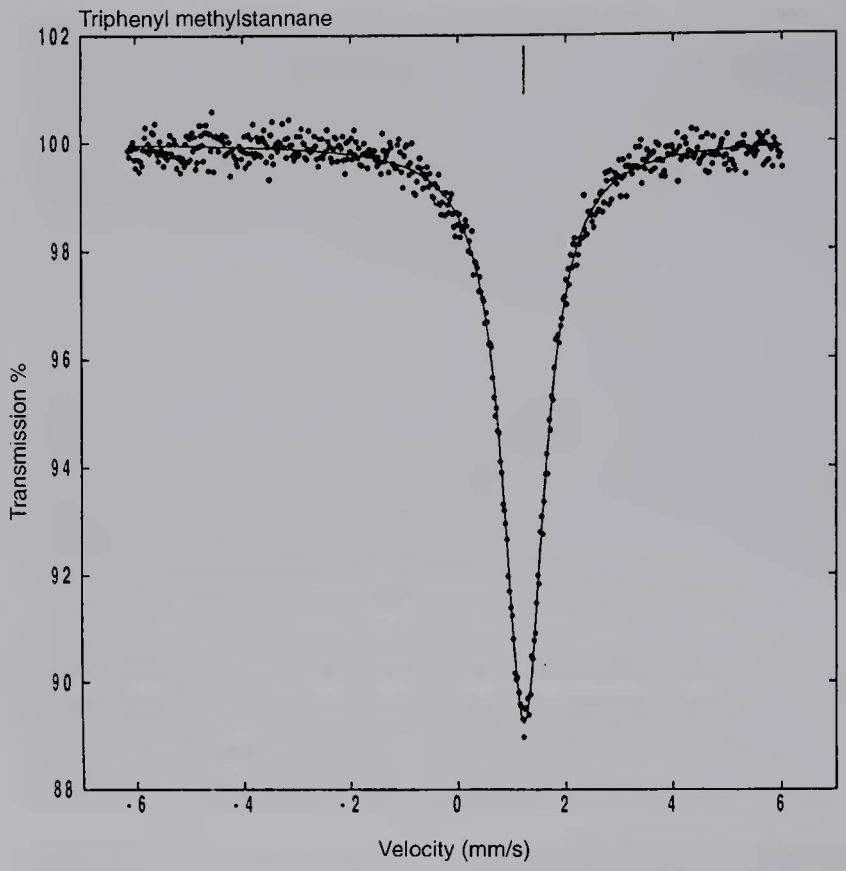


Fig. 3.17-1 Mössbauer spectrum of $Ph_3(Me)Sn$.

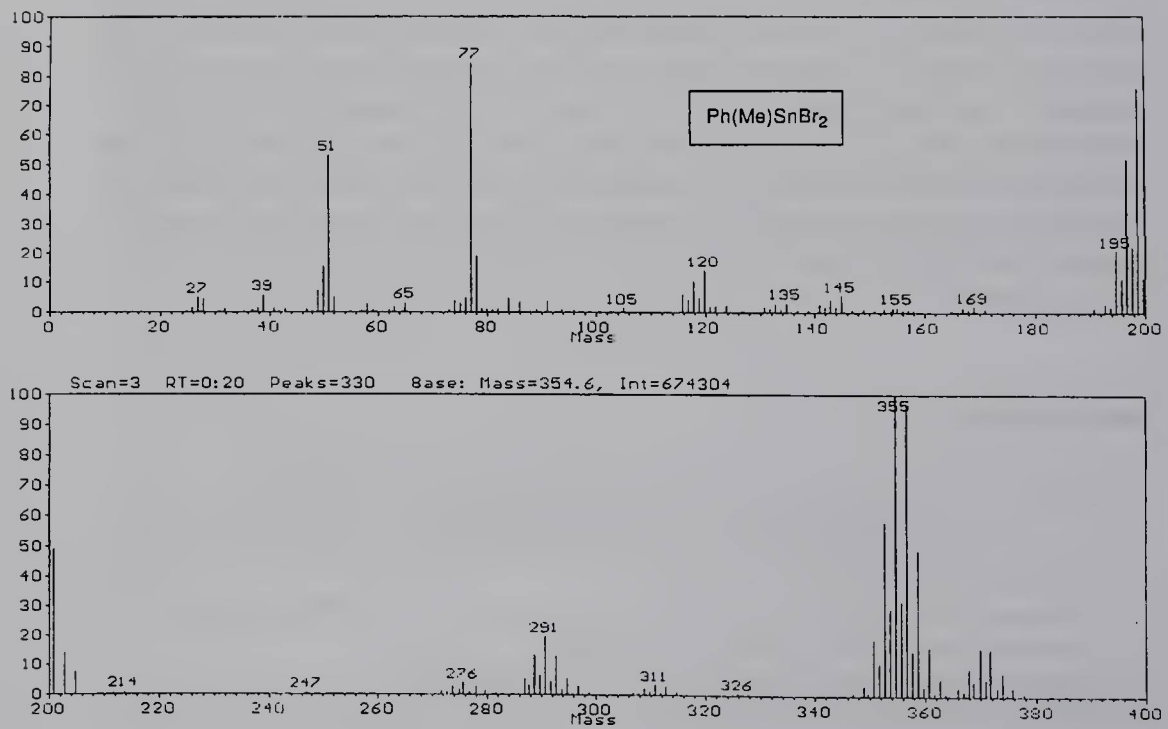


Fig. 3.17-2 Mass spectrum of $Ph(Me)SnBr_2$.

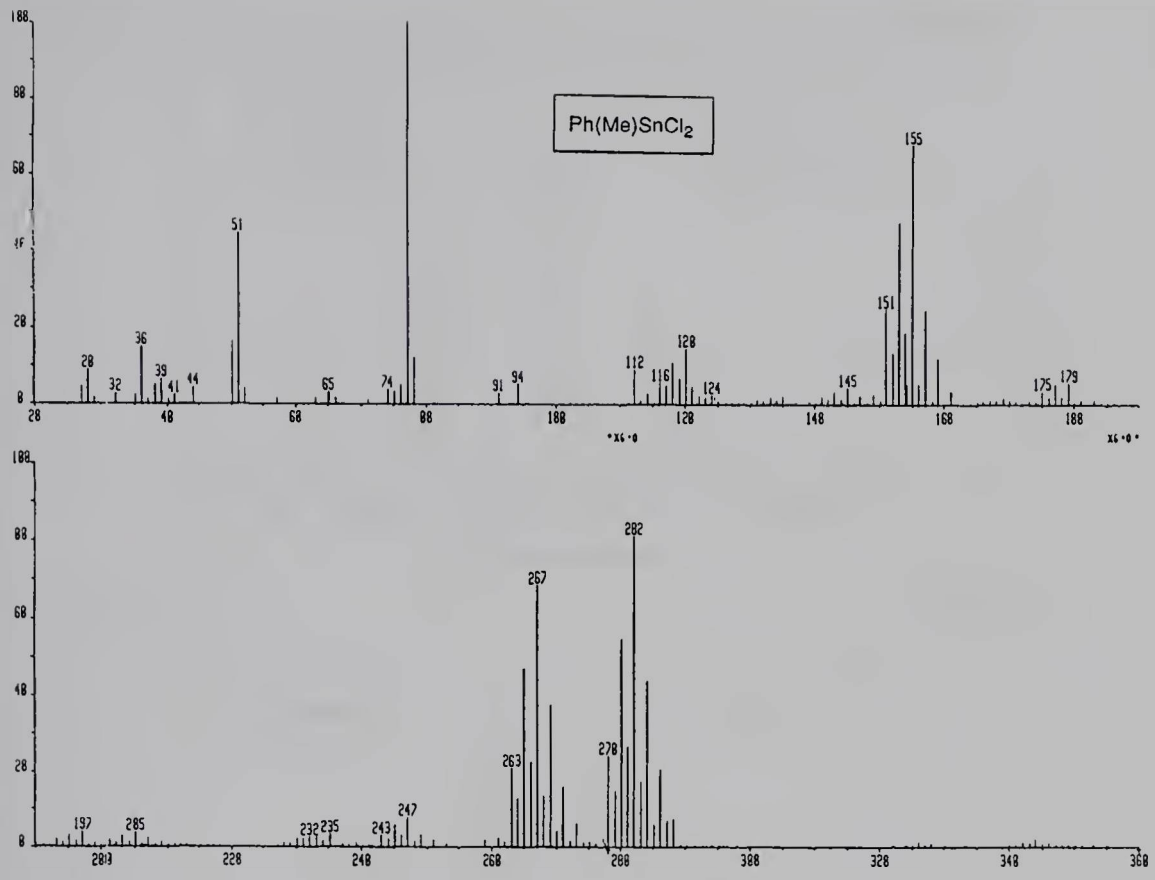


Fig. 3.17-3 Mass spectrum of Ph(Me)$SnCl_2$.

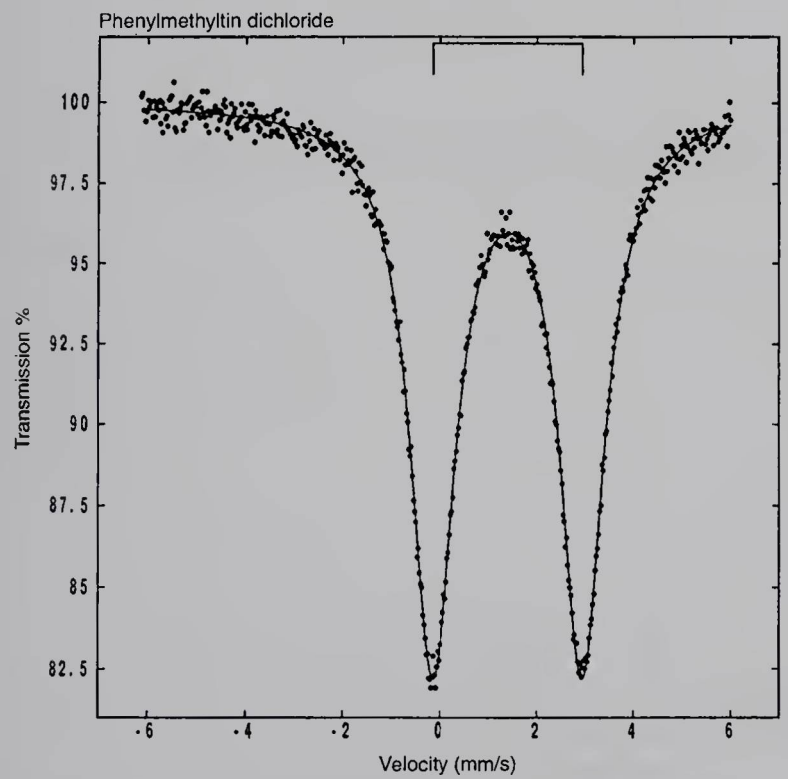


Fig. 3.17-4 Mössbauer spectrum of Ph(Me)$SnCl_2$.

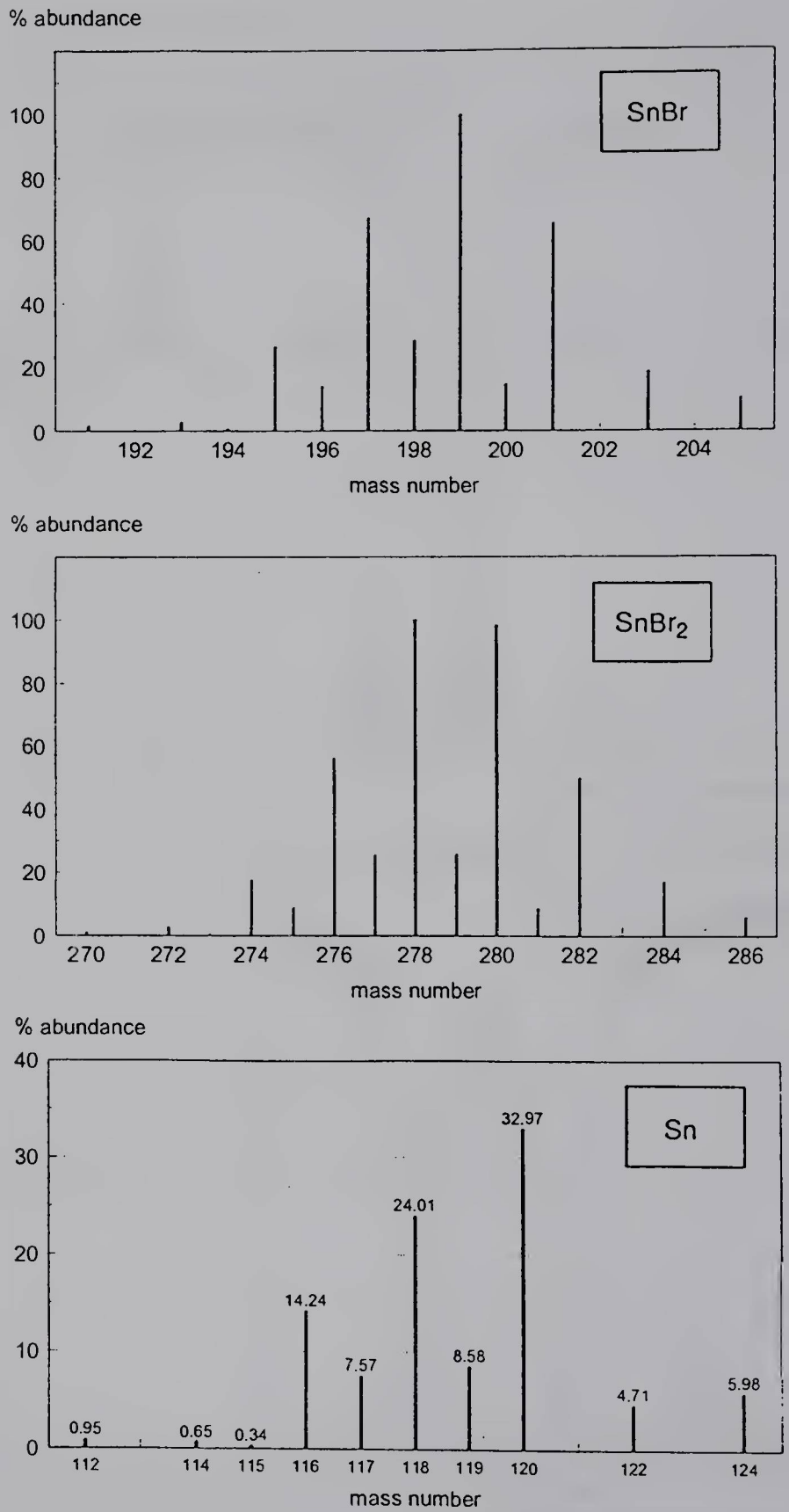
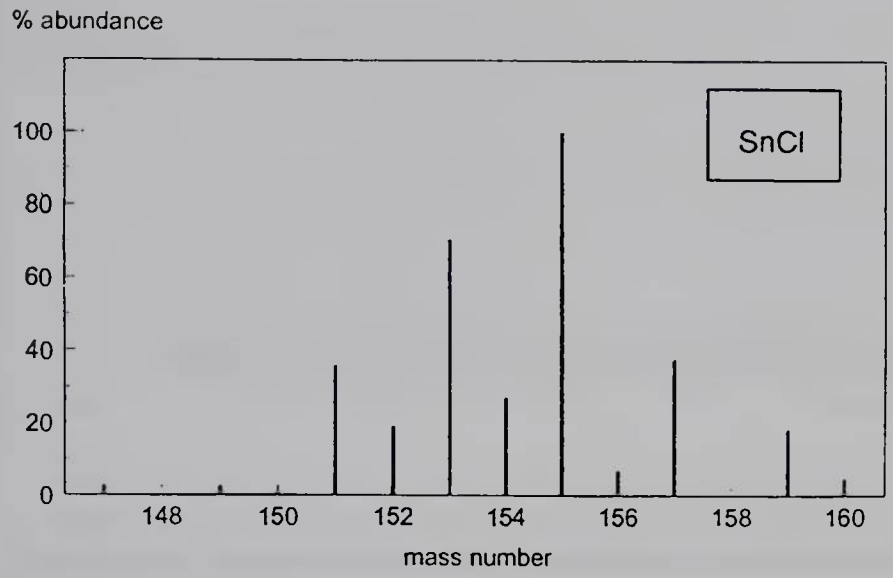


Fig. 3.17-5 Isotope distribution patterns for Sn, SnX and SnX_2 (X = Br, Cl).



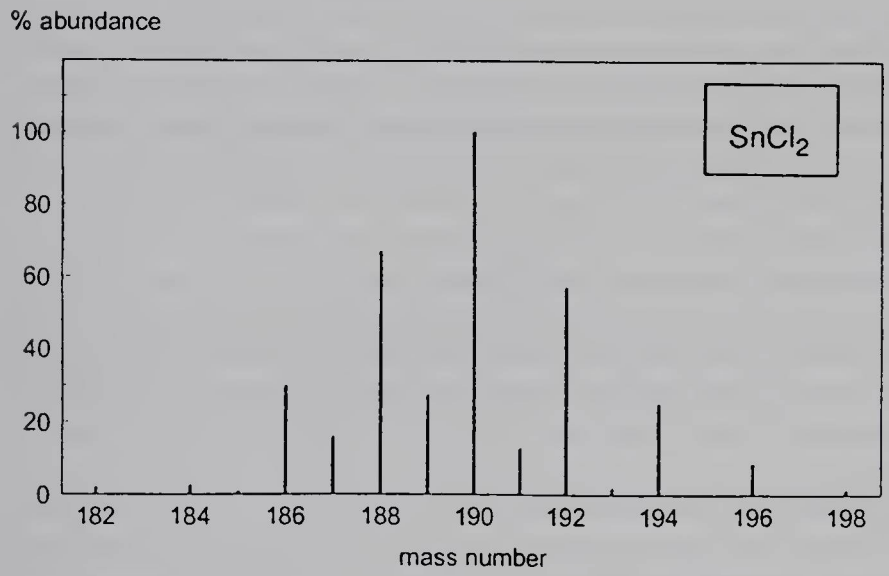


Fig. 3.17-5 (continued)

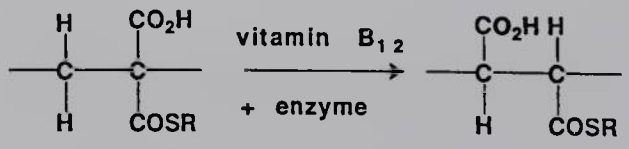
3.18
Transition Metal-Carbon Bonds in Chemistry and Biology

Christopher J. Jones

The 'classical' coordination chemistry which was developed in the first half of the 20th century was primarily concerned with compounds containing bonds between transition-metal ions and nitrogen, oxygen or halogen donor atoms. In the second half of that century, there was increasing interest in the use of so-called 'soft ligands' containing donor atoms such as sulfur, phosphorus, arsenic or selenium. Such ligands tend to form complexes with metals in their lower oxidation states; phosphine ligands in particular may often be found in compounds containing carbon monoxide or unsaturated hydrocarbons as co-ligands. To some extent these developments occured in parallel with a large expansion of organometallic chemistry, which is concerned with compounds containing metal-carbon bonds and which has become a major field of research. The study of metal complexes containing alkyl, alkenyl, acyl, carbonyl and hydride ligands has led to the discovery of many novel reactions, some of which have important industrial applications in catalytic processes. These include alkene hydrogenation, alkene isomerisation, alkene metathesis, the hydroformylation of alkenes and the carbonylation of methanol to produce acetic acid.

Although organometallic chemistry may appear to be a human invention, for millions of years biology has exploited the reactivity of a metal-carbon bond in the vitamin B_{12} coenzyme. Among other things, B_{12} is involved in effecting reactions such as the group migration shown in Eq. (1).

This practical exercise is primarily intended to provide experience in compound synthesis and characterisation using spectroscopic methods. However, it also illustrates some chemical aspects of organometallic chemistry which relate to both biological inorganic chemistry and homogeneous catalysis. In Section 3.18.1 a simple model compound is prepared which recreates the basic coordination environment of cobalt in vitamin B_{12}. In Section 3.18.2, two ruthenium carbonyl hydride complexes are prepared using a primary alcohol and formaldehyde as the source of the hydride and carbonyl ligands. In each case, the nature of the reaction products is determined using spectroscopic data.



(1)

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3.18.1
Methylcobaloxime: A Model for Vitamin B_{12} Coenzyme

Although the average human contains only 2 to 5 mg of cobalt, concentrated in the liver, it is an essential trace element whose absence causes serious illness. The cobalt is present as vitamin B_{12}, a coenzyme which, among other roles, is associated with biosynthetic methylation reactions in organisms ranging from man to bacteria. Vitamin B_{12} is necessary for the proper development of red blood cells. It is also the agent responsible for the microbial conversion of environmental Hg^{2+} to highly toxic CH_3Hg^+ derivatives. These concentrate in fish and have lead to serious outbreaks of poisoning among human populations eating fish from mercury contaminated waters.

Because vitamin B_{12} is present in animals in such small quantities, it proved extremely difficult to isolate. However, in 1957 Hodgkin and her associates reported a successful structure determination on cyanocobalamin, the cyanide derivative of B_{12}, using X-ray diffraction techniques. This structure is shown in Figure 3.18-1 and consists of two main components. The first is a planar tetradentate macrocyclic ligand, similar in some ways to the porphyrin unit found complexing the iron in haemoglobin. This highly substituted macrocyclic ring chelates the cobalt atom via four nitrogen atoms and, in the deprotonated form, is formally anionic.

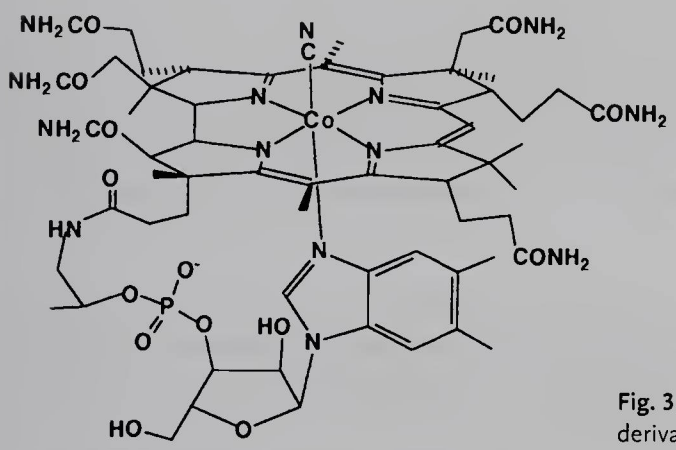


Fig. 3.18-1 Cyanocobalamin – the cyano derivative of vitamin B_{12}.

Attached to this ring via a sugar-phosphate linkage is the second component, a benzimidazole base, which also bonds to the cobalt. The sixth position in the octahedral coordination sphere of the cobalt is occupied by a cyanide ion. However, the active coenzyme would normally have either a water molecule or a CH_2 group from a sugar residue occupying this site.

The coordination sphere of cobalt in vitamin B_{12} is rather similar to that in cyanopyridine-bis(dimethylglyoximato)cobalt(III), i.e. cyanopyridine cobaloxime, whose structure is shown in Figure 3.18-2. This much simpler molecule may easily be synthesised in the laboratory and provides a chemical model for vitamin B_{12}. Instead of working with small amounts of expensive coenzyme, it is possible to study the

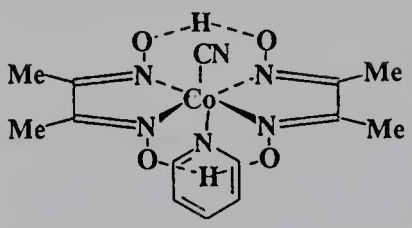
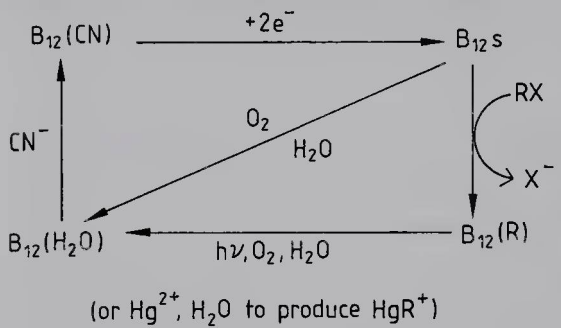


Fig. 3.18-2 Cyanopyridinecobaloxime or cyanopyridinebis(dimethylglyoximato)cobalt(III).

chemistry of cobalt in a similar, though not identical, environment using cobaloximes as models.

Using this model system, it is possible to demonstrate that reduction of Co(III) to Co(I) produces a nucleophilic metal centre, which may be methylated using CH_3I to give an analogue of the methylcobalamin involved in the biomethylation of mercury as mentioned earlier. The reactivity of the Co(I) model complex may be contrasted with the inert behaviour of the Co(III) complex, which may only be methylated with difficulty using CH_3MgI. The reactions of vitamin B_{12} (VB_{12}), copied using the cobaloxime model, may be summarised as shown in Scheme 3.18-1.



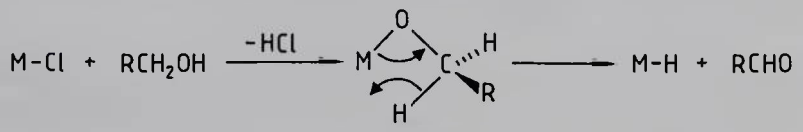
Scheme 3.18-1

Following the procedure described in the Experimental section, prepare a sample of chloropyridinecobaloxime. This material is then reduced and reacted with iodomethane to give methylpyridinecobaloxime, a model for the cobalt alkyl moiety in the vitamin B_{12} coenzyme. Infrared and ^1H NMR spectra may be used to demonstrate the formation of the metal-alkyl complex.

3.18.2
Formation of Metal-Hydrogen and Metal-Carbonyl Bonds

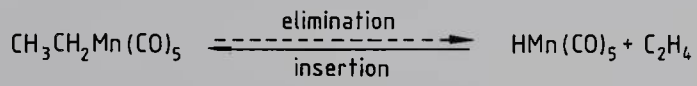
Ruthenium has a very extensive chemistry involving oxidation states –2 to +8 and serves to illustrate some of the chemistry found for the later 2nd and 3rd row *d*-block transition metals. Several ruthenium complexes show catalytic behaviour in hydrogenation and hydroformylation processes which are of commerical importance. The experiments described below illustrate decarbonylation reactions of alcohols and aldehydes with the concomitant formation of ruthenium carbonyl hydrides.

It has been known for many years that halides of the platinum metals can be reduced by alcohols or aldehydes in the presence of ligands (e.g. tertiary phosphines) to give carbonyl and/or hydrido complexes. Using isotopic labelling techniques, it is possible to show that the mechanism of metal-hydride formation from the alcohol involves a so-called β-elimination step (Eq. 2).



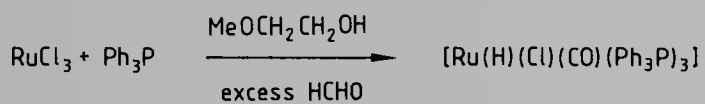
(2)

It should be noted that in the addition of transition-metal hydrides to olefins the reverse of β-elimination takes place (Eq. 3).



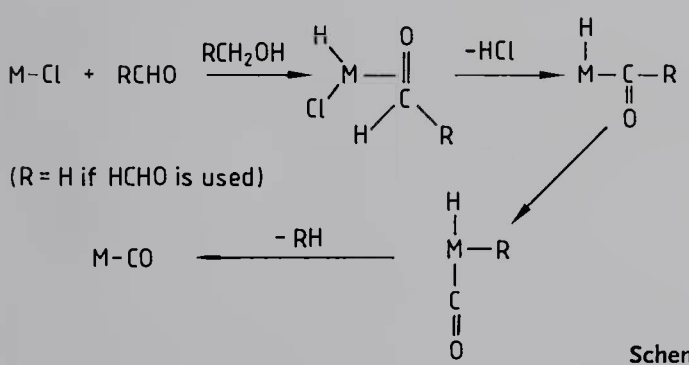
(3)

The complex $[Ru(H)(Cl)(CO)(Ph_3P)_3]$ is obtained by the reaction in Eq. (4).



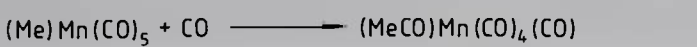
(4)

In this synthesis of $[Ru(H)(Cl)(CO)(Ph_3P)_3]$, the source of the hydride is the CH_2 group of the primary alcohol and the source of the CO ligand is the aldehyde. The steps of the mechanistic pathway for M-CO formation are uncertain, but are believed to involve "oxidative-addition" and "reductive-elimination" processes (Scheme 3.18-2), i.e. to depend upon the ability of the metal to exist in various oxidation states differing relatively little in energy.



Scheme 3.18-2

The transformation {M · CO · R} into {M(R)(CO)} involves migration of the R group from carbon to the metal. This can be a reversible process and is well established both in the "hydroformylation" of olefins and in carbonyl insertion reactions (e.g. Eq. 5).



(5)

A further example of this type of chemistry is provided by the synthesis of the iridium(I) complex *trans*-[IrCl(CO)(Ph_3P)$_2$], commonly known as Vaska's compound (Eq. 6). This material exhibits an extensive oxidative addition chemistry and is of historical importance in the development of this area of chemistry.

$$IrCl_3 \cdot 3H_2O + Ph_3P + Me_2NCHO \xrightarrow[-Ph_3PHCl]{-Me_2NH} [Ir(Cl)(CO)(Ph_3P)_2] \qquad (6)$$

Following the procedures described in the Experimental section, prepare samples of carbonylhydridotris(triphenylphosphine)ruthenium(II) and carbonyldihydridotris-(triphenylphosphine)ruthenium(II). Infrared, ^{1}H NMR and ^{31}P NMR spectra may be used to determine the formulae and structures of the products.

Special Safety Precautions

If any chemicals in this experiment should come in contact with your skin, wash them off immediately with copious amounts of water and then consult a demonstrator.

In the event that formaldehyde solution, pyridine or methanol are spilled outside a fume cupboard, keep others away from the area of the spill and consult a demonstrator. The liquid should be absorbed on an inert absorbent (e.g. vermiculite) and removed to a fume cupboard to be packaged for disposal. Consult a demonstrator about spillage of any other chemicals involved. Skin contamination by, or inhalation of, these materials must be avoided.

Material	*Hazards*
Hexa-aquocobalt(II)chloride, $CoCl_2 \cdot 6H_2O$	Toxic, Irritant
Dimethylglyoxime	Harmful
Ethanol	Harmful, Flammable
Pyridine	Harmful, Flammable
Diethyl ether	Highly Flammable, Harmful
Dichloromethane	Harmful
[Chloropyridinebis(dimethylglyoximato)-cobalt(III)]	Properties unknown, Assume toxic
Sodium borohydride	Toxic, Flammable
Iodomethane	Highly toxic, Cancer suspect agent
Methanol	Toxic, Flammable
Petroleum ether 40/60	Irritant, Flammable
Ruthenium trichloride trihydrate	Harmful by skin absorption, Corrosive
2-Methoxyethanol	Toxic, Mutagenic
Triphenylphosphine	Irritant
Potassium hydroxide	Corrosive
40% aqueous formaldehyde solution	Toxic, Cancer suspect agent

Disposal of Wastes

Waste solvents must be disposed of into the containers provided, in the fume cupboard. These must be removed before commencing the next reactions.

3.18.3 Experimental

Part 1

Avoid skin contact with, or inhalation of, any of the materials used. All operations should be performed in a fume cupboard. Wash all contaminated apparatus thoroughly with water before removing it from the fume cupboard. In the event of spillage, see the *Special Safety Precautions.*

Chloropyridinebis(butane-2,3-dioximato)cobalt(III)

In a fume cupboard place 95% ethanol (200 cm^3) in a 400 cm^3 beaker and add butane-2,3-dioxime (5.5 g). Warm the mixture on a steam bath and stir the mixture to dissolve the solid then add $CoCl_2 \cdot 6H_2O$ (5.0 g). When this too has dissolved, add pyridine (4 cm^3) to the mixture and allow it to cool to room temperature. Transfer the solution to a 500 cm^3 Büchner flask and fit a rubber bung with a dip tube which projects to just below the surface of the liquid in the flask. Using a water pump draw a slow steam of air through the solution *via* the dip tube for about 30 minutes. Allow the solution to stand for 30 minutes then collect the deposited brown solid by filtration. Wash the brown product with aliquots (5 cm^3) of water, then ethanol and finally diethyl ether. Allow the product to air dry. Record the yield. Redissolve the product in the minimum volume of dichloromethane necessary, filter the solution and add an equal volume of 95% ethanol. Using a rotary evaporator, reduce the volume of solvent to about 1/3 the original volume. A brown crystalline product should be deposited and may be collected by filtration and dried in air. Record your yield of purified product and submit all of your unused product for assessment. Obtain IR (KBr disc) and ^1H NMR ($CDCl_3$) spectra of your product.

Methylpyridinebis(butane-2,3-dioximato)cobalt(III)

In a fume cupboard set up equipment for carrying out a reaction under nitrogen as shown in Figure 3.18-3. Allow nitrogen to pass through the system for 5 minutes, escaping via a loosened stopper in the flask. Place methanol (10 cm^3) in the round-bottomed flask and bubble nitrogen slowly through the liquid for 30 seconds using a glass tube. Remove the tube, stopper the flask and allow nitrogen to pass over the apparatus and out through the bubbler.

Remove a stopper only briefly to add reagents, the nitrogen escaping when a stopper is removed should limit the entry of air into the flask. Add chloropyridine-bis-(dimethylglyoximato)cobalt(III) (0.8 g) to the methanol followed by iodomethane

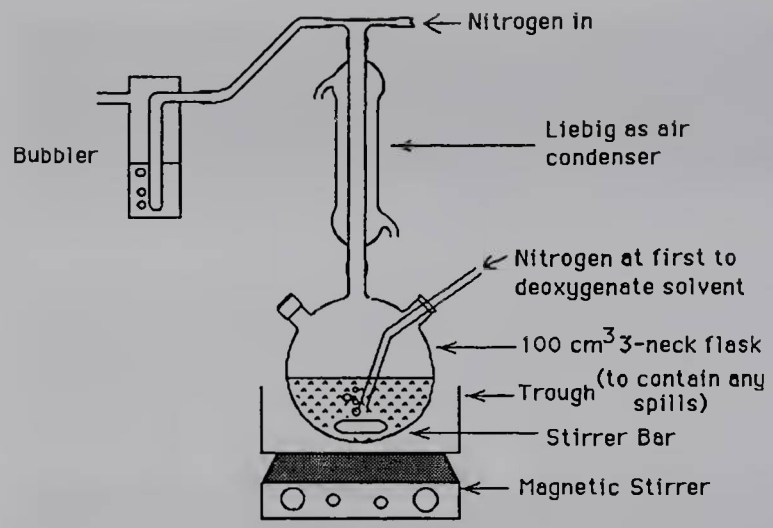


Fig. 3.18-3 Apparatus for the methylation of chloropyridine cobaloxime.

(2 cm^3). While stirring the mixture, slowly add sodium borohydride (0.4 g) in portions. Stir the mixture for 10 minutes, allowing the evolved gas to vent through the bubbler. After this time, remove the condenser and other fittings and add water dropwise to the reaction mixture to precipitate the orange product. Do not add too much water. Collect the orange solid by filtration and wash it with aliquots (5 cm^3) of petroleum ether (boiling range 40–60 °C). Allow the product to air dry, then record the yield and submit all of your product in a tube wrapped in aluminum foil as the compound is light sensitive. Obtain IR (KBr disc) and ^1H NMR spectra ($CDCl_3$) of your product.

Part 2

Avoid skin contact with, or inhalation of, any of the materials used and wear protective gloves. Ruthenium trichloride is highly coloured and will stain skin and clothing. The solvents used are flammable and iodo methane and formaldehyde are toxic so that all operations must be performed in a fume cupboard. Wash all contaminated apparatus thoroughly with water before removing it from the fume cupboard. In the event of spillage, see the *Special Safety Precautions*.

Chlorohydridocarbonyltris(triphenylphosphine)ruthenium(II)

In a fume cupboard, set up a 100 cm^3 round-bottomed flask fitted with a reflux condenser and small magnetic stirrer bar above a stirrer hotplate and small oil bath. To the flask add triphenylphosphine (1.0 g) followed by 2-methoxyethanol (30 cm^3). While stirring, heat the mixture under reflux. Shake the sample of ruthenium trichloride hydrate (0.15 g) provided with 2-methoxyethanol (10 cm^3) in a stoppered 50 cm^3 flask to produce a solution. Using a dropping pipette, add this solution to the reaction vessel *via* the condenser. Immediately afterwards add the 40% aqueous formaldehyde solution (10 cm^3), again added via the condenser using a dropping pip-

ette. Continue to heat the mixture under reflux for 20 minutes. After this time, remove the flask from the oil bath and slowly add ethanol (25 cm^3) via the condenser. Remove the condenser and allow the flask to stand on a cork ring to cool to room temperature. A cream solid should be desposited. If not, cool the mixture further in ice and allow to stand longer. Collect the solid product by filtration and wash it with a little water (10 cm^3), followed by ethanol (20 cm^3). Place the filtrate in the bottle provided for Ru wastes in the fume cupboard. Dry the product in a vacuum dessicator, then record the yield and submit all of your product in a tube wrapped in aluminum foil as the compound is light sensitive. Obtain the IR (KBr disc) spectrum of your product.

Dihydridocarbonyltris(triphenylphosphine)ruthenium(II)

In a fume cupboard, set up a 100 cm^3 round-bottomed flask fitted with a reflux condenser and small magnetic stirrer bar above a stirrer hotplate and small oil bath. Prepare the following three solutions in 25 cm^3 conical flasks: a) ruthenium trichloride trihydrate (0.15 g) in ethanol (10 cm^3), b) 40% aqueous formaldehyde (10 cm^3) (available in prepared form), c) postassium hydroxide (0.5 g) in ethanol (10 cm^3). To the round-bottomed flask add triphenylphosphine (1.0 g) followed by ethanol (20 cm^3). While stirring, heat the mixture to reflux, then quickly and successively add solutions a), b) and c) via the condenser. Continue to heat the mixture under reflux for 15 minutes. After this time, remove the flask from the oil bath and allow the reaction mixture to cool to room temperature. Collect the deposited white solid product by filtration and wash it with a little ethanol (5 cm^3), then water (5 cm^3) followed by ethanol (5 cm^3). Place the filtrate in the waste bottle provided. Redissolve the product in the minimum volume of dichloromethane necessary, filter the solution and add ethanol dropwise to induce precipitation of the purified material. Allow the mixture to stand to complete the crystallisation, then collect the product by filtration. Dry the product in a vacuum desiccator, then record the yield and submit all of your product in a tube wrapped in aluminum foil as the compound is light sensitive. Obtain IR (KBr disc), ^1H NMR and $^{31}P\text{-}\{^1H\}$ NMR spectra ($CDCl_3$ and C_6D_6) on your product.
(*Note:* $^{31}P\text{-}\{^1H\}$ NMR means the ^{31}P NMR spectrum is recorded with the coupling to ^1H removed by irradiation of the sample at the frequency of the ^1H signals).

3.18.4 Exercises

Examine the IR, ^1H NMR and $^{31}P\text{-}\{^1H\}$ NMR spectra obtained, list the bands or signals observed and identify which bands or signals arise from which groups in the molecules you have synthesised. Your report on this experiment should also contain the following information:

Part 1

1. The equations of the reactions carried out indicating the reference molecular masses of the compounds on which your yield calculation is based. Cite the mass of product obtained and calculate the % yield for each product.
2. A list of the principle infrared bands for each product identifying which vibration they arise from. In each case, indicate how the spectral bands confirm the presence of particular groups in the molecule (e.g. Co-Cl, C=N).
3. A list of the shifts, integrations and, where appropriate, coupling constants for each signal in the ^1H NMR spectra, along with its assignment indicating how the ^1H NMR spectra confirm the formulations of your products.
4. A brief comment on the limitations of cobaloximes as models for B_{12} coenzyme.

Part 2

1. The equations of the reactions carried out indicating the reference molecular masses of the compounds on which your yield calculation is based. Cite the mass of product obtained and calculate the % yield for each product.
2. A list of the principle infrared bands for each product indentifying which vibration they arise from. In each case, indicate how the spectral bands confirm the presence of particular groups in the molecule (e.g. Ru-H, Ru-CO, PPh_3).

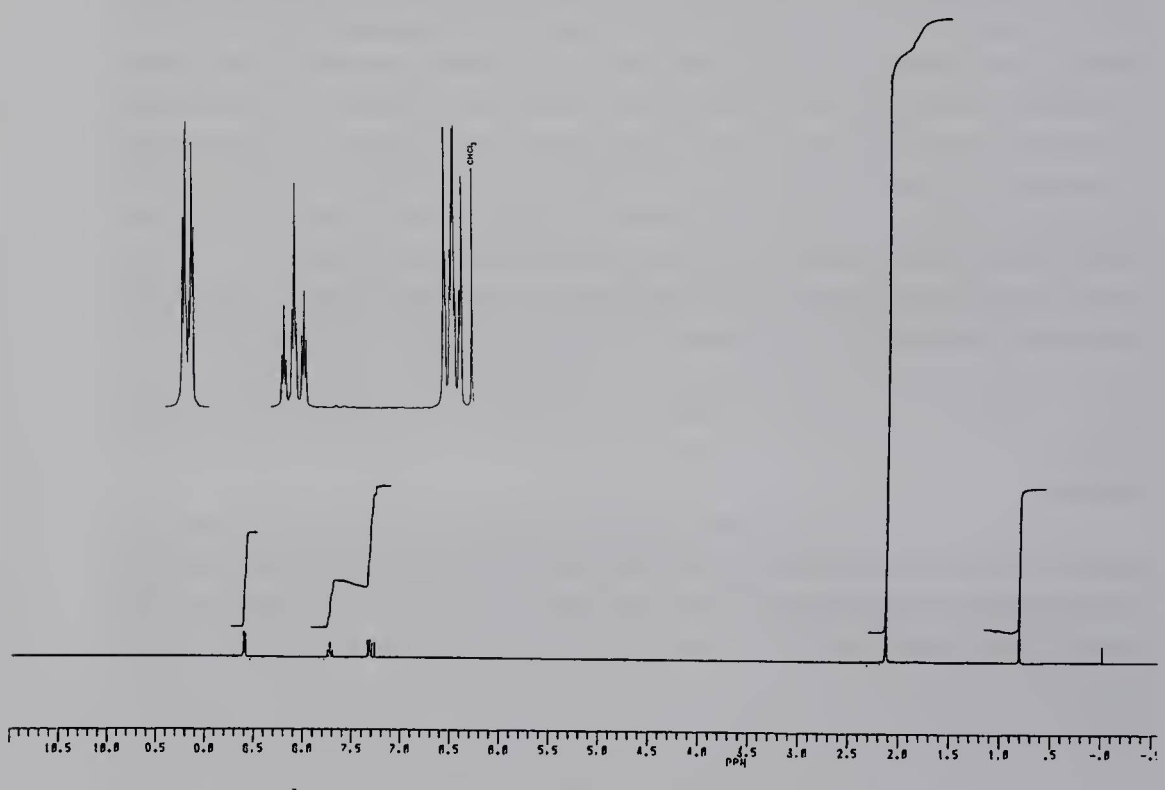


Fig. 3.18-4 The 300 MHz ^1H NMR spectrum of methylpyridinecobaloxime in $CDCl_3$. The inset shows an expansion of the aromatic region.

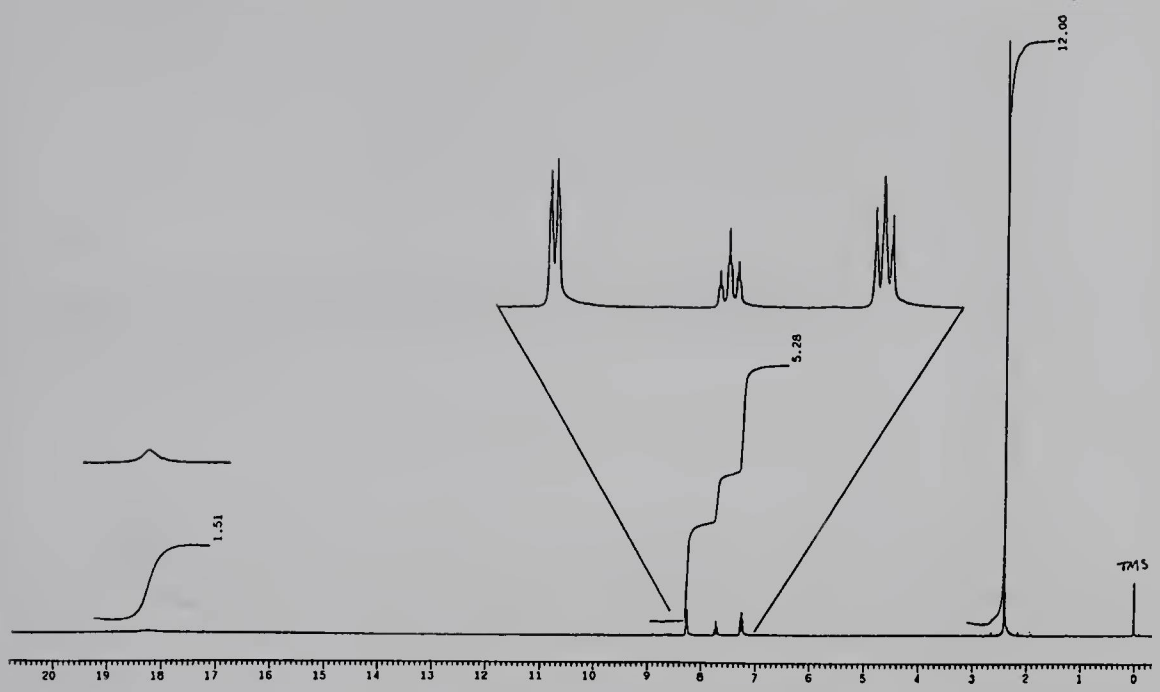


Fig. 3.18-5 The 270 MHz ^{1}H NMR spectrum of chloropyridinecobaloxime recorded in $CDCl_3$ solution.

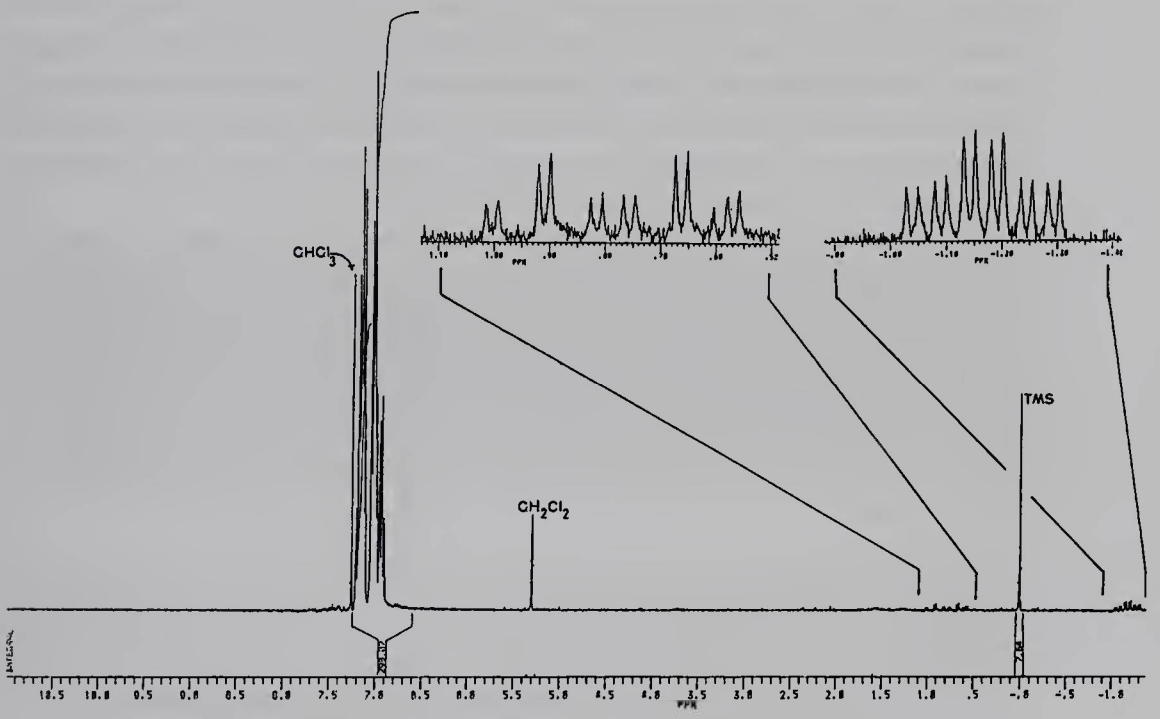


Fig. 3.18-6 ^{1}H NMR spectrum of $[Ru(H)_2(CO)(PPh_3)_3]$ in $CDCl_3$ at 300 MHz.

Fig. 3.18-7 109 MHz ^{31}P-{^{1}H} NMR spectrum of $[Ru(H)_2(CO)(PPh_3)_3]$ in $CDCl_3$.

3. A list of the shift and coupling constants for each hydride signal in the ^{1}H NMR spectrum and the signals in the ^{31}P-{^{1}H} NMR spectrum, along with its assignment indicating how the NMR spectra confirm the formulations of your products. You should measure the P–H and P–P coupling constants from the NMR spectra obtained. (The signals due to the aryl protons in PPh_3 may not be well resolved, do not try to analyse these).
4. An explanation of why more than one carbonyl stretching frequency is observed in the IR spectrum of $Ru(CO)(H)(Cl)(PPh_3)_3$.
5. A suggestion about how you could determine which of the bands in the 2000 cm^{-1} region of the IR spectra of these carbonyl hydrides is due to Ru-H and which to C–O stretching vibrations.

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3.19
Nickel-Catalysed Cross-Coupling of Alkylmagnesium with Haloarene

G. Brent Young

The metal mediated formation of carbon-carbon bonds is an important aspect of organic synthesis. In this experiment, selective coupling of two precursors can be achieved by the formation and rearrangement of labile organonickel species participating in a catalytic cycle. Organonickel complexes, though, may have a variety of rearrangement options which may depend, for example, on the nature of the ancillary ligands (phosphines, in this case) and which may lead to loss of regioselectivity. You will make and study two dichlorobis(phosphine)nickel(II) complexes and examine their suitability as catalysts for coupling of 2-propylmagnesium chloride with chlorobenzene. Most of the manipulations must be carried out with strict exclusion of oxygen, and this experiment is intended as a preparation for sophisticated anaerobic handling techniques. It is *especially important* to read the experimental procedure throughly before embarking on this experiment. Careful planning is vital to smooth operation.

Special Safety Precautions

All halocarbons, phosphines and nickel compounds should be regarded as irritant and toxic. Wear gloves and avoid inhalation. Diethyl ether is highly flammable. Organomagnesium solutions are caustic and may be flammable and toxic. Avoid ingestion.

3.19.1
Experimental

a) The Dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II) Catalyst

Equip a 100 cm^3 round-bottomed flask with a reflux condenser and magnetic stirrer bar. Add $NiCl_2 \cdot 6H_2O$ (0.71 g) to ethanol (10 cm^3) in the flask and warm the mixture in an oil bath, with stirring, until all the nickel complex has dissolved. Remove the oil bath and carefully add 1,2-bis(diphenylphosphino)ethane (dppe, 1.20 g) to the

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warm *but not boiling* solution. Precipitation of product should occur immediately. Replace the condenser and restore the oil bath and continue stirring at reflux for two hours. Allow the mixture to cool, filter off the product and wash with ethanol and diethyl ether before drying in a vacuum desiccator. Record the yield.

b) The Dichlorobis(triphenylphosphine)nickel(II) Catalyst

$NiCl_2 \cdot 6H_2O$ (1.5 g) is dissolved in water (1.5 cm^3) and added to glacial acetic acid (30 cm^3). To this solution is added a suspension/solution of triphenylphosphine (3.25 g) in glacial acetic acid (15 cm^3) and the mixture stirred until all the phosphine has dissolved (ca. 1 hour). Keep the precipitate in contact with the solution for ca. 24 hours, filter and wash thoroughly with diethyl ether. Dry at 70 °C under vacuum for 2–3 hours.

c) 2-(Chloromagnesio)propane

All glassware should be oven dried (but do not place plastic stopcock keys in ovens). Equip a 250 cm^3 2- (or 3-)necked flask with reflux condenser, pressure-equalising addition funnel and magnetic stirrer bar. A glass T-piece adaptor should be fitted to the top of the reflux condenser, one arm connected to the nitrogen supply and the other to a mineral oil (Nujol) bubbler (a Drechsel bottle is best). Any remaining openings can be closed by glass stoppers. The whole apparatus can be flushed with nitrogen by removing the stopper(s) for ca. 2 minutes while a brisk current of nitrogen is flowing.

Magnesium turnings (8.3 g) are placed in the flask and dry diethyl ether (45 cm^3) is added. (Nitrogen is kept flowing during addition). A solution of 2-chloropropane (9.5 cm^3) in dry ether (40 cm^3) is prepared and thoroughly mixed in the addition funnel, and a small quantity (ca. 5 cm^3) is added to the magnesium. Reaction is initiated by introduction of a few drops of 1,2-dibromoethane. Once effervesence is observed, the chloropropane solution is added at a rate sufficient to maintain a gentle reflux. During reflux, the nitrogen supply should be reduced to a slow steady flow. Continue stirring for 15–30 minutes after addition is complete. Increase the nitrogen flow, remove the additon funnel and replace it by a rubber (Suba-Seal) septum.

Immediately before employing any organomagnesium reagent it should be standard practice to estimate its concentration. Using a 5 cm^3 syringe with a narrow gauge 18 cm needle, withdraw exactly 2 cm^3 of the solution and inject into distilled water (20 cm^3) in a 100 cm^3 conical flask. Add a few drops of a suitable indicator (phenolphthalein or bromothymol blue) and titrate against 0.1 M aqueous HCl. Hence, estimate the concentration of RMgCl, assuming that OH^- arises only from Mg–C hydrolysis. Dismantle and clean the syringe (see next section).

d) Catalysed Cross-Couplings

This apparatus should be set up during preparation of the organomagnesium reagent. All glassware should be oven dried. Equip each of two 100 cm^3 3-necked

round-bottomed flasks with a pressure-equalising addition funnel, a reflux condenser and a magnetic stirrer bar. A plug of glass wool should be wedged (not *too* tightly) in the outlet tube from the reservoir of each funnel, above the stopcock. Each condenser should be fitted with a glass T-piece adaptor, one arm of which is connected to the nitrogen supply and the other to a mineral oil bubbler vent (the two assemblies can be joined "in-series").

Fit Suba-Seal septa to both additon funnels and close any other openings with glass stoppers. Make sure the whole apparatus is thoroughly flushed with briskly flowing nitrogen (the Suba-Seals should each be removed for ca. 1 minute to allow flushing of the funnel).

To each flask, add chlorobenzene (4.15 cm^3) and diethyl ether (10 cm^3). Into one flask, place (dppe)$NiCl_2$ (0.36 g) and into the other $(Ph_3P)_2NiCl_2$ (0.44 g). Stir both mixtures and cool in ice.

After determination of the concentration of *i*PrMgCl in ether, introduce equal portions of this solution (40×10^{-3} moles) to each addition funnel, using a syringe with a wide bore 18 cm needle. Try not to draw up large solid particles in the syringe. *Care* should also be taken at this stage *not* to (1) inject yourself or anyone else with the solution and (2) spill the solution, especially on your skin. Spillage is best avoided by measuring the correct amount into the syringe by ejecting gas bubbles back into the source flask with the syringe pointing upwards, and then drawing enough nitrogen into the syringe to fill the needle and introduce a little gas above the solution. The needle is now removed from the source flask and inserted into the addition funnel, and then, with the barrel still pointing up, the gas is expelled first, followed by the liquid. (Ensure that the stopcock on the funnel is already closed). Draw some gas back into the syringe and remove the needle from the septum. The procedure (which is standard practice for anaerobic manipulation) is repeated for the other funnel. If in *any* doubt, *ask a demonstrator.* As soon as transfer is complete, take the syringe to a fume cupboard and *remove the plunger.* Leave the assembly for 5–10 minutes, then wash both components with water, followed by IMS (or methanol).

Add the organomagnesium solution – cautiously at first in case of an exothermic reaction – to the cooled, stirred solution of PhCl. The glass wool will act as a filter for any suspended solids. When addition is complete, remove the ice bath. Dry the exteriors of the flasks and substitute oil baths. Heat the mixtures at gentle reflux with stirring for 4 hours. During reflux, reduce the nitrogen flow to a slow steady trickle (ca. one bubble per second).

Unused organomagnesium solution must be quenched by cooling and slow (at first) addition of water (the hydrolysis is exothermic). Unreacted magnesium metal can be destroyed by introduction of dilute aqueous HCl (fume cupboard).

e) Analysis of Cross-Coupling Reactions

After cooling the reactions in ice baths (be careful to turn up the nitrogen supply during cooling so as to avoid sucking the bubbler oil back into the flasks), water (20 cm^3) is introduced first into the addition funnels *via* syringe, then into the reaction mixtures, slowly at first, to quench any unreacted *i*PrMgCl. More ether

($20-30\ cm^3$) can now be added to aid in separation. Anaerobic handling is no longer necessary. Each reaction flask is treated identically. The contents are poured into a separatory funnel (filtration may be necessary to remove excessive amounts of solid) and the organic layer separated. The aqueous phase is shaken with fresh diethyl ether ($25\ cm^3$) and the ether fractions combined and washed successively with saturated aqueous sodium thiosulfate ($2 \times 20\ cm^3$) and distilled water ($2 \times 20\ cm^3$). The organic phase is then dried over anhydrous $MgSO_4$. Relative quantities of propylbenzenes and benzene as well as any residual chlorobenzene can now be analysed by glc using an OV-11 (or related silicone gum) column. Set the injection port and detector temperatures to 150 °C and the column oven to 90 °C. Adjust the mobile phase (nitrogen) gas pressure to 30–35 psi. Identify components by comparison of their retention times with those in a standard mixture (provided). Integrate the peak areas by cutting them from the chart paper and weighing them on an analytical balance. (Two chromatograms for each sample will be necessary so that one of each can be included in your report). Tabulate your results. (Assume that the detector response-factor for each of your components is 1.0; a flame ionisation detector responds to the *mass* of each solute present).

3.19.2 Exercises

1. Comment on the notable colour difference between the two catalysts. How could you verify your explanation?
2. Estimate (a) the relative extent of overall coupling and (b) the relative extent of regioretention for the two catalysts, noting any other reactions which are evident.
3. Suggest a plausible catalytic cycle for the cross-coupling reaction, explaining, by way of a suitable scheme, the nature of each step (the reference literature will help).
4. Suggest why the two catalysts differ in their activity, particularly with respect to the regioselectivity of the coupling reaction. Give a mechanistic explanation for the observed rearrangement.

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3.20
Transition Metal Catalysis

Neil M. Boag

Transition metal complexes may be used as catalysts for a wide variety of organic syntheses. In this experiment, a catalyst precursor is prepared and used to prepare an alkyne.

Diarylacetylenes may be prepared by a variety of routes. In recent years, two methods based on transition metals have been developed. The first method devised by Castro involves the use of copper acetylides. These reagents are prepared by treatment of an aqueous ammonia solution of cuprous iodide with an ethanol solution of mono-substituted aryl acetylenes (Eq. 1).

$$n\mathrm{CuI} + n\mathrm{ArC{\equiv}CH} \rightarrow (\mathrm{CuC{\equiv}CAr})_n + n\mathrm{HI} \quad (1)$$

Treatment of these cuprous acetylides with aryl iodides in refluxing pyridine under nitrogen yields diaryl acetylenes stoichiometrically (Eq. 2).

$$(\mathrm{CuC{\equiv}CAr})_n + n\mathrm{Ar'I} \rightarrow n\mathrm{Ar'C{\equiv}CAr} + n\mathrm{CuI} \quad (2)$$

The second method, developed independently by Cassar and Heck, utilises a palladium complex to effect this reaction catalytically (Eq. 3).

$$\mathrm{ArC{\equiv}CH} + \mathrm{Ar'X} + \mathrm{NaOMe} \rightarrow \mathrm{ArC{\equiv}CAr'} + \mathrm{NaX} + \mathrm{HOMe} \quad (3)$$

The early procedure has been modified through the use of amines as solvents with CuI as a co-catalyst. These modifications allow the reaction to proceed at room temperature and has enabled the introduction of alkyl substituents. The mild conditions have resulted in this method being used for the introduction of carbon-carbon triple bonds during the synthesis of natural products.

In this experiment, a catalytic precursor is prepared which may be identified. This precursor is then be used to catalytically synthesise an alkyne using the conditions devised by Cassar. Under these conditions, the precursor generates the active species $\mathrm{Pd(PPh_3)_4}$.

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3.20.1 Experimental

a) The Catalytic Precursor

Note: It is important to determine the yield of product as accurately as possible (Exercise 1).

Add water (5 cm^3) to a mixture of palladous chloride (0.15 g) and sodium chloride (0.12 g). Stir the slurry and slowly warm to about 50 °C. While the resultant solution is cooling, prepare a solution of triphenylphosphine (0.5 g) in ethanol (75 cm^3). Add the palladous chloride solution to the triphenylphosphine solution dropwise with stirring using a Pasteur pipette. Be careful not to add any residue which may remain. When the addition is complete, use an extra 1 cm^3 of water to ensure all the palladium salts are transferred. Warm the resultant slurry to about 50 °C over 30 minutes to coagulate the precipitate, cool and filter. Wash well with water, acetone and ether. Dry the product in a 50 °C oven for 30 minutes. Weigh the product.

b) The Catalytic Reaction

Add the following reagents to a B14 100 cm^3 round-bottomed flask.

4-bromoacetophenone (note 1)	2.00 g
palladium complex	0.42 g
sodium methoxide	0.60 g
triphenylphosphine	0.31 g
phenylacetylene	1.00 g
dimethylformamide (dmf)	40 cm^3
magnetic stirrer bar	

Using a Pasteur pipette, bubble nitrogen through the solution for ten minutes. Attach a condenser to the flask. To the top of the condenser attach a B14 T-piece. Connect one end of the T-piece to a nitrogen cylinder and the other to an outlet bubbler consisting of a Drechsel bottle 1/4 full of water. Using a water bath, heat the reaction mixture with stirring to 100 °C and maintain this temperature for four hours. Cool and pour into 200 cm^3 of water. Extract with 3 × 40 cm^3 of diethyl ether. Wash the ether extracts with 2 × 30 cm^3 of water and dry with sodium sulfate. Filter and take to dryness on a rotary evaporator. Dissolve the residue in the minimum of hot methanol, add decolourising charcoal and filter. Cool in ice and filter off the product. Wash with a little cold methanol. Air dry.

3.20.2 Exercises

1. Deduce a structure for the catalytic precursor based on the yield of product (which is essentially quantitative) and the fact that only one palladium chloride stretch is observed in the IR spectrum of this material. What physical measurement could be made to support the structural formulation?
2. Record an IR spectrum of the product of the catalytic reaction as a Nujol mull and identify any important absorption bands.
3. Record a proton NMR spectrum of the product from the catalytic reaction in $CDCl_3$. Integrate the spectrum. (A better result will be obtained if the sample is left overnight or dried in a vacuum desiccator to ensuure complete removal of the recrystallisation solvent which can interfere).
4. A $^{13}C\{^1H\}$ NMR spectrum of the catalytic product is reproduced in Figure 3.20-1. Use all the spectroscopic information to confirm the identity of this material.

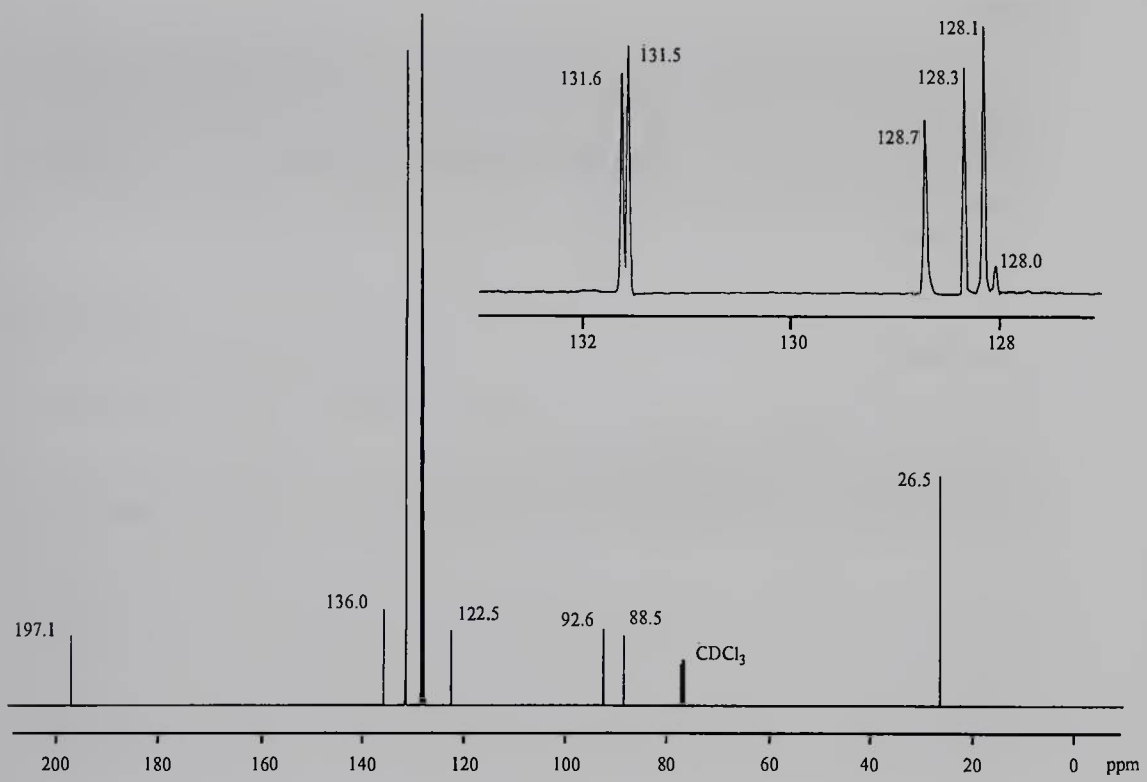
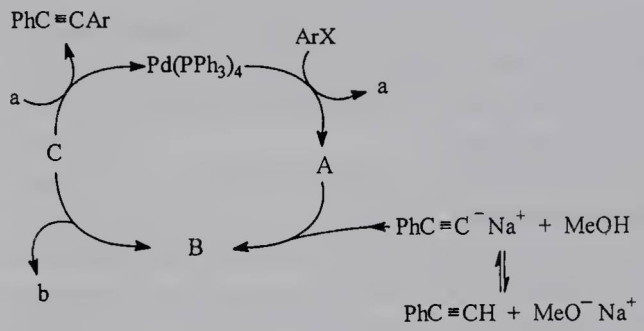


Fig. 3.20-1. $^{13}C\{^1H\}$ NMR spectrum of catalytic product.

5. Complete the following catalytic cycle. Calculate the electron counts and oxidation states of the transition metal intermediates.



6. Based on the yield of product from the catalytic reaction, calculate the number of turnovers obtained.

3.20.3 Notes

1. A large variety of alkynes can be prepared (see references by Cassar and Heck for details).
2. Copies of proton, carbon-13 and infrared spectra of the catalytic product are available from the author. These can be supplied as HPGL or Word for Windows files if required.

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3.21
Nitration of Cobalt(III) Acetylacetonate

David J. Otway

Coordination of organic molecules to metal ions frequently modifies the nature of their chemical reactions. In this experiment coordinated acetylacetone can be readily nitrated.

Special Safety Precautions

Acetic anhydride is an irritant. Avoid contact, handle in a fume cupboard. Chloroform should be used in a fume cupboard.

3.21.1
Experimental

a) Preparation of Cobalt(III) Acetylacetonate

A mixture of cobalt(II)carbonate (1.25 g) and acetylacetone (10 cm^3) in a 100 cm^3 conical flask is heated to 90 to 100 °C. Heating is stopped while 12% hydrogen peroxide (kept in a refrigerator) – *avoid skin contact* – (15 cm^3) is added dropwise with rapid stirring over a period of 10–15 min. (Do not add the hydrogen peroxide rapidly or the heat evolved will cause frothing). When addition is complete, cool the mixture in an ice-bath and then filter off the green solid and dry it at 110 °C. Dissolve the product in the minimum amount of hot toluene, filter if necessary, and then add 80–100 petroleum ether (ca. 75 cm^3) to the warm toluene solution. Cool in an ice-bath and filter off and air-dry the dark green crystals. Record the m.p.

b) Nitration of Cobalt(III) Acetylacetonate

A mixture of finely ground copper(II) nitrate trihydrate (2.7 g) and acetic anhydride (50 cm^3) is stirred for 15 minutes at 0 °C in a conical flask fitted with a calcium chloride drying tube. To the resulting slurry add cobalt(III) acetylacetonate (1.25 g) and then stir for 2 hours at 0 °C, followed by 1 h at room temperature. The blue-green so-

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lution is then mixed with water (150 cm^3), ice (150 g), and sodium acetate (4 g). Stir the two-phase liquid for 2 hours, during which time a finely divided green precipitate appears. Continue stirring until any gummy substance has gone (the mixture should consist of a green solution and a fine green powder). Filter off the green solid, wash it with two portions of water (15 cm^3) and one portion of cold ethanol (15 cm^3) and then air-dry it. Dissolve the *dry* solid in boiling chloroform (10 cm^3) in a beaker (in a fume cupboard as chloroform is toxic and flammable). Add hot ethanol (10 cm^3) and boil the mixture carefully, allowing the chloroform to distil off until crystals appear in the solution. Allow the mixture to cool, chill in an ice bath and then filter off the green solid. Wash with two portions of cold ethanol (5 cm^3) and air dry. Record the decomposition point of the product.

Record the IR spectrum of both complexes and make band assignments [1]. Record the ^{1}H-NMR spectra of both complexes in $CDCl_3$.

3.21.2 Report

1. Briefly indicate the aims of the experiment.
2. Do not reproduce the experimental procedure unless your experiment differed.
3. Write balanced equations for both reactions giving yields and m.p. of the products.
4. Tabulate the IR spectra of both complexes and give full band assignments [1, 2].
5. What are the point groups for both $Co(acac)_3$ and the product from the nitration?
6. Tabulate and fully assign the ^{1}H NMR of both complexes.
7. Write a short conclusion.

Hand in with the report:

Samples of cobalt(III) acetylacetonate and its nitration product.
Infrared spectra of both samples.
Fully labelled NMR spectra of both samples.

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3.22
Phenyllithium and Tetraphenylsilane

Petr Kilian

The most widely used synthesis of organo-element derivatives involves the reaction of a preformed organolithium with a covalent halide. Metal–carbon and non-metal–carbon bonds can vary greatly in their reactivity with water and oxygen. Highly oxygen/moisture-sensitive lithium alkyls and aryls are relatively easy to prepare provided that an atmosphere of argon is used. In this experiment, phenyllithium is prepared and used for the synthesis of (moisture- and air-stable) tetraphenylsilane:

$$PhBr + 2Li \rightarrow PhLi + LiBr$$

$$4PhLi + SiCl_4 \rightarrow Ph_4Si + 4LiCl$$

Tetraphenylsilane is characterised by m.p., ^1H and ^{13}C NMR measurements. In order to exercise manipulation of structural data and discussion of molecular structural parameters in a form used in a journal paper, output files from a single-crystal X-ray diffraction experiment are supplied. Furthermore, an experimental powder diffraction pattern is provided, which can be compared with the powder pattern generated from single-crystal X-ray data. The molecular geometry of Ph_4Si is optimised using quantum chemical calculations and the optimised geometry is compared with that from the single-crystal X-ray diffraction experiment.

Special Safety Precautions

Diethyl ether is highly flammable; silicon tetrachloride releases hydrogen chloride fumes on contact with atmospheric moisture. Perform the reactions in a fume cupboard.

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3.22.1 Experimental

a) Phenyllithium

The apparatus required is shown in Figure 3.22-1; use a 250 cm^3 round-bottomed flask. The apparatus should be set up empty, using glassware pre-dried by heating in an oven. At this stage do not attach the addition funnel, keep the side neck stoppered. Set it up quickly, while the glassware is still hot. Use thick gloves to protect yourself from burns. Think ahead: prepare everything you will need before taking the preheated glassware out from the oven. Connect the apparatus quickly to the argon and purge it well.

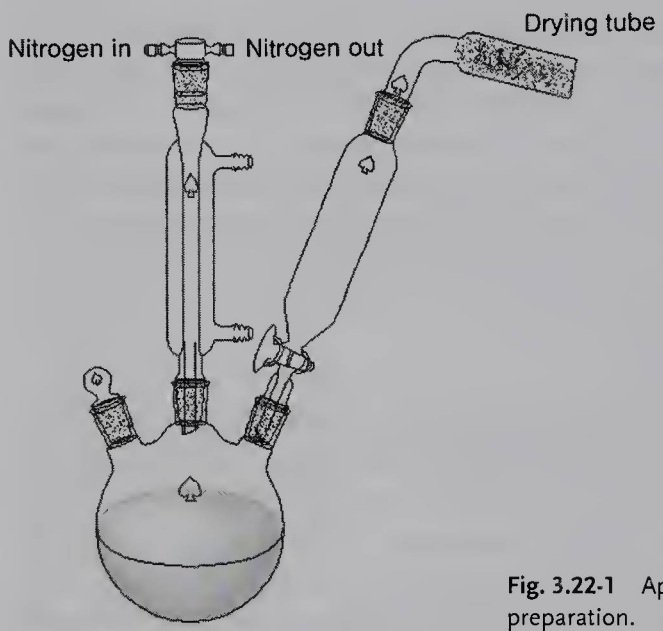


Fig. 3.22-1 Apparatus for phenyllithium preparation.

Under a flow of argon, pour in dry diethyl ether (100 cm^3) via the side neck. Weigh 3 g of lithium wire, wash it quickly with diethyl ether and rapidly cut the metal into small (1–2 mm) lengths with the aid of scissors, allowing each freshly cut piece to fall into the flask containing the dry ether. Stopper the side neck with a glass stopper. All this should be done as quickly as possible as this ensures the presence of fresh, clean metal surfaces which will subsequently react easily with bromobenzene. Mix anhydrous bromobenzene (20.6 cm^3, 31.4 g) with dry diethyl ether (30 cm^3) in the addition funnel. Attach it quickly to one side neck with a drying tube as shown in Figure 3.22-1. Add a few cm^3 of bromobenzene solution at once to the reaction mixture stirred with a magnetic stirrer. The reaction soon begins and boiling is observed in the vicinity of the metal fragments. If the reaction fails to start, warm the flask with a hair dryer until boiling continues in the absence of the heat. The bright, clean metal surfaces develop black spots. The ethereal solution of bromobenzene is then added in small portions (several cm^3 at a time) from the addition funnel at a rate

sufficient to enable the exothermic reaction to maintain a reasonable rate of reflux (the addition should be complete in about 30 minutes). The solution becomes grey–black. When the addition of bromobenzene is complete and the ebullition is weakening, reflux the mixture on an electric heating mantle or using an oil bath for about 30 minutes. Cool the mixture (ice–water) to about room temperature and, having dried the outside of the reaction flask, carefully filter the mixture as rapidly as possible through a filter funnel containing a loose glass-wool plug into a dry three-necked 250 cm^3 flask. To protect the phenyllithium solution, the filtration can be performed under a flow of argon via a gas inlet adaptor in one of the side necks.

Dispose of the excess lithium. Using a spatula, transfer the unreacted metal and glass-wool from the filter funnel into a beaker and cover with ethanol. Beware of the vigorous reaction between the phenyllithium (some of which is bound to remain on the glass-wool) and the ethanol. The metal dissolves in the ethanol, with liberation of hydrogen. Cautiously add water (1 cm^3), wait until reaction has ceased, then further water (5 cm^3, then 10 cm^3). When there is no further reaction, the beaker can be washed out.

b) Tetraphenylsilane

Silicon tetrachloride deposits a hard layer of silica on glass, and it is therefore recommended to use dedicated glassware for this reaction repeatedly. Add slowly and cautiously silicon tetrachloride (4.6 cm^3, 6.9 g; use a plastic syringe to measure) to 40 cm^3 of dry diethyl ether in the unstoppered addition funnel. Do not shake the addition funnel to mix as the reaction is exothermic and diethyl ether is a highly volatile solvent. Place a drying tube on the addition funnel, swirl the contents gently to mix and attach the funnel to the flask containing phenyllithium (to one of the side necks). Keeping the reaction mixture cool in a bath of ice and water and under a flow of argon, add the silicon tetrachloride dropwise, with stirring. When the addition is complete, boil the mixture for 1 minute, cool it and pour it on to crushed ice in a suitable beaker. When the ice has melted, filter off the solid tetraphenylsilane (note its water-repellent properties) and wash it thoroughly with water.

Recrystallise the crude product from boiling toluene (about 200 cm^3; quickly filter hot through a dry, warmed sinter to remove any insoluble SiO_2 impurity) to give pure tetraphenylsilane as white, needle-like crystals. The typical yield is about 4.7 g or 30–40%. Concentration of mother liquors will yield a further small quantity.

c) Characterisation

Record the m.p. and ^1H NMR spectrum ($CDCl_3$) of tetraphenylsilane. Figure 3.22-2 shows the $^{13}C\{^1H\}$ NMR spectrum. Assign the spectra as far as possible.

Prepare samples for single crystal X-ray diffraction (several milligrams of crystalline material will be needed) and submit your sample for a measurement. Alternatively, SiPh4.cif and SiPh4.rtf files, containing the crystallographic data, are available as supplementary material from the web site (http://www.wiley-vch.de/books/sample/students/p00.php?p=3527324720&lang=en). The molecule can be visualised

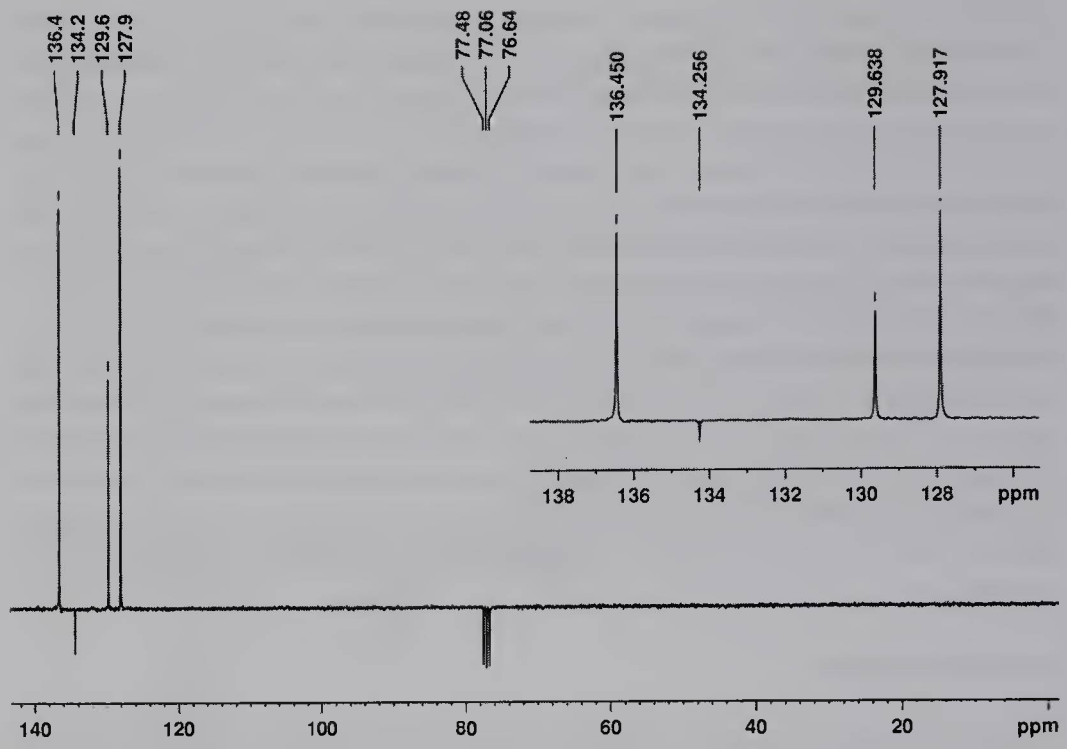
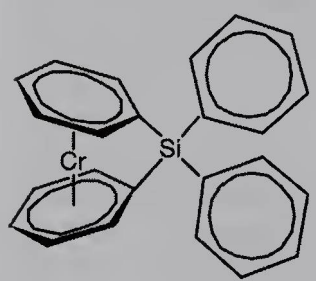


Fig. 3.22-2 $^{13}C\{^1H\}$ NMR spectrum (DEPT-Q) of $SiPh_4$ (in $CDCl_3$).

on a computer using Mercury software.[1)] Label important atoms and print a picture of the molecule from which the geometry of the molecule is observable, and attach it to your report. Discuss the molecular structure in a few sentences. You should start with a description of the overall shape of the molecule (planar, tetrahedral coordination of Si, etc.) and the position of the phenyl rings with respect to each other. Discuss briefly the bonding around the central atom (C–Si bond lengths, C–Si–C–bond angles). Compare the bonding situation around the silicon atom with that in the related chelated molecule $[(C_6H_5)_2Si(\eta^6\text{-}C_6H_5)_2]Cr$ (see the structure below), the X-ray structure of which has been published in the literature.[2)]



1) Freeware for your own PC: download from www.ccdc.cam.ac.uk.
2) C. Elschenbroich, J. Hurley, B. Metz, W. Massa, G. Baum, *Organometallics*, **1990**, *9*, 889–897.

Powder diffraction data can be calculated from single-crystal X-ray data. Generate the powder data of $SiPh_4$ using Mercury software (Fig. 3.22-4) and compare it with the experimental pattern (Fig. 3.22-3).

Build and optimise the structure of $SiPh_4$ using suitable chemistry calculations software. We used GaussView to build the initial model of the $SiPh_4$ molecule, which was then submitted for optimisation to Gaussian03 software, using the DFT/B3LYP method and 3–21G* basis set (the calculation runs for several hours). Open the resulting log file in GaussView and briefly compare the optimised geometry from the calculations with that obtained from X-ray structure determination. Focus on discussing the Si–C bond lengths and geometry around the silicon atom.

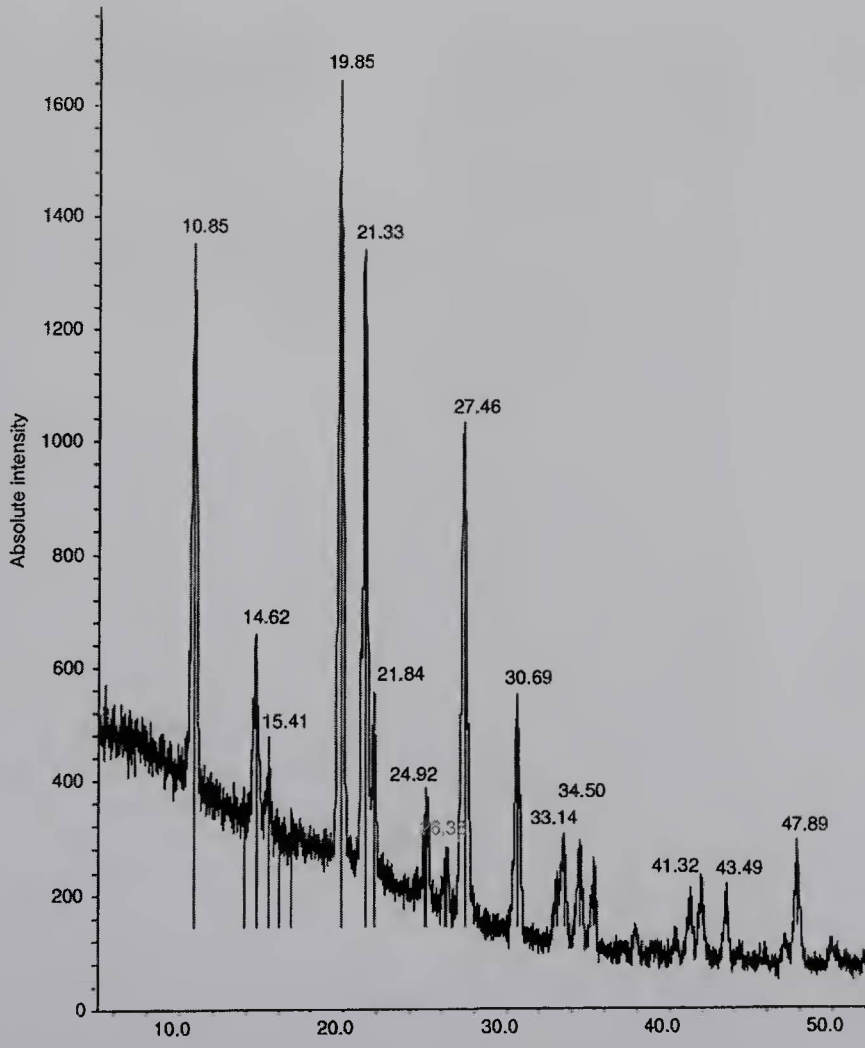


Fig. 3.22-3 Experimentally obtained powder pattern of $SiPh_4$.

55.81
60.0
70.0
80.0
90.0
2Theta

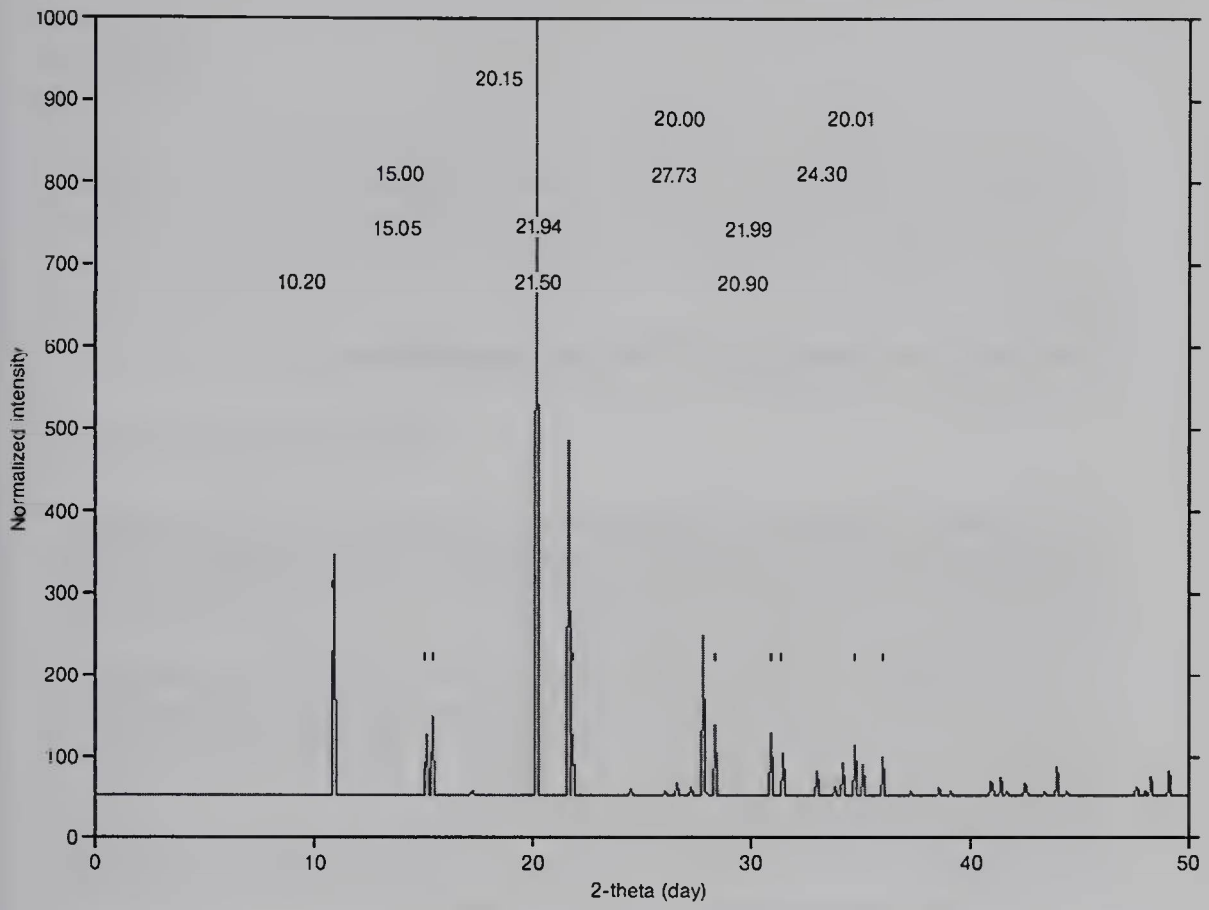


Fig. 3.22-4 Calculated powder X-Ray pattern of $SiPh_4$.

3.23
Synthesis and Reactivity of Tertiary Phosphines

Neil M. Boag

The common oxidation states of phosphorus are P(III) and P(V). A particularly important class of complexes are the tertiary phosphines PR_3 and phosphites $P(OR)_3$. These species have an extensive chemistry in their own right, but are often encountered in their common role as $2e^-$ Lewis bases.

Organophosphine complexes are generally unstable towards oxidation and are notoriously malodorous. However, the triarylphosphines are relatively air-stable compounds with no discernible smell. In this experiment, you will synthesise an example of this type of species and investigate its chemistry.

An important feature of phosphorus is that it exists as a single isotope, ^{31}P, with a nuclear spin of 1/2. The nucleus may be easily detected by NMR spectroscopy and $^{31}P\{^1H\}$ NMR spectroscopy will be used as a diagnostic tool.

Triarylphosphines are generally synthesised from halophosphines by metathesis using aryl Grignard reagents (Eqs. 1 to 3).

$$PCl_3 + 3\,ArMgCl \rightarrow PAr_3 + 3\,MgCl_3 \quad (1)$$

$$PhPCl_2 + 2\,ArMgCl \rightarrow PhPAr_2 + 2\,MgCl_2 \quad (2)$$

$$Ph_2PCl + ArMgCl \rightarrow Ph_2PAr + MgCl_2 \quad (3)$$

The experiment makes use of this reaction to synthesise an example of a triarylphosphine and explores the chemistry of these species.

Special Safety Precautions

Phosphine halides are colourless fuming liquids with a penetrating, obnoxious odour. They react violently with water, liberating hydrochloric acid. When using, calculate quantities as volumes using the appropriate densities (Aldrich or Merck catalogue) and **only** use in a fume cupboard.

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3.23.1 Experimental

Important: This method is applicable to PPh_2Ar, $PPhAr_2$ and PAr_3. The reaction conditions given below are for the synthesis of PPh_2Ar and uses one equivalent of ArMgBr. If $PhPAr_2$ is to be synthesised, then the scale of the Grignard synthesis must be doubled. If PAr_3 is to be synthesised, the scale of the Grignard reaction should be tripled.

Perform this synthesis in a fume cupboard

a) Grignard (Scale as Appropriate)

Set up an apparatus consisting of a 250 cm^3 3-neck flask containing a magnetic stirring bar, a dropping funnel and a condenser equipped with a $CaCl_2$ drying tube. Add magnesium turnings (1.2 g) to the flask and just cover the magnesium with dry THF (see Section 3.23.3, Note 1). Place 0.05 moles of the appropriate aryl bromide dissolved in 25 cm^3 of dry THF in the dropping funnel. Add a little of this solution to the magnesium followed by one crystal of iodine. Do not stir at this stage. Surround the reaction flask with a warm water bath (about 40 °C). After a few minutes, the iodine crystal should dissolve and lose colour and the reaction mixture start to reflux. Start the magnetic stirrer and drop the aryl bromide solution into the reaction mixture at ca. 1 drop per second. After addition, remove the warm water bath and stir the solution for a further hour.

b) Phosphine

Add a solution of 0.045 moles of the appropriate phosphine halide in 10 cm^3 of dry THF to the dropping funnel. Add the solution of phosphine halide dropwise to the Grignard solution with stirring. When the addition is complete, surround the flask with a hot water bath and reflux the solution for 3 hours. Cool the solution and pour onto 100 cm^3 of ice. Neutralise the resultant solution with dilute hydrochloric acid and remove the THF on a rotary evaporator. Extract the solution with 3 × 40 cm^3 of toluene and then extract the toluene solution with 4 × 40 cm^3 on conc. hydrochloric acid (**care!**)

Carefully (**dropwise – strong acid/strong base neutralisation generates a lot of heat**) neutralise the acid with 0.880 ammonia (more than 100 cm^3 required). An oil should result which, upon cooling, will solidify (see Section 3.23.3, Note 2). Filter the solid, wash well with water (break up the lumps) and air dry. Recrystallise from hot methanol.

Measure the infrared spectrum of the product as a Nujol mull and record its melting point. Use Chemical Abstracts to obtain a literature value of the melting point.

c) Phosphine Oxide

Prepare a solution/suspension of the phosphine (1 g) in acetone (10 cm^3). Dissolve sufficient hydrogen peroxide to furnish 1.1 moles of peroxide per mole of phosphine in a few cm^3 of water and slowly add this solution to the acetone solution of phosphine. After five minutes, remove the acetone on a rotary evaporator and extract the phosphine oxide with 2 × 20 cm^3 of toluene. Wash the toluene extracts with ferrous ammonium sulfate solution and dry with anhydrous magnesium sulfate. Remove the toluene on a rotary evaporator. Recrystallise the product (try methanol first, if this is not successful try toluene/petroleum ether).

Record the infrared spectrum of the product as a Nujol mull. Identify the P=O stretching frequency by comparing the infra-red spectrum with that of the phosphine.

d) Phosphine Plus Methyl Iodide Reaction

Add approx. 0.2 g of the phosphine to a small ignition tube (which should fit in a centrifuge). Add toluene to the tube until it is 3/4 full and dissolve the phosphine by warming gently (water bath). Using a Pasteur pipette, add six drops of methyl iodide and seal the tube with a stopper.

Heat in a 40 °C water bath for thirty minutes. A white solid should form. Decant off the supernatant liquid (centrifuge if necessary) and wash the solid three times with diethyl ether. Break up any lumps to ensure the material is well washed. Air dry and store in a desiccator (see Section 3.23.3, Note 3).

Record proton NMR spectra of the three phosphorus compounds you have synthesised using approx. 50 mg of sample in $CDCl_3$. It is better if the products are left to dry for at least several hours (or *in vacuo*) before the NMR samples are prepared so as to ensure there is no residual solvent which would complicate the spectra.

Record $^{31}P\{^1H\}$ spectra of the three phosphorus compounds (spectra of a typical phosphine, P(4-MePh)$_3$, and its products are reproduced in Figure 3.23-1).

3.23.2 Exercises

1. Assign the resonances in the proton NMR spectra of the phosphine and phosphine oxide. Use the NMR spectra to identify the product formed by the reaction of the phosphine with methyl iodide. What is the oxidation state of the phosphorus in this complex? Are the $^{31}P\{^1H\}$ spectra useful in assigning oxidation states?
2. What is the chemistry behind the *conc.* HCl extraction and why is it undertaken?
3. How would a phosphite, P(OR)$_3$, be prepared? A particularly important reaction of phosphites is the Arbusov reaction. What is the Arbusov reaction?

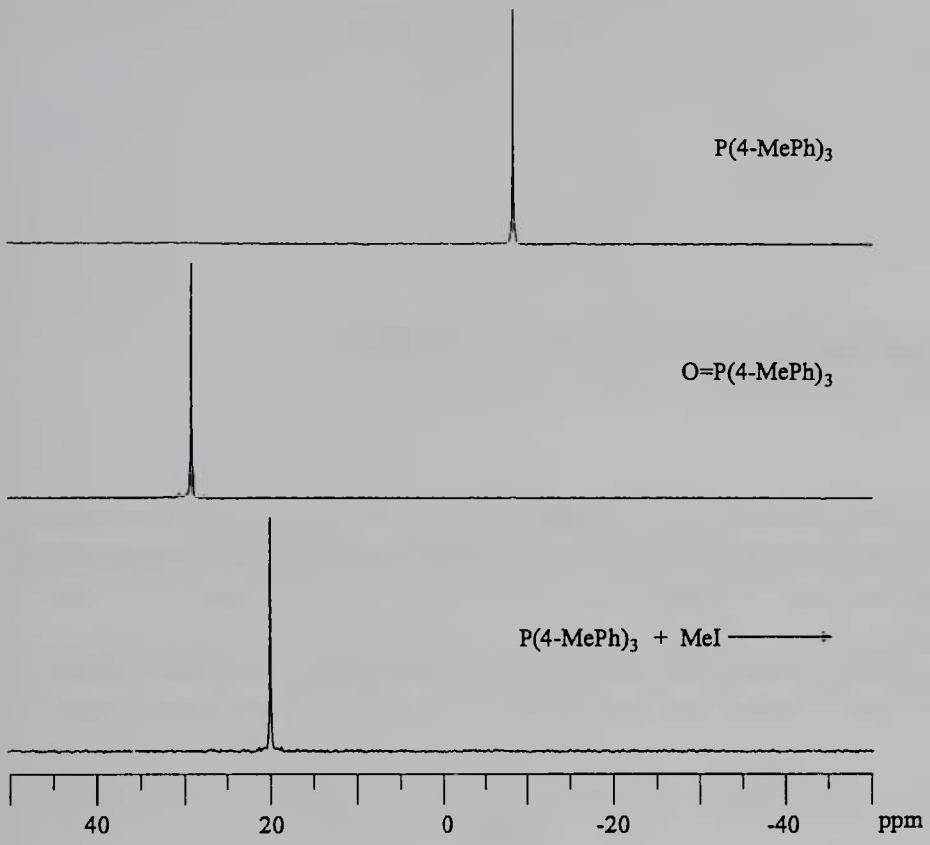


Fig. 3.23-1 $^{31}P\{^{1}H\}$ NMR spectra of P(4-MePh)$_3$ and its derivatives.

3.23.3 Notes

1. Tetrahydrofuran may be dried and stored over molecular sieves.
2. The oil can sometimes take several hours to solidify, particularly if it is hot.
3. The product can be very hygroscopic and oily. It may be prepared *in situ* by the addition of a drop of methyl iodide to a $CDCl_3$ solution of the phosphine in an NMR tube.
4. Copies of proton and phosphorus NMR as well as infrared spectra of P(4-MePh)$_3$ and its derivatives are available from the author. These can be supplied as HPGL or Word for Windows files if required.

Further Reading

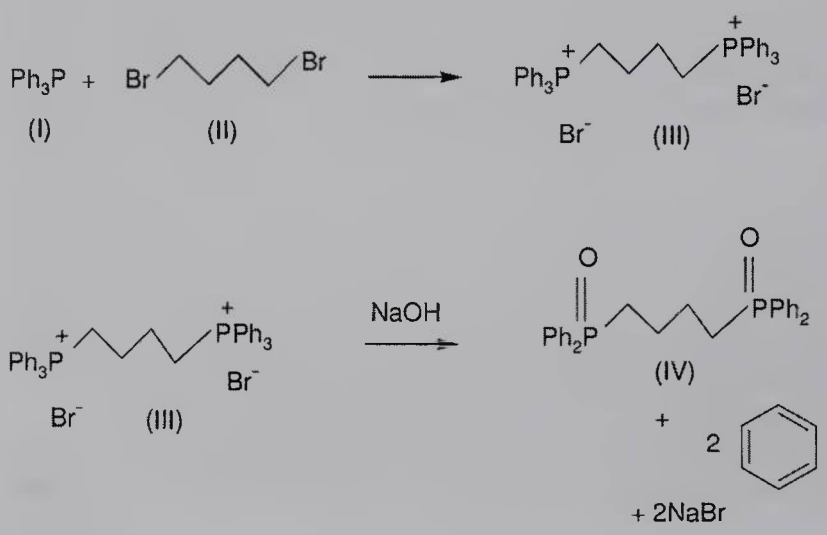
F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., pp. 404–415 and 421–423.
F. A. Cotton, G. Wilkinson, *Inorganic Chemistry*, 4th ed., pp. 459–473.

3.24
Two-stage Synthesis of $Ph_2P(O)(CH_2)_4P(O)Ph_2$

Andrew G. Platt

Phosphine oxides have the general formula $R_3P{=}O$ and have applications ranging from fungicides to extractants in nuclear fuels reprocessing. They are generally very stable molecules and can tolerate a wide variety of functional groups in the R part of the molecule.

This experiment involves the formation of compounds with two phosphine oxide groups linked by a chain of methylene groups as illustrated in the scheme below:



In this example, 1,4-dibromobutane (II) reacts with excess triphenylphosphine (I). The reaction can be considered as an oxidation of the phosphorus centre giving the bis-phosphonium salt (III).

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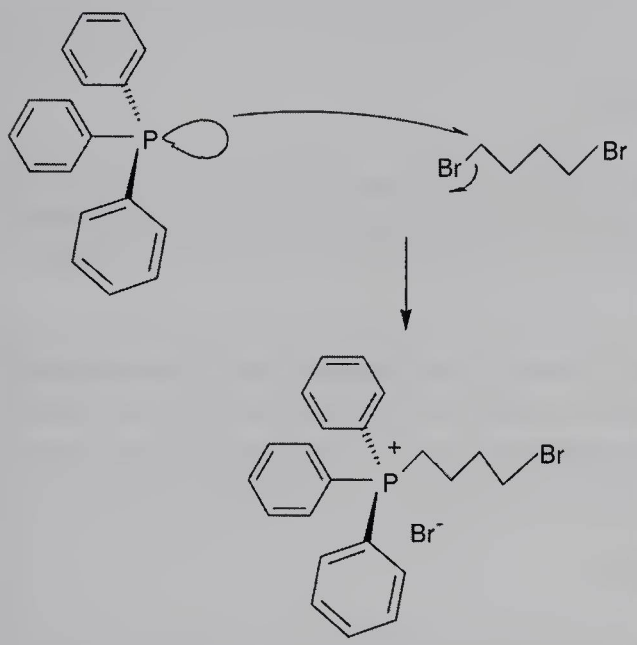
The mechanism can be thought of as a nucleophilic substitution:



Phosphonium salts can be hydrolysed by strong sodium hydroxide solution to give the corresponding phosphine oxides.

Special Safety Precautions

Haloalkanes have the potential to be mutagenic. Handle dibromobutane and dibromopentane with care. Dispense in a fume cupboard, using a clean pipette – do not pour from the bottle. In the event of contact with the skin, wash with plenty of soapy water. Phosphonium salts have the potential to be lipophilic and can be absorbed through the skin. Avoid all contact and in the event of contamination wash immediately with plenty of soapy water. Sodium hydroxide solutions are extremely corrosive. Any spillage should be washed immediately with plenty of running water. Although phosphine oxides have not been evaluated for their toxic or long-term effects, it is prudent to assume that they have high toxicity and they should be treated accordingly.

3.24.1 Experimental

3.24.1.1 Preparation of the Diphosphonium Salt

Weigh 5 g of triphenylphosphine into a 100 cm^3 round-bottomed flask and add a small piece of porous pot to aid smooth boiling. Add 1 cm^3 of dibromobutane, 10 cm^3 of dimethylformamide (DMF), equip the flask for reflux and boil the mixture for 1 hour.

Allow to cool to room temperature and pour the contents into 100 cm^3 of diethyl ether. Stir the resulting solid until complete crystallisation occurs. Filter the solid, wash with diethyl ether and dry at the pump. Record the weight obtained. Record the infrared spectrum of the diphosphonium salt.

3.24.1.2 Hydrolysis of the Diphosphonium Salt

Place the solid from the first stage in a 100 cm^3 round-bottomed flask, add 20 cm^3 of methylated spirits and 5 cm^3 of water, then add 5 g of sodium hydroxide. Reflux the mixture for 1 hour. Cool and pour into 100 cm^3 of 2 M HCl. Filter the solid, dry at the pump and record the weight and the infrared spectrum of the product.

3.24.2 Exercises

1. Electrospray mass spectrometry (ESMS) is a means of obtaining mass spectra from substances that are insufficiently volatile or too unstable for other forms of mass spectrometry. For ESMS, a dilute solution of the sample is evaporated in the mass spectrometer. During evaporation, charging of the droplet occurs by application of a voltage to the sample. For materials which are not readily charged, ionisation can be achieved by binding to ionic impurities in the solvent such as H^+, Na^+ and NH_4^+ ions. The electrospray mass spectrum of $Ph_2P(O)C_4H_8P(O)Ph_2$ is shown below. Assign as many of the peaks as possible. A useful website for helping predict the mass spectrum from a given formula is http://www.shef.ac.uk/chemistry/chemputer/– click on the isotope match icon.
2. Assign the bands due to the C–H absorptions in the infrared spectra of $[Ph_3PC_4H_8PPh_3]^{2+}$ $2[Br]^-$ and $Ph_2P(O)C_4H_8P(O)Ph_2$. You should quote the wavenumber and assign the absorption as a stretch or bending mode.
3. By comparing the two infrared spectra, identify the P=O stretch in the infrared spectrum of the final product. The P=O stretch is generally intense and found in the region below 2000 cm^{-1}.

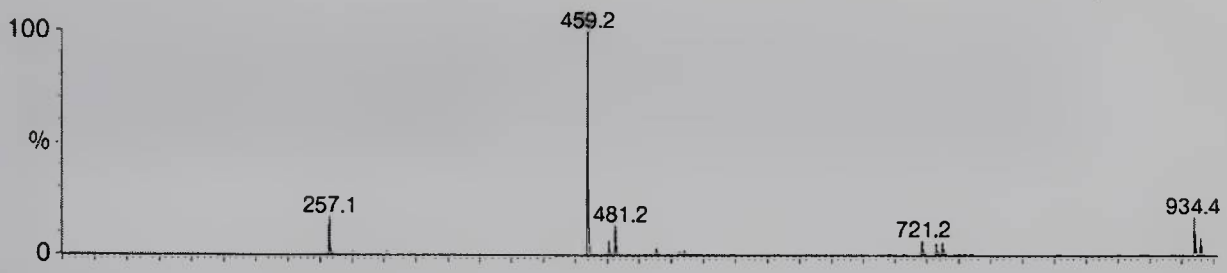


Fig. 3.24-1 Electrospray mass spectrum of $Ph_2P(O)C_4H_8P(O)Ph_2$.

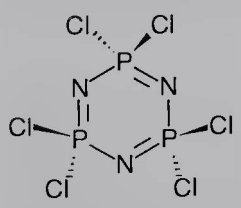
Further Reading

This section is adapted from P. Calcagno, B. M. Kariuki, S. J. Kitchin, J. M. A. Robinson, D. Philp, K. D. M. Harris, *Chem. Eur. J.* **2000**, *6* (13), 2338.

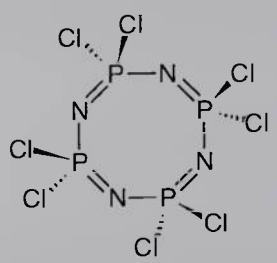
3.25
Inorganic Heterocycles: Cyclophosphazenes

Josef Novosad and Milan Alberti

Cyclophosphazenes constitute an important class of inorganic heterocyclic ring systems. Hexachlorocyclotriphosphazene. $(NPCl_2)_3$, is the earliest reported inorganic heterocycle, dating back to 1834. The ring system is made up of alternating phosphorus and nitrogen atoms. Phosphorus is pentavalent and tetracoordinate while nitrogen is trivalent and dicoordinate. The phosphorus atom has two exocyclic substitutents but the ring nitrogen atom has none. The best studied examples are hexachlorocyclophosphazene, $(NPCl_2)_3$ (**1**), and octachlorocyclotetraphosphazene, $(NPCl_2)_4$ (**2**).



1



2

Nucleophilic substitution reactions involving replacement of the labile P–Cl bonds in **1** and **2** by nucleophiles such as aliphatic and aromatic amines, alcohols, phenols and organometallic reagents are known.

Cyclophosphazenes are interesting as inorganic pseudo-aromatic systems, as well as being commercially important. Polymers derived from $(NPCl_2)_3$ are useful, for example, in high temperature applications. This experiment involves the preparation of two cyclotriphosphazenes: $(NPCl_2)_3$ and its anilino analogue.

Special Safety Precautions

- Aniline: highly toxic, cancer suspect agent.
- Phosphorus Pentachloride: violently decomposed by water with formation of hydrochloric acid and phosphoric acid; corrosive, moisture-sensitive.
- Phosphorus Oxychloride: violently decomposed by water with formation of hydrochloric acid and phosphoric acid; corrosive, moisture-sensitive.

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- 1,1,2,2 Tetrachloroethane: highly toxic, suspect cancer agent.
- Dichloromethane: toxic, irritant.
- Methanol: flammable liquid, toxic.

3.25.1 Experimental

a) Hexachlorocyclotriphosphazene, [1,3,5-triaza-2,4,6-triphosphorin-2,2,4,4,6,6-hexachloride]

Caution: Carry out this procedure in a fume cupboard. PCl_5 is corrosive and HCl is liberated during the reaction.

The reaction of phosphorus pentachloride with ammonium chloride produces a mixture of cyclic and linear chlorophosphazenes (Eq. 1).

$$n PCl_5 + n NH_4Cl \rightarrow (NPCl_2)_n + 4n HCl \quad (1)$$

Equip a 250 cm^3 three necked round-bottomed flask with a reflux condenser, a heating mantle, a scrubbing train consisting of one empty Drechsel bottle (reversed) and one half-filled with 2 M aqueous NaOH solution. Place in the flask 150 ml of 1,1,2,2-tetrachloroethane, *powdered* ammonium chloride NH_4Cl (75 mmol, 4 g), phosphorus pentachloride PCl_5 (75 mmol, 15.6 g) and phosphorus oxychloride $POCl_3$ (0.75 mmol, 1.15 g). After addition, heat the mixture at reflux for 3.5 hours until no more HCl is evolved. Disconnect the scrubbing assembly, allow the mixture to cool and filter off any excess NH_4Cl. Evaporate the filtrate using a rotary evaporator. Cool the crude product (in a refrigerator) and extract the solid with 60–80 °C petroleum ether (3 × 25 cm^3). Combine the extracts and reduce in volume (rotary evaporator) to ca. 10 cm^3. Cool this solution to recover the product as an off-white solid. Filter and vacuum dry the product. Record its yield, melting point and infrared spectrum. The mass spectrum of a pure sample of $(NPCl_2)_3$ is given in Figure 3.25-1. Assign the major features of the IR and mass spectra.

b) Hexakis(anilino)cyclotriphosphazene, [1,3,5-triaza-2,4,6-triphosphorin-2,2,4,4,6,6-hexaaniline]

$(NPCl_2)_3$ reacts with $C_6H_5NH_2$ to give hexakis(anilino)cyclotriphosphazene and aniline hydrochloride (Eq. 2).

$$(NPCl_2)_3 + 12 C_6H_5NH_2 \rightarrow N_3P_3(C_6H_5NH)_6 + 6 C_6H_5NH_2 \cdot HCl \quad (2)$$

In a 100 cm^3 round-bottomed flask equipped with a reflux condenser, place 2.5 g (7.2 mmol) of $(NPCl_2)_3$ and 32 cm^3 (0.35 mol) of aniline. Using an oil bath, heat the

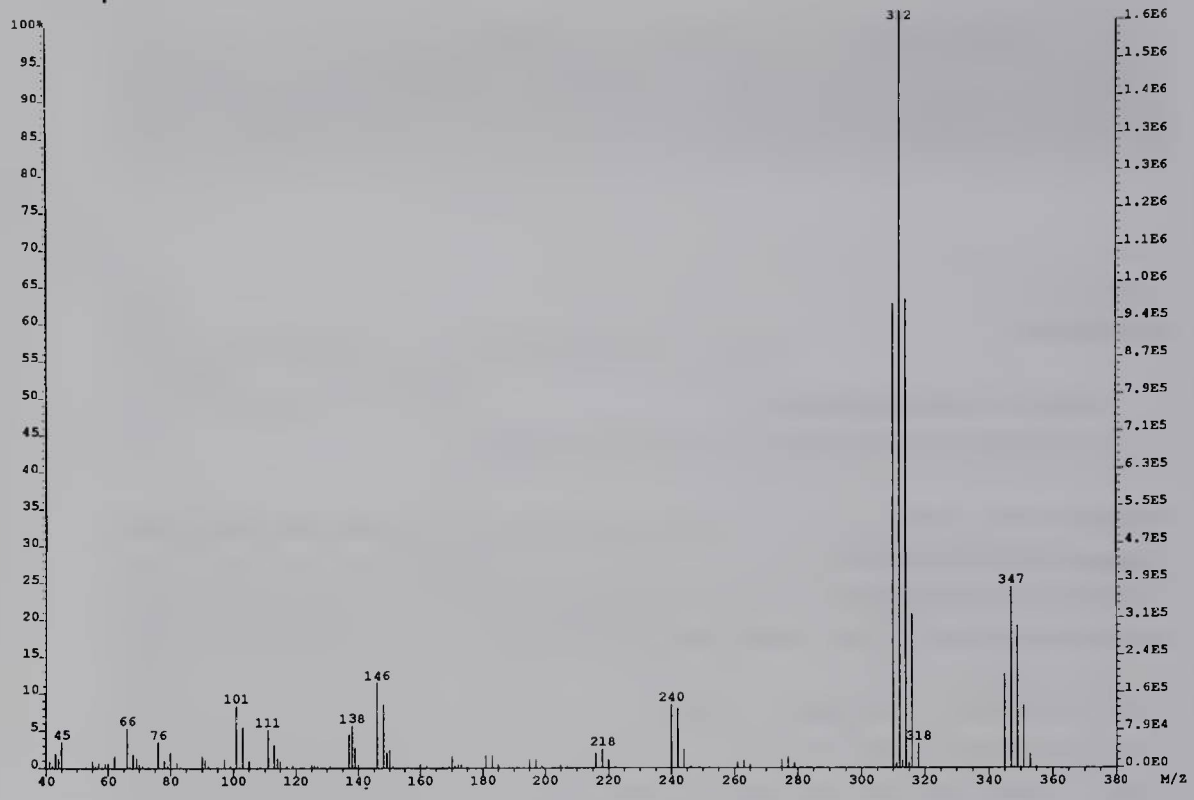

Fig. 3.25-1

mixture at reflux, with stirring, for 6 hours. The resulting red-purple semicrystalline mass is allowed to cool, then washed successively with water (3×30 cm^3) and ethanol (3×30 cm^3), and air dried. Recrystallise part of this crude product by dissolving in a minimum volume of hot dichloromethane and adding up to an equivalent volume of methanol, cooling subsequently if necessary. Record the yields and melting points of both the crude and purified products and the infra-red spectrum of the pure phosphazene. Assign characteristic infrared frequencies.

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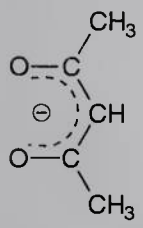
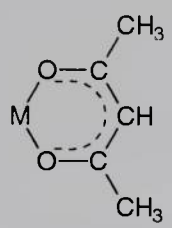
3.26
Inorganic (Carbon-Free) Chelate Rings: A Dithioimidodiphosphinato Ligand and Some of its Metal Complexes

Ionel Haiduc

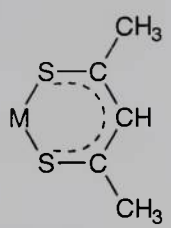
Every coordination chemistry textbook describes [1, 2] the very stable chelate ring complexes of β-diketones, of which acetylacetone (pentane-2,4-dione, abbreviated *acac*) is the best known. This ligand forms a uninegative anion, **a**, with delocalized π-electrons, which is able to form neutral chelate rings, **b**, in complexes of the type $M(acac)_n$ (n = the oxidation state of the metal). These six-membered rings are very stable and even exhibit some aromatic character. Replacement of oxygen by sulfur results in the formation of a dithio analogue (abbreviated *sacsac*), which is also able to form similar sulfur based chelate rings, **c**.



a

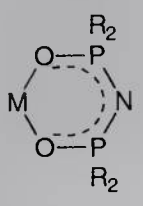


b

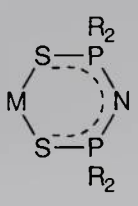


c

Whilst the oxygen/sulfur replacement is known by almost any student of inorganic chemistry, fewer people are aware that in the six-membered chelate rings **b** and **c**, the carbon atoms can also be replaced, leading to fully inorganic, carbon-free chelate rings. Thus, the C···C···C sequence can be replaced [3] by a P···N···P sequence to produce rings **d**, and **e**.



d



e

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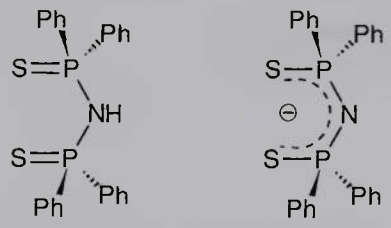
In this case, the phosphorus atoms will bear organic groups (exocyclic substituents), e.g. R = CH_3 or C_6H_5.

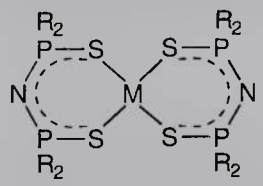
In this experiment, you will prepare the free ligand as the neutral compound **f**, tetraphenyldithiodiphosphinylimide, which is readily converted to a potassium or ammonium salt as the delocalized anion **g**, and from this, the chelate ring complexes **e** (m = Pb, Fe, Co, Ni).



f **g**

The structures of the neutral ligand **f**, and of the potassium salt, have been confirmed by X-ray diffraction.

The ligand described here forms the spirobicyclic complexes **h** with divalent metals, but other types of compounds are also known.



h

Special Safety Precautions

1. Chlorodiphenylphosphine, Ph_2PCl, is corrosive, irritating and very toxic by inhalation. *Always* use it in a good fume cupboard. Spillages should be treated with solid sodium carbonate and washed with large amounts of water.
2. Carbon disulfide is a foul smelling, toxic and very flammable liquid. Petroleum ether and diethyl ether are also very flammable, volatile liquids. Keep these properties in mind when handling these solvents. Don't keep large amounts around.
3. Grease the glass joints with silicone grease.

3.26.1 Experimental

a) $HN(PPh_2S)_2$

$$2Ph_2PCl + Me_3SiNHSiMe_3 \rightarrow Ph_2P{-}NH{-}PPh_2 + 2Me_3SiCl$$

$$Ph_2P{-}NH{-}PPh_2 + 2S \rightarrow \underset{\underset{S}{\|}}{Ph_2P}{-}NH{-}\underset{\underset{S}{\|}}{PPh_2}$$

Refer to the setup in Figure 3.26-1. A solution of hexamethyldisilazane (8.4 g) in 75 cm^3 of toluene is placed in a two-neck round-bottomed flask (250 cm^3) provided with a pressure-equalised dropping funnel on one neck and a condenser adapted for distillation on the second neck. The distillate (see further) will be collected in a round-bottomed flask (200 cm^3) and the system is closed with a calcium chloride tube. The flask is heated with a heating mantle and the contents stirred with a Teflon-coated magnetic stirrer.

A solution of chlorodiphenylphosphine (23 g) in toluene (75 cm^3) is placed in the dropping funnel. This is added dropwise to the solution of hexamethyldisilazane while heating. As the chlorotrimethylsilane forms, it distills out. The toluene solvent boils at 110 °C and the heating is maintained below this temperature (preferably at 80–90 °C). The heating at 80–90 °C is maintained for ca. 3 hours, to completely remove chlorotrimethylsilane. Then, the mixture is allowed to warm up to the boiling

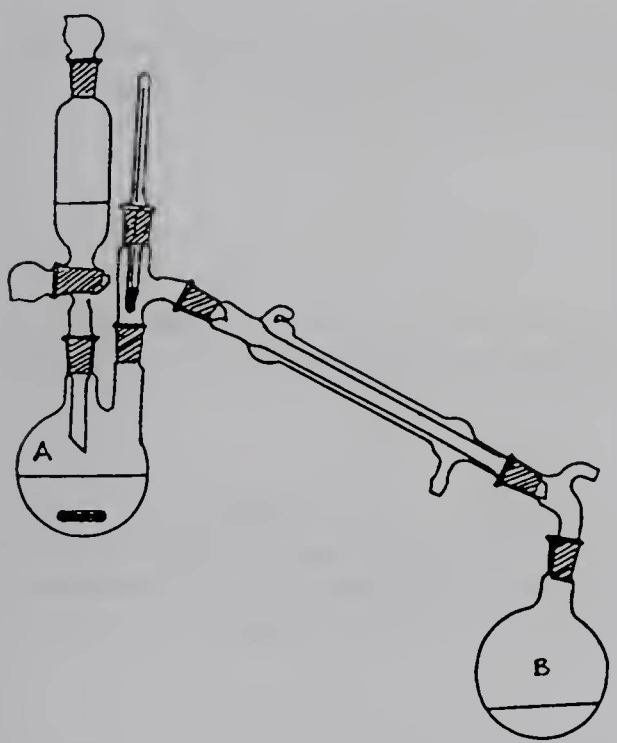


Fig. 3.26-1 Apparatus for $HN(PPh_2S)_2$ synthesis.

temperature of toluene and ca. 70–80 cm^3 of toluene is distilled out. The mixture is cooled to room temperature, the dropping funnel is removed and replaced with a stopper. Now 3.3 g elemental sulfur are added to flask A and the mixture is heated again to 80–90 °C and stirred for another 3 hours, until almost all sulfur is dissolved. Upon cooling, the precipitated solid is filtered on a glass frit, thoroughly washed with cold toluene, carbon disulfide (to remove unreacted sulfur from the product) and petroleum ether, and dried in air.

Calculate the yield of the first crop and compare the melting point of your product with the literature value (m.p.: 213.5–214.5 °C). Record and interpret the infrared spectrum, identifying the P–N, P–S and N–H vibration bands.

b) $K^+[N(PPh_2S)_2]^-$

$$Ph_2(S)PNHP(S)Ph_2 + KO^tBu \rightarrow K^+[N(PPh_2S)_2]^- + {}^tBuOH$$

In a round-bottomed flask (200 ml), 10 g of $HN(PPh_2S)_2$ in 100 ml methanol is treated with 2.5 g potassium *tert*-butoxide. The solution is evaporated to dryness and the product is recrystallised from methanol to give the colorless crystalline potassium salt (m.p.: 363–366 °C).

c) $NH_4^+[N(PPh_2S)_2]^-$

$$Ph_2(S)PNHP(S)Ph_2 + NH_3 \rightarrow NH_4^+[N(PPh_2S)_2]^-$$

Dry ammonia gas is bubbled through a solution of 1 g $HN(PPh_2S)_2$ in 100 ml CH_2Cl_2. The ammonium salt precipitates as a needle-like crystalline solid, which decomposes on heating with evolution of ammonia and regeneration of the neutral ligand. Therefore, the melting point will be that of the ligand.

d) Some Metal Complexes

Lead

Lead acetate (0.4 g) is treated with the potassium salt (1 g) in 20 cm^3 methanol. The bright yellow precipitate which is formed can be recrystallised from a methylene chloride/diethyl ether mixture (1:1). m.p.: 239–241 °C.

Iron

A pale green precipitate is formed by adding an excess of $[Et_4N][FeCl_4]$ (ca. 1 g) to a solution of the potassium salt (0.9 g) in 100 cm^3 methanol. The solid is filtered, washed with methanol and dried. The complex $Fe[(SPPh_2)_2N]_2$ can be recrystallised from a mixture of CH_2Cl_2 and petroleum ether to give pale green crystals (m.p.: 285–286 °C).

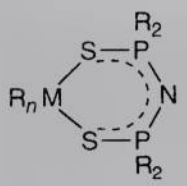
Cobalt

The cobalt complex can be prepared similarly, from $CoCl_2 \cdot 6H_2O$ and the potassium salt of the ligand, in the form of green, air-stable crystals (m.p.: 304–309 °C).

Nickel

This brown complex (m.p. 265–266 °C (dec)) can be obtained as above, from $[Et_4N][NiCl_4]$ and the potassium salt. Calculate yourself the amounts of reagents required.

Other metal complexes described in the literature contain manganese, palladium, platinum, copper, gold, silver, indium, zinc, bismuth and tellurium. The structures of some of these metal compounds have been confirmed by X-ray diffraction. Organometallic derivatives i, with R_nM = PhTe, R_2Au, Me_3Sn and Me_2Sn have also been reported.



i

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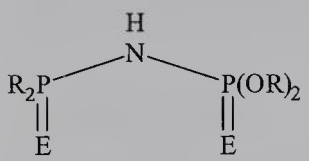
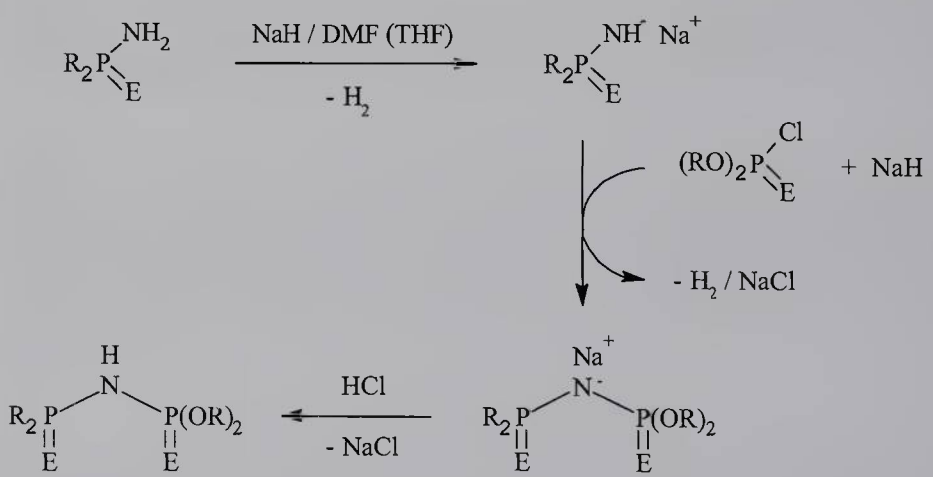
3.27
Inorganic (Carbon-Free) Chelate Rings II: Asymmetric Mixed-Donor P-N-P Ligand and its Palladium Complex

David J. Birdsall and Josef Novosad

In the previous experiment the preparation of symmetrically substituted P–N–P ligand is described, the following method deals with the synthesis of ligands with the phosphorus atoms bearing different organic substituents, particularly of electronically unequivalent natures.



Whilst the condensation reaction using Ph_2PCl and hexamethyldisilazane is suitable for the preparation of $Ph_2P–NH–PPh_2$, the usage of such method would most probably lead to a mixture of at least three different ligands when starting with two different chlorides. Instead, the reaction of $R_2P(E)NH_2$ and $R'_2P(E)Cl$ using sodium hydride was introduced. The amino compound is deprotonated in the first step to give its sodium salt which is then reacted with an equimolar amount of the chloro compound. The effervescence of the hydrogen gas liberating in both reaction steps can be used as an indication of the reaction progress. The salt of the ligand formed can be readily converted into protonated form using water solution of hydrogen chloride.



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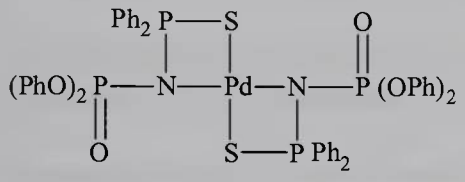
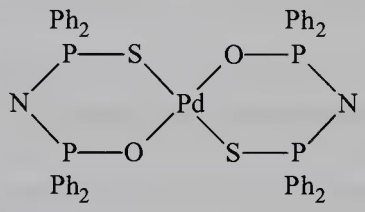
Similarly to imidodiphoshinates, the asymmetric analogues are easily coordinated to a variety of metals. Interestingly, there are two kinds of chelate rings in the square-planar palladium complexes. While most P–N–P compounds form two six-membered chelate rings [$Pd(E–P)_2N$], there are a few examples of four-membered chelate rings [Pd–S–P–N] found, with nitrogen and chalcogen as donor atoms. Most probably this phenomenon is related to electronically different organic substituents bound to the phosphorus atoms of the ligand.





Special Safety Precautions

1. Chlorodiphenylphosphine, Ph_2PCl, and similar tertiary phosphines are corrosive, irritating and toxic by inhalation. Always use them in a good fume cupboard.
2. Sodium hydride, NaH, is corrosive, pyrophoric matter, which must be treated in the absence of water, both liquid and gaseous in the air. These unpleasant properties can be reduced by mixing NaH with paraffin oil as a precautionary agent. Nevertheless, handle such dispersion with care too.
3. A violent exothermic reaction between sodium hydride and hot DMF has been reported earlier. Take care when using sodium hydride suspension in DMF and avoid the excessive increase in reaction temperature.

3.27.1 Experimental

All glassware should be carefully dried to eliminate the traces of water, the storage in the hot oven (125–130 °C) before the experiment is preferred. The synthesis must be carried out under dry nitrogen or argon except the final part when diluted hydrochloric acid is involved in the protonation of the sodium salt of the ligand.

The experiment is designed as almost 'total' synthesis of the asymmetrical ligand from basic starting materials, $POCl_3$ and Ph_2PCl.

a) $(PhO)_2P(O)Cl$

$$POCl_3 + 2\ PhOH \rightarrow (PhO)_2P(O)Cl + 2\ HCl$$

Perform the synthesis in fume cupboard! Place 50 cm^3 $POCl_3$ (0.54 mol, 82.4 g) and 102.8 g (1.09 mol) phenol into a 250 cm^3 round bottomed flask and attach a reflux

condenser. The condenser has to be equipped with a drying tube filled with phosphorus pentoxide. Keep in mind the tube has not to be blocked since the hydrogen chloride is liberated during the reaction. While stirring maintain the temperature around 200 °C for next 24 hours. Then increase the temperature up to 230 °C shortly (for 15 minutes approximately). Replace the reflux condenser and distil the mixture *in vacuo* (0.1 Torr/13.3 Pa). The fraction between 148–155 °C should be collected.

b) $(PhO)_2P(O)NH_2$

Perform the ammonolysis in a fume cupboard! Dissolve 10.0 g $(PhO)_2P(O)Cl$ (0.037 mol) in dry diethyl ether (50 cm^3) in two- or three-necked 100 cm^3 round-bottomed flask and bubble the dried ammonia gas through the solution for 20 minutes (the gas flow should be adjusted above the level allowing the counting of ammonia bubbles). The mixture has to be stirred and the inlet tube should be checked for ammonium chloride plugs. After the ammonolysis is completed, the mixture is filtered using celite, and the filtrate is evaporated to dryness using rotary evaporator.

c) $Ph_2P(S)Cl$

$$Ph_2PCl + S \rightarrow Ph_2P(S)Cl$$

Using a syringe, add 5 cm^3 95% Ph_2PCl (6.15 g, 26.5 mmol) into a mixture of toluene (15 cm^3) and sulfur powder (0.85 g, 26.5 mmol) in a Schlenk tube of appropriate size. Heat the mixture under reflux for 3 hours, then filter any excess sulfur, and evaporate the toluene to dryness using a vacuum line.

d) $(PhO)_2P(O)-NH-P(S)Ph_2$

$$(PhO)_2P(O)NH_2 + NaH \rightarrow [(PhO)_2P(O)NH]^-Na^+ + H_2$$

$$[(PhO)_2P(O)NH]^-Na^+ + Ph_2P(S)Cl + NaH \rightarrow [(PhO)_2P(O)\text{-}N\text{-}P(S)Ph_2]^-Na^+ + H_2$$

$$[(PhO)_2P(O)\text{-}N\text{-}P(S)Ph_2]^-Na^+ + HCl \rightarrow (PhO)_2P(O)\text{-}NH\text{-}P(S)Ph_2 + NaCl$$

Place 100 cm^3 THF and 3.20 g of the NaH (60% dispersion in paraffin oil, 80 mmol) in a 250 cm^3 three-necked, round-bottomed flask. Add slowly 6.60 g (26.5 mmol) $(PhO)_2P(O)NH_2$ while stirring the suspension intensively. After the hydrogen effervescence is complete, use a syringe to introduce previously prepared $Ph_2P(S)Cl$ (6.70 g, 26.5 mmol) dropwise. Then attach a reflux condenser and bring the mixture to its boiling temperature and continue the heating for 3 hours. After cooling add 5 ml methanol to destroy any excess sodium hydride. Reduce the volume of the THF by half under vacuum using a rotary evaporator and add 150 cm^3 2 M aqueous hydrochloric acid. Extract the mixture with dichloromethane (3 × 50 cm^3). Dry the combined dichloromethane extracts over Na_2SO_4 for 30 minutes, then distil the solvent off partially (50 cm^3), and store the extract in a freezer.

You will obtain the product as a crystalline white solid, which should be collected by vacuum filtration and washed with cold ether (2×5 cm^3).

Since the resulting compound is air and water stable, it can be stored without additional precautions.

e) $[(PhO)_2P(O)-N-P(S)Ph_2]_2Pd$

$$(PhO)_2P(O)-NH-P(S)Ph_2 + KO^tBu \rightarrow [(PhO)_2P(O)-N-P(S)Ph_2]^- K^+ + {}^tBuOH$$

$$2\,[(PhO)_2P(O)-N-P(S)Ph_2]^- K^+ + Pd(OAc)_2 \rightarrow [(PhO)_2P(O)-N-P(S)Ph_2]_2Pd + 2\,KOAc$$

The potassium salt of the ligand is prepared in methanol (10 cm^3) stirring $(PhO)_2P(O)-NH-P(S)Ph_2$ (0.233 g, 0.5 mmol) along with potassium *tert*-butoxide (0.056 g, 0.5 mmol) in a 50 cm^3 one-necked flask, until the suspension turns into a clear solution. Then palladium acetate (0.056 g, 0.25 mmol) in MeOH (30 cm^3) is added, and the mixture is stirred for next 6 hours at room temperature. The red precipitate is filtered, washed with methanol (5 cm^3), and dried in air.

f) Crystal Preparation

Both $(PhO)_2P(O)-NH-P(S)Ph_2$ and $[(PhO)_2P(O)-N-P(S)Ph_2]_2Pd$ can be prepared as monocrystals, suitable for X-ray structure analysis, by slow diffusion of hexane into a dichloromethane solutions of the compounds. The crystallization can be performed in a small test-tube, where the dichloromethane solution is carefully overlaid by hexane (in volume ratio 1:5 – 1:7). If the interphase turns cloudy when adding hexane, it is necessary to dilute the dichloromethane solution. The final arrangement is depicted in Figure 3.27-1.

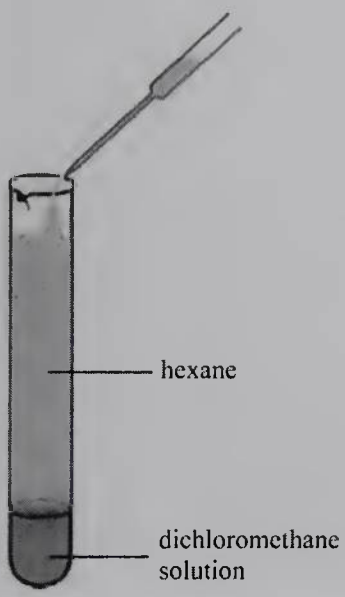


Fig. 3.27-1 The arrangement of the liquid diffusion process.

3.37.2
Exercises

Measure the melting points of the monocrystals prepared by the diffusion process. Record the proton-decoupled ^{31}P NMR spectrum of both the ligand and its complex dissolved in dichloromethane and discuss the result. Read the chemical shift(s) and calculate the coupling constant. Try to assign the signals and compare obtained values to the literature data of starting phosphorus materials and similar compounds.

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3.28
Amidosulfuric Acid, Trisilveramidosulfate Monohydrate and $SO_3 \cdot N(CH_3)_3$ Complexes

Antonín Růžička and Zdirad Žák

Amidosulfuric acid, HSO_3NH_2, is a white non-hygroscopic crystalline solid. It is a strong acid and serves *inter alia* as a titrimetric standard substance for acidimetry. In strongly alkaline solutions, it is possible to exchange up to all three H atoms in its molecule by metal ions. Thus, various salts have been prepared e.g. $KSO_3NHAg \cdot H_2O$, $NaSO_3NHAg$, KSO_3NHAg and $AgSO_3NAg_2 \cdot H_2O$.

This experiment involves the preparation of HSO_3NH_2, $AgSO_3NAg_2 \cdot H_2O$ and, by the reaction of the trisilver salt with CH_3I, $SO_3 \cdot N(CH_3)_3$. This donor-acceptor complex is usually prepared by the direct reaction of SO_3 with $N(CH_3)_3$ and its formation during the action of CH_3I on $AgSO_3NAg_2 \cdot H_2O$ indicates that all three Ag ions of the trisilver salt are bonded to the nitrogen atom as has been confirmed by X-ray structure analysis. A large excess of $AgNO_3$ is required for the preparation of $AgSO_3NAg_2 \cdot H_2O$, but silver can be recovered from the mother liquid in elemental form.

Special Safety Precautions

1. a) Fuming sulfuric acid (30% SO_3, oleum) is a very corrosive substance and reacts violently with water. Extensive care must be taken to avoid contact with skin — it can cause severe burns.
   b) You must work in a fume cupboard.
   c) Protective clothing, gloves and goggles should be worn at all times, do not inhale the vapours.
   d) For measuring, use only a dry graduated cylinder.
2. Clamp securely the Erlenmeyer flask with the reaction mixture in the water bath to prevent overturning.
3. The residue of oleum after the isolation of HSO_3NH_2 may be destroyed by adding it *dropwise* to a large amount of cold water.
4. CH_3I and HCOH are highly toxic and mutagenic. All manipulations should be done in a fume cupboard, do not inhale the vapours.
5. Solutions of $AgNO_3$ leave black stains of elemental silver on contact.

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3.28.1
Experimental

a) HSO_3NH_2

The formation of the amidosulfuric acid can be expressed by the overall Eq. (1).

$$OC(NH_2)_2 + H_2SO_4 \cdot SO_3 \rightarrow 2HSO_3NH_2 + CO_2 \quad (1)$$

15 g of urea is dissolved in 25 cm^3 of concentrated H_2SO_4 (*caution* – the mixture warms up strongly!) in a 500 ml Erlenmeyer flask. The flask is immersed in a boiling water bath (clamp securely!) and 60–70 cm^3 of 30% oleum is added in small quantities (5–10 cm^3). After approx. 30 ml of oleum has been added to the flask, it is necessary to stop the addition of oleum and wait until the reaction starts (CO_2 evolves), otherwise a violent evolution of CO_2 can occur and the reaction mixture will be lost in the water bath. When the reaction proceeds, the addition of oleum is continued in the same manner. After all oleum has been added, leave the flask in the boiling water bath for a further 30 minutes. Then remove it from the bath and cool it down in an ice bath (ice water bath). HSO_3NH_2 crystallises out of the solution. Filter the product off through a sintered glass funnel, placing a trap between the filtering medium and the suction pump, and press out all the mother liquid you can. This raw amidosulfuric acid is contaminated by sulfuric acid which can be removed by recrystallisation from water as follows.

Dissolve the crude HSO_3NH_2 at 70 °C in as little water as possible (see Note), filter if necessary through a sintered glass funnel and cool in an ice bath to 0–2 °C. Vacuum filter the crystallised acid using a sintered glass funnel and a suction flask, wash with ethanol (15 cm^3), ether (15 cm^3) and allow to dry in air.

Note: The solubility of HSO_3NH_2 at 70 °C is 40 g of HSO_3NH_2 in 100 g of H_2O.

Test for SO_4^{2-} ions: Dissolve a pea-sized quantity of dry HSO_3NH_2 in 2–3 cm^3 water in a test tube. Add a few drops of a 5% solution of $BaCl_2$. The presence of SO_4^{2-} ions is manifested by the formation of a white precipitate of $BaSO_4$ (barium amidosulfate is soluble in water).

Acidimetric titration of HSO_3NH_2 with a 0.1 M solution of NaOH: Use standard procedure and calculate the purity of the prepared acid.

b) $AgSO_3NAg_2 \cdot H_2O$

The preparation proceeds according to Eqs. (2) and (3).

$$2HSO_3NH_2 + K_2CO_3 \rightarrow 2KSO_3NH_2 + H_2O + CO_2 \quad (2)$$

$$KSO_3NH_2 + 3AgNO_3 + 2NH_4OH \rightarrow AgSO_3NAg_2 \cdot H_2O + KNO_3 + 2NH_4NO_3 + H_2O \quad (3)$$

Dissolve 3.0 g HSO_3NH_2 in 50 cm^3 water in a beaker and neutralise the solution with solid K_2CO_3. Add 5 ml of conc. NH_4OH solution and then, under continuous stirring with a magnetic stirrer, add slowly the solution of 25 g $AgNO_3$ in 100 cm^3 of water. A yellow precipitate of an amorphous form of $AgSO_3NAg_2 \cdot H_2O$ is formed immediately. Filter off approx. 1/2 of the precipitate using a sintered glass funnel. Return the filtrate to the remaining unfiltered precipitate, cover the beaker with a watch glass and allow to stand for several days in a dark place. The bright yellow amorphous precipitate will recrystallise into a yellow-green crystalline product.

Wash the amorphous salt on the filter with a small amount of water (25 cm^3), ethanol (15 cm^3) and ether (15 cm^3), and allow to dry in air. Isolate the crystalline product in the same way.

Note: Before washing the crystalline product with ethanol and ether, save the mother liquid for silver revovery!

c) $SO_3 \cdot N(CH_3)_3$

The reaction scheme is given by Eq. (4).

$$AgSO_3NAg_2 \cdot H_2O + 3CH_3I \rightarrow SO_3 \cdot N(CH_3)_3 + 3AgI + H_2O \quad (4)$$

Transfer 2.0 g of the dry amorphous salt to a 25 cm^3 distillation round-bottomed flask with a ground joint. Attach a reflux condenser to the flask and using a funnel, pour 3.0 cm^3 of CH_3I down the condenser onto the silver salt. After a few seconds, an exothermic reaction starts and the contents of the flask warms up to the boiling point of CH_3I. (*Note:* The crystalline yellow-green salt reacts with CH_3I very slowly). After 15 minutes, distill off under vacuum the unreacted methyl iodide and the water formed into a cold trap until dry (use a water vacuum pump). (Dispose of the distillate as instructed by the supervisor).

Sublime $SO_3 \cdot N(CH_3)_3$ from the dry reaction product *in vacuo* at 160–170 °C (use an oil bath) using an oil vacuum pump and the apparatus depicted in Figure 3.28-1. The crystals of the complex thus obtained are up to several centimeters long.

Determine the melting point in a sealed glass capillary (240 °C). Record the IR spectrum and compare it (400–1600 cm^{-1}, KBr pellet) with that in the literature.

d) Recovery of Silver

$$2AgNO_3 + NaOH \xrightarrow{H_2O} Ag_2O \cdot xH_2O + 2NaNO_3 \quad (5)$$

$$Ag_2O + NaOH + HCOH \rightarrow 2Ag + HCOONa + H_2O \quad (6)$$

Transfer the mother liquid from the filtration of $AgSO_3NAg_2 \cdot H_2O$ into a 1000 cm^3 beaker and keep adding a 10% solution of NaOH until all the silver is precipitated as hydrated silver oxide. Then add the same amount of 10% hydroxide solution as was required for the silver oxide precipitation and bring the contents to boil. Add *dropwise* under continuous stirring a 37% water solution of formaldehyde until all the Ag_2O

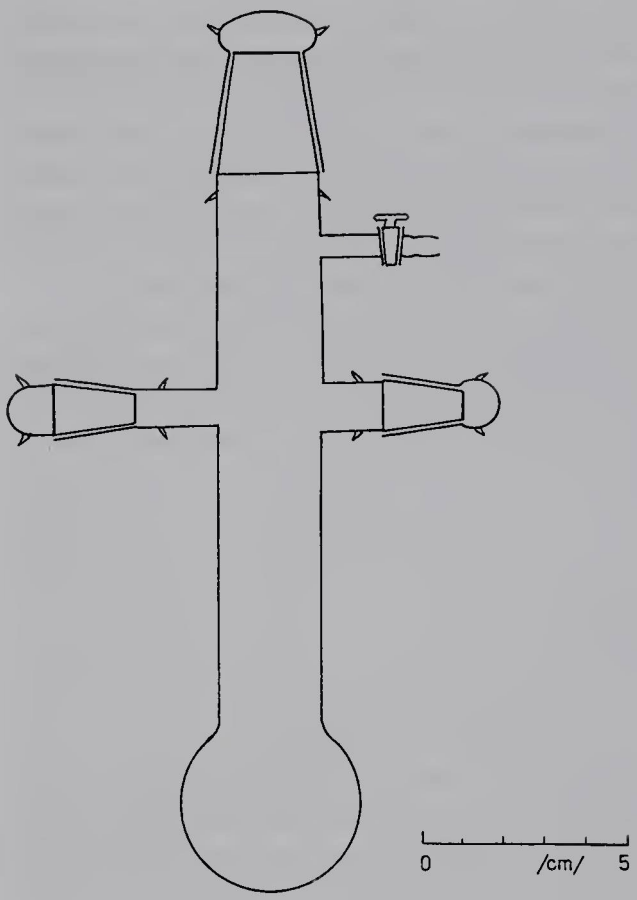

Fig. 3.28-1 Sublimation apparatus.

is reduced to elemental silver – the colour of the suspension will change from dark brown to greyish and the supernatant will clear rapidly when stirring is interrupted. Allow the contents to cool, decant the supernatant, fill the beaker with distilled water, stir, leave to settle and decant. Repeat this procedure several times until the neutral reaction of the liquid is reached. Vacuum filter, wash the silver with water and dry in an oven at 100 °C.

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3.29
Anomalous Paramagnetism in Some Iron(III) Chelates Studied by the Evans NMR Method

David J. Otway

Crawford and Swanson have described the use of the nuclear magnetic resonance technique to determine magnetic moments in solution [1] based on the original Evans method. The method relies on measuring the separation (Δf) in the resonance positions of two identical protons in two solutions. One of the solutions contains the paramagnetic material and the other contains pure solvent. The separation (Δf in hertz) is related to the mass susceptibility, χ_g, of the dissolved paramagnetic substance by the following relationship

$$\chi_g = \frac{3\,\Delta f}{2\pi f m} \tag{1}$$

where f is the frequency of operation of the machine, m is the concentration of paramagnetic substance (g cm^{-3}) and χ_o is the mass susceptibility of the pure solvent. The magnetic moment is then calculated using Eqs. (2) and (4).

$$\chi_M = \chi_g \cdot M \tag{2}$$

where χ_M is the molar susceptibility and M is the molar weight of the complex. This gives your answer in cgs. units. Convert it to SI using Eq. (3).

$$\chi_M\,(\mathrm{SI}) = \chi_M\,\mathrm{cgs} \times 4\pi \times 10^{-6} \tag{3}$$

χ'_M is obtained from χ_M by including a diamagnetic correction for the ligands. This is done by summing the diamagnetic corrections for each ligand atom [2]. Calculate μ_{eff} from Eq. (4).

$$\mu_{eff} = 797\,(\chi'_M T)^{1/2} \tag{4}$$

where T is the temperature of the NMR probe.

In this experiment the technique is applied to the study of the anomalous paramagnetism of iron(III) *N,N*-dialkyldithiocarbamates. These complexes are anomalous in that their behaviour is neither "high spin" nor "low spin" [3, 4]. Depending

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on the nature of the alkyl substituents on the ligand, the value of the magnetic moments can be pure low spin, pure high spin, or intermediate between these values.

The explanation is that the ligand field energies for these complexes lie close to the crossover between the high-spin, weak field ground state configuration ($t_{2g}^3 e_g^2$) and low-spin strong-field (t_{2g}^5) states. Thus the spin pairing energy for these complexes must be close to the ligand field strength. The high-spin configuration has 5 unpaired electrons and the low-spin configuration has one unpaired electron. For $Fe(S_2CNR_2)_3$ complexes, the low-spin case occurs for R = isopropyl, and isobutyl, and high spin for 2R = pyrrolidyl. Intermediate magnetic moments are observed for R = methyl, ethyl, benzyl. A spin equilibrium is suggested for these complexes [3].

The iron dithiocarbamates also have the advantage of being easy to prepare and purify and of having good solubility in solvents such as chloroform. As paramagnetic shift, Δf, in Eq. (1) depends on concentration, it is an advantage to have as high a concentration as possible for accurate measurement of the shift. Make sure that you carry out all of the measurements for the spectroscopic part of the experiment as carefully as possible. For these complexes, shifts of 5–40 Hz are observed for 0.02 g cm^{-3} chloroform solutions.

Special Safety Precautions

Chloroform should be used in a fume cupboard. Carbon disulfide is toxic and *must* be used in a fume cupboard (wear gloves too). Both amines are irritating to eyes, face and respiratory system, again use gloves and work in a fume cupboard.

3.29.1 Experimental

Make $Fe(S_2CNR_2)_3$ for NR_2 = *N,N*-dicyclohexyl and *N,N*-dibenzyl as follows: solutions of sodium salts of the ligands are prepared by adding CS_2 (0.05 mol) to a stirred solution of the amine (0.05 mol) in ethanol (50 cm^3). 6 M NaOH (10 cm^3) is then added with stirring.

The complexes are prepared by mixing 0.017 mol of 60% w/v $FeCl_3$ aqueous solution with the solution from the ligand preparation. A black-brown precipitate immediately forms. This should be recovered by vacuum filtration, the precipitate washed with ethanol and air-dried. The complex is recrystallized by dissolution in hot $CHCl_3$ (30 cm^3) **(in a fume hood)**, vacuum filtration, and addition of ethanol (30 cm^3) to the filtrate. Black or dark brown crystals form on cooling; the crystals are recovered by vacuum filtration and are washed with ethanol and air-dried.

The magnetic moments are determined by preparing a chloroform solution of accurately known concentration of the complex (0.1 g in ca. 0.5 cm^3 – use a pipette). An internal reference is used by placing a sealed capillary containing pure $CHCl_3$ (provided by technicians) in an NMR tube containing the complex solution. The NMR spectrum is then recorded in the region of the $CHCl_3$ peak. A large, broad sol-

vent peak is observed due to paramagnetic broadening by the complex and a smaller, sharp peak is observed downfield to this peak. A high spinning rate (>40 Hz) is recommended as this creates a good vortex, which keeps the capillary in the middle of the tube and minimizes nonhomogeneity effects. The magnetic moments can then be calculated [1, 2].

N.B.: For the purposes of this experiment you may calculate the susceptibility of the solvent using the values in [2].

3.29.2 Report

1. Briefly indicate the aims of the experiment.
2. Do not reproduce the experimental procedure unless your experiment differed.
3. Give balanced equations for the formation of the complexes and yields.
4. Give the magnetic moments (as determined by the Evans NMR method) of the two complexes. Comment on the values obtained.
5. What are the point groups of the compounds that you have made?
6. What sources of both systematic and random error are there in this experiment? Which are most significant errors and how might they be minimised?

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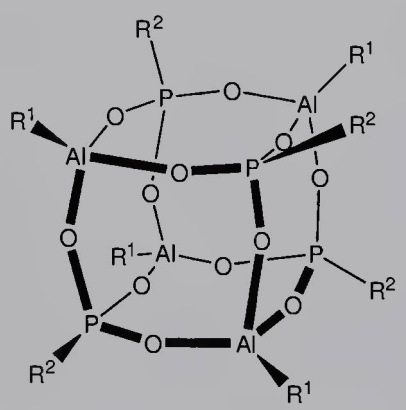
3.30
Cubic Molecular Aluminophosphonates

Jiri Pinkas

Framework aluminophosphates are crystalline microporous materials related to zeolites by the isoelectronic relationship between the $[AlPO_4]$ and $[AlSiO_4]^-$ formula units. The multitude of known three-dimensional structures is composed of a relatively small number of structural moieties, such as $Al_4O_{12}P_4$ cubes or $Al_6O_{18}P_6$ hexagonal prisms that are termed secondary building units (SBUs). The concept of SBUs was originally derived from the solid-state structures of zeolites and aluminophosphates with tetrahedral frameworks. However, it was shown that in some cases the SBUs and their analogues are present in the reaction mixture during the synthesis and their isomerisation and condensation lead to the formation of extended framework structures. Molecular aluminophosphates and -phosphonates with polyhedral cores are synthesized as structural and spectroscopic models for the secondary building units. These experiments are motivated by the effort to develop rational synthetic routes to new porous materials of several types. One area is microporous materials where the goal is to use these molecules as precursors and control the course of reaction to a particular architecture. Of special interest is the connection of cubic molecules through all eight vertices to form a network with a body-centred cubic topology. Moreover, these polyhedral units can serve as nodes in the construction of coordination polymers after suitable derivatisation of their vertices with functional linker groups. Connection of aluminophosphonate cubic units with the linkers positioned at four tetrahedrally arranged vertices should result in a diamond-type network. Therefore, these cubic molecules hold promise as potential precursors to porous materials.



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Special Safety Precautions

Trialkylaluminium compounds are highly flammable and react violently with water. Aluminophosphonates are sensitive to moisture. Use purified nitrogen and a drying column.

3.30.1 Experimental

Standard techniques and equipment for the manipulation of air- and moisture-sensitive compounds, such as dry-box, Schlenk flasks, syringes, rubber septa and cannulas, should be used in this preparation. Distil toluene and tetrahydrofuran from Na–benzophenone under dry nitrogen. A solution of Et_3Al in toluene can be purchased from commercial vendors. Prepare a solution of $C_6H_{11}PO(OH)_2$ (2.00 g, 12.2 mmol) in tetrahydrofuran (60 cm^3). Fill a syringe with the Et_3Al solution in toluene (1.9 M, 6.4 cm^3, 12 mmol). Add both solutions simultaneously by syringes through a septum dropwise to freshly distilled toluene (60 ml) which is vigorously stirred at 50 °C in a 250 crn^3 Schlenk flask. Stir for 1 hour and than leave the reaction mixture to cool to room temperature. Continue stirring with a magnetic stirrer for an additional 20 hours. Reduce the volume of the clear, colourless reaction mixture slowly to 10 cm^3 and then cool to –20 °C in a freezer. After the first fraction of colourless crystals has formed (ca. 2 days), decant the mother liquor by a syringe and use it to obtain next fractions. Wash the crystals with a small amount of hexane and dry *in vacuo*. Transfer the evacuated reaction flask into a dry=box. Weigh the resulting product and calculate the reaction yield (the first fraction 15%, total usually 50%). Prepare the samples for ^1H and ^{13}C NMR spectrometric measurements in $CDCl_3$ or CD_2Cl_2. Place a small amount of the product in capillaries and seal them with Apiezon wax to record mass spectra. Flame-seal the capillaries outside the box with a small gas torch. Record the IR spectrum in a KBr pellet prepared with a mini-press.

The crystalline solid from the first fraction is identified as $[EtAl(\mu\text{-}O)_3PC_6H_{11}]_4$ (yield 0.410 g, 0.47 mmol, 15%), m.p. >300 °C. ^1H NMR (300 MHz, CD_2Cl_2): δ –0.18 (q, $^3J_{HH}$ = 8.2 Hz, 8H, $AlCH_2$), 1.02 (t, $^3J_{HH}$ = 8.1 Hz, 12H, $AlCH_2CH_3$), 1.29–1.35, 1.78, 1.86, 2.00 (br m, 44H, C_6H_{11}). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ –3.9 (br s, CH_3CH_2Al), 9.02 (s, CH_3CH_2Al), 26.41 (s, C4-C_6H_{11}), 26.44 (d, $^3J_{PC}$ = 4.7 Hz, C3-C_6H_{11}), 26.54 (d, $^2J_{PC}$ = 17.6 Hz, C2-C_6H_{11}), 35.74 (d, $^1J_{CP}$ = 162.6 Hz, P-CH). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 12.7 (s, $^1J_{PC}$ = 162.6 Hz, ^{13}C satellites). IR (KBr pellet, cm^{-1}): ν 2936 (s), 2863 (m), 2793 (w), 1283 (w), 1204 (s), 1176 (vs), 1126 (s), 1099 (s), 1003 (m), 898 (w), 669 (m), 628 (w), 581 (w), 503 (s). MS (EI, 70 eV), m/z (relative intensity, ion): 871 (10, M – H^+), 843 (100, M – Et^+), 731 (10, M – 2Et – $cHex^+$), 407 (10, 1/2M – Et^+), 393 (15, 1/2M – Pr^+).

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3.31

Preparation and Optical Properties of Zinc Sulfide Quantum Dots

Andrew L. Hector

Quantum dots are nanoparticles (crystals with dimensions of a few nanometres) of a semiconducting material. They are of particular interest for optical applications due to the higher *quantum yield* that they exhibit for fluorescence (light emission) compared with bulk semiconductors. This is a measure of the likelihood of a photon being produced after absorption of a higher energy photon. Often their emission is brighter and they are stable for longer time periods than organic fluorescent dyes. Research into their applications is focused on light-emitting diodes, diode lasers, solar cells, optical amplifiers, photocatalysis and biological labels.

At particle sizes below the Bohr exciton radius, the band structure of semiconductors is incompletely developed. The properties are therefore intermediate between those of molecules and of bulk semiconductor materials. The most obvious sign of this is an increased band gap compared with the bulk semiconductor, which increases (is 'blue-shifted') as the particle size is reduced (Fig. 3.31-1).

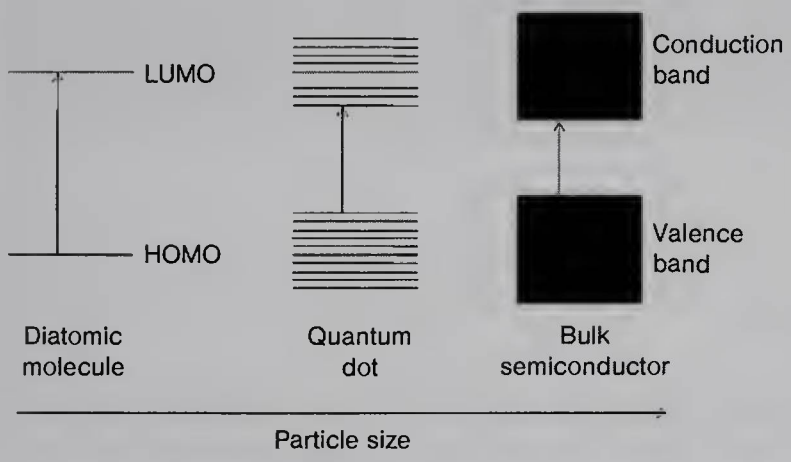

Fig. 3.31-1 Band structure diagrams showing the intermediate properties of semiconductor nanoparticles between molecules and bulk materials.

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This reduction in the observed band gap is an effect referred to as *quantum confinement*. A good approximation to the relationship between particle size r (nm) to the energy of the band gap E in electronvolts (eV) is given by the Brus equation, which simplifies for cubic ZnS to

$$r = \frac{0.31 - 2.91\sqrt{E - 3.53}}{2(3.54 - E)}$$

Colloidal quantum dots can be synthesised in solution by controlled growth of the very small crystallites. This may be achieved through thermal decomposition of a precursor compound or simply by controlling a precipitation process. In order to take advantage of the high quantum yield and of quantum confinement effects, it is essential to produce particles of a controlled size that do not aggregate (stick together). As the surface energy of these very small particles is high, aggregation occurs readily and is often irreversible. Hence the particles need to be synthesised with a coating on the surface – this helps to control the particle size in addition to inhibiting aggregation. The choice of this capping agent determines the solubility of the particles – often a surfactant is used with a hydrophilic end group that sticks to the growing particle and an organic chain which provides solubility in an organic solvent. The aim of this experiment is to synthesise zinc sulfide quantum dots capped with polyphosphate groups, which results in water-soluble particles. These will also be doped with other metal ions to modify their optical properties.

Special Safety Precautions

Sodium sulfide is corrosive, is toxic in contact with the skin and liberates toxic H_2S on contact with acids. Wear gloves, work in a fume cupboard and destroy sulfide residues with sodium hypochlorite (bleach) solution. Salts of Zn, Cu and Mn are harmful and irritants. Manganese acetate is also a possible teratogen. Contact with the skin, eyes, etc., should be avoided. Ethanol is highly flammable.

3.31.1 Experimental

a) Quantum Dot Synthesis

First prepare the following standard solutions using 100 cm^3 volumetric flasks and deionised water. Note that Na_2S should be handled in a fume hood with a plastic spatula.

1.00 mol dm^{-3} sodium sulfide from the solid $Na_2S \cdot 9H_2O$ (MW 219.5)
1.00 mol dm^{-3} zinc acetate from $Zn(O_2CCH_3)_2 \cdot 2H_2O$ (MW 240.2)
0.10 mol dm^{-3} manganese acetate from $Mn(O_2CCH_3)_2$ (MW 173.0)
0.01 mol dm^{-3} copper acetate from $Cu(O_2CCH_3)_2$ (MW 181.6).

The three quantum dot samples (A–C) are produced by the same method. Dissolve sodium polyphosphate in deionised water immediately before use in a 250 cm^3 conical flask. Stir *rapidly* while adding the zinc acetate solution using a graduated pipette, followed by any copper or manganese acetate and finally the sodium sulfide in one quick addition. Stir the mixture for a further 5 minutes. Place the mixture in a 50 cm^3 centrifuge tube with a screw-top lid. Centrifuge for 5 minutes at 3500 min^{-1}. Decant the solution into a sulfide waste beaker for disposal after bleach treatment.

Component	Sample		
	A	B	C
Deionised water (cm^3)	40	35	35
$Na(PO_3)_n$ (g)	5.10	5.10	5.10
1.00 M $Zn(O_2CCH_3)_2$ (cm^3)	5.50	5.45	5.00
0.01 M $Cu(O_2CCH_3)_2$ (cm^3)	0	5.00	0
0.10 M $Mn(O_2CCH_3)_2$ (cm^3)	0	0	5.00
1.00 M Na_2S (cm^3)	5.00	5.00	5.00

Wash the samples with deionised water and then with ethanol. To do this, add 40 cm^3 of solvent to the centrifuge tube, screw the lid on firmly and shake thoroughly until the solid is finely suspended in the solvent. Balance the tube weights and centrifuge (60 minutes with water or 5 minutes with ethanol, both at 3500 min^{-1}) and decant the solvent into the sulfide waste beaker. Dry the sample in a desiccator under vacuum. When dry, gently powder with a pestle and mortar.

b) Particle Size Analysis Using X-Ray Diffraction

Record X-ray diffraction patterns over a 2θ range of 20–70 ° (Cu $K_{\alpha 1}$) for your samples. Peaks or reflections are observed in the diffraction patterns when constructive interference between scattered X-ray photons occurs. This requires an ordered arrangement of the atoms. Sharp peaks arise because interference is destructive when the angle is changed by a small amount from that at which constructive interference occurs. This requires ordering over a large number of unit cells and the lattice can be considered infinite. With small crystals, both constructive and destructive interferences are weaker and the peaks are broadened. This is a useful phenomenon in the study of nanocrystals as the broadening can be related to the average crystallite size (t) in nm using the Scherrer equation:

$$t = \frac{0.891\lambda}{\left(\sqrt{B_M^2 - B_S^2}\right)\cos\theta}$$

where λ is the X-ray wavelength (0.154 nm), B_M is the peak width at half-height in radians (180° = π rad), B_S is the peak width for a highly crystalline standard and hence a measure of diffractometer resolution and θ is the diffraction angle in degrees (usually measured in 2θ).

Calculate the size of your particles, using the 111 reflection at ~28° and the data provided for bulk ZnS powder and a silica diffraction standard.

Sample data:

Sample	PXD linewidth, ° (rad)	Crystallite size (nm)
SiO_2 standard	0.1 (0.002)	–
Bulk ZnS	0.67 (0.012)	12
Sample A, ZnS	4.0 (0.070)	2.0
Sample B, ZnS:Cu	4.0 (0.070)	2.0
Sample C, ZnS:Mn	3.67 (0.064)	2.2

c) Optical Band Gap Measurement

The energy difference between the valence and conduction bands in zinc sulfide is similar to that of a photon of ultraviolet light, hence exposing ZnS to such photons can excite an electron from the filled valence to the empty conduction band. Thus, UV–visible spectroscopy can be used to measure the band gap. A step function is observed in the absorption at the band gap energy and this is usually converted to and expressed in electronvolts (1 nm = 1240 eV). Large cubic ZnS crystals have a band gap of 3.54 eV.

Samples for spectroscopic analysis should be made up in deionised water as dilute solutions. Weigh 3 mg of quantum dots, wash into a 25 cm^3 standard flask and make up to the fill line. Dissolve using an ultrasound bath (this may take ~15 min) and shake well. Collect UV–visible spectra from 600 to 250 nm using quartz cells, with deionised water in the second beam as standard.

Measure the wavelength at half the height of the step in the absorbance and convert this to electronvolts to obtain the band gap. Use the Brus equation to obtain an estimate of the particle size of the quantum dot samples.

Sample data:

Sample	Band gap (nm)	Band gap E (eV)	Particle size (nm)
Bulk ZnS[a)]	350	3.54	∞
Sample A, ZnS	318	3.90	2.0
Sample B, ZnS:Cu	314	3.95	1.9
Sample C, ZnS:Mn	317	3.91	2.0

[a)] For bulk ZnS a diffuse reflectance spectrum was provided; the particle size calculation shows that its size is above the Bohr exciton radius.

d) Photoluminescence Behaviour

Light can be re-emitted from semiconductors by various mechanisms (Fig. 3.31-2) and this can be investigated using photoluminescence spectroscopy. Relaxation di-

rectly from the conduction band to the valence band is referred to as band edge emission and is only observed in very high-quality semiconductors. More commonly, the electron transfers to a defect state, in this case associated with S^{2-} ion vacancies. Emitted photons are then of lower energy than the absorption band gap, in the violet region. If particles are doped with other ions, dopant states can also become involved in the relaxation mechanism, reducing still further the energy of emitted photons. Doping tetrahedral Cu^{2+} into ZnS provides an energy state just above the valence band, the t_2 level of Cu^{2+}. When Mn^{2+} ions are doped into ZnS, a higher energy state is also available and relaxation between the two Mn^{2+} states results in red emission.

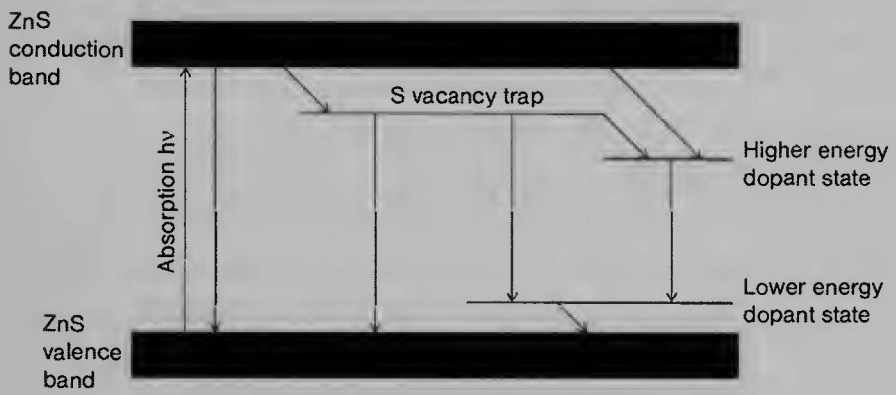

Fig. 3.31-2 Relaxation mechanisms for ZnS and doped ZnS.

Collect photoluminescence spectra using the solutions prepared for part c) using quartz cells. Use a 300 nm excitation wavelength and an emission range of 350–700 nm. Your data should contain a strong emission peak above 400 nm. Note the position of the maximum and convert the emission wavelength to electronvolts. If any other strong peaks are observed, note their energies.

Discuss the photoluminescence data with respect to the band theory description above. Comparing the photoluminescence data on samples 1 and 3, what can we learn about the relative rates of electron transfer to the S^{2-} defect state compared with the higher energy Mn^{2+} state?

Sample data:

ZnS	408 nm, 3.04 eV
ZnS:Cu	421 nm, 2.95 eV
ZnS:Mn	421 and 593 nm, 2.95 and 2.09 eV

Further Reading

This section is adapted from an experiment described in A. F. Lynch, D. A Nivens, B. C. Helmly, M. Richardson, R. R. Williams, *Chem. Educator*, **2004**, *9*, 159–162.

Basic description of nanoparticles: P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, F. A. Armstrong, *Inorganic Chemistry*, 4th edn, Oxford University Press, Oxford, **2006**, Chapters 24.1–24.7, pp. 643–655.

Brus equation and original description of the ZnS:Mn particles: J. F. Suyver, S. F. Wuister, J. J. Kelly, A. Meijerink, *Nano Lett.* **2001**, *1*, 429–433.

Original description of the ZnS:Cu particles: A.A. Bol, J. Ferwerda, J. A. Bergwerff, A. Meijerink, *J. Lumin.* **2002**, *99*, 325–334.

Scherrer equation: S. E. Dann, *Reactions and Characterisation of Solids*, Tutorial Chemistry Texts, Royal Society of Chemistry, Cambridge, **2000**.

Bulk cubic ZnS band gap: A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford Science Publications, Oxford, **1984**.

3.32
Four Methods for Analysing First Order Kinetics

Véronique Pimienta, Dominique Lavabre, Jean-Claude Micheau, and Gaston Levy

A chemical reaction always corresponds to the relaxation of a nonequilibrium situation ($\Delta G \rightarrow 0$). The concentrations of the substrates, intermediates and products change as a function of time. The simplest method to induce a chemical reaction is to mix two compounds with different chemical potentials. An alternative and convenient way is to exploit the property of photochromism (a single compound + light). A photochromic compound is one that undergoes a reversible colour change under UV or visible irradiation. Photochromic compounds are used in such diverse applications as optical information storage, imaging and in the construction of sunglasses.

The purposes of this study is to familiarise yourself with four general methods for analysing first-order kinetics and investigating reaction mechanisms. In this experiment, you will be examining the thermally reversible orange/blue photochromism of the mercury dithizonate bis(1,5-diphenylthiocarbazonato-*NS*)mercury(II)). The kinetic study is based on the first-order thermal return reaction blue → orange. The colour change is easily monitored using a UV/visible spectrophotometer or a colorimeter (Fig. 3.32-1).

A typical pattern of the absorbance at 606 nm (blue isomer) prior to, during and after irradiation of mercury dithizonate in xylene solution is shown in Figure 3.32-2.

As the process can be repeated many times without appreciable fatigue, a single sealed or stoppered cell can be used for several kinetic runs.

Special Safety Precautions

1. Mercury acetate is toxic. Its toxicity stems from the ability of mercury to combine with sulfhydryl groups (–SH) that are essential for enzymatic activity.
2. Diphenylthiocarbazone ($C_{13}H_{12}N_4S$) is known as dithizone and has long been used as a reagent for the colorimetric analysis of metal traces. Exercise caution as it is potentially dangerous.
3. Concentrated ammonia solutions must always be used in a fume cupboard.

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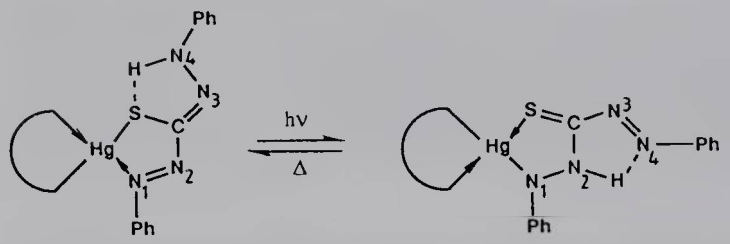
4. Xylene is flammable and toxic. Significant neuro and cardiac toxicity is described for this compound.
5. Limit exposure values: mercury vapour (0.05 mg m^{-3}); ammonia: (18 mg m^{-3}); xylene (130 mg m^{-3}).



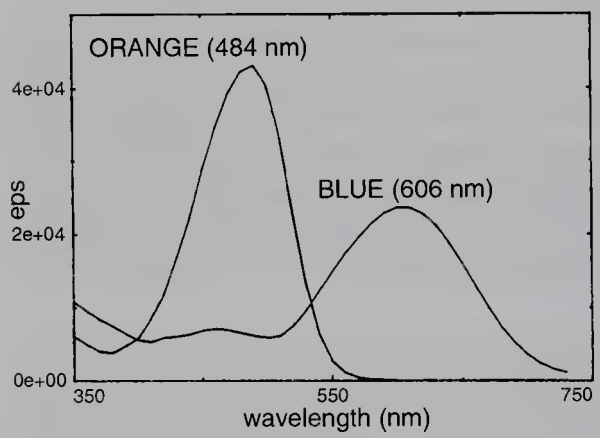


Fig. 3.32-1 The photochromic mechanism of mercury dithizonate involves a N_4 to N_2 H-transfer and a *cis-trans* isomerisation about the $C{=}N_3$ bond. There is an S-H hydrogen bond and a $PhN_1N_2CN_3$ conjugated system in the stable orange isomer and an N_4-H bond and a Ph_4N_3CS conjugated system in the blue form.

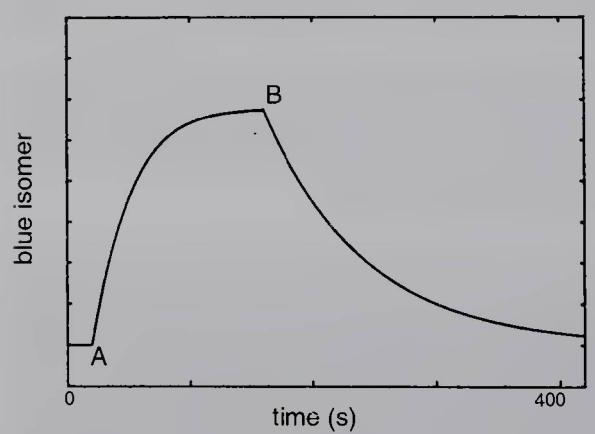


Fig. 3.32-2. Photochemical formation and thermal decay of the blue isomer of mercury dithizonate. *A* = light on; *B* = light off. Note that under irradiation, the system reaches a steady state during which the thermal return rate exactly counterblances the photochemical rate. If is not necessary to start from the steady state for kinetic measurements.

3.32.1 Experimental

a) Mercury(II) Dithizonate

3.2 g (0.01 mol) of mercury(II) acetate are dissolved in 6 M aqueous ammonia and added to 5.1 g (0.02 mol) of dithizone in hot 6 M ammonia. The solution is then poured onto ground ice and the mercury dithizonate precipitate filtered. The product is purified by recrystallisation from chloroform and is dried under vacuum. Red crystals are obtained (m.p.: 225–226 °C dec.) Analysis for $C_{26}H_{22}N_8S_2Hg$, FW = 710.6 (theoretical): C, 43.91; H, 3.10; N, 15.76; S, 9.01; Hg, 28.22 (found): C, 43.8; H, 3.2; N, 15.6; S, 9.5; Hg, 27.2.

b) Kinetic and Spectrophotometric Measurements

Dry xylene is a good solvent for kinetic and spectrophotometric measurements. A 2×10^{-5} M mercury dithizonate solution exhibits an absorbance of about 0.86 at 484 nm ($\varepsilon(484) = 43000\ M^{-1}\ cm^{-1}$). Under irridiation (sunlight, overhead projector or flashlamp), the orange isomer is converted to the blue isomer and the solution turns deep blue ($\lambda_{max} = 606$ nm). After vigorous shaking, the cuvette (1 cm × 1 cm) is placed in the compartment of a spectrophotometer and the evolution of the absorbance at 606 nm (decreasing) or at 484 nm (increasing) is recorded continuously. In the dark, the blue complex reverts spontaneously to the stable orange isomer, following first-order kinetics. Be careful to screen from stray light which could induce partial rephotolysis.

c) Data Processing

All studies of first-order kinetics are based on Eq. (1).

$$y_t - y_\infty = (y_0 - y_\infty) \exp(-k_{obs}\, t) \tag{1}$$

in which y_t, y_0 and y_∞ are the magnitudes of the observed signal (here the absorbance) at time t, 0 and ∞; k_{obs} is the apparent first-order rate constant.

There are several methods for determining an accurate value of k_{obs}. Four main methods are presented here. If an estimation of y_∞ is easily available, the half-time and semi-log methods can be used.

Half-time Method

The half-time equation (Eq. 2) is derived directly from Eq. (1) since at $t = t_{1/2}$, $(y_t - y_\infty)/(y_0 - y_\infty) = 1/2$. For pure first-order kinetics, the successive values of $t_{1/2}$ must be independent of the choice of y_0 (Fig. 3.32-3).

$$k_{obs} = \ln 2 / t_{1/2} \tag{2}$$

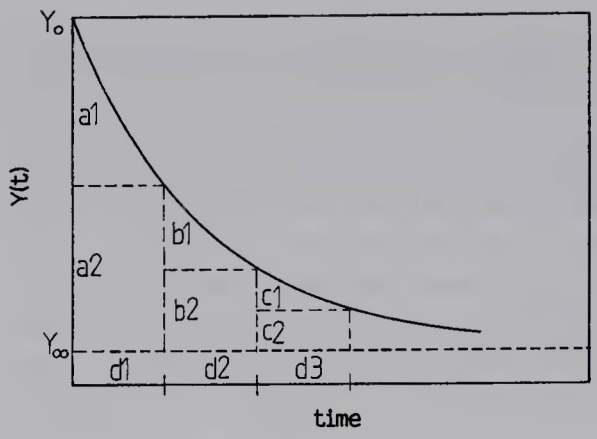


Fig. 3.32-3. First-order decay leading to a good estimation of y_∞. Half-time method ($a_1 = a_2$; $b_1 = b_2$; $c_1 = c_2$). Note the regularity of the successive half-time ($d_1 = d_2 = d_3$).

Semi-log Method

The semi-log equation (Eq. 3) is also easily derived from Eq. (1).

$$\ln|y_t - y_\infty| = -k_{obs}\,t + \ln|y_0 - y_\infty| \tag{3}$$

In the semi-log plot (Fig. 3.32-4), since all the experimental points are (in principle) included in the linear regression analysis, it is more accurate than the simple half-time method.

If an estimation of y_∞ is not possible, one must use a time-lag method whereby the reaction time is divided into regular intervals (Δ), the value of which being chosen so as to obtain around six or more regular intervals over the whole reaction curve. Guggenheim's and the R/R_D methods are time-lag methods.

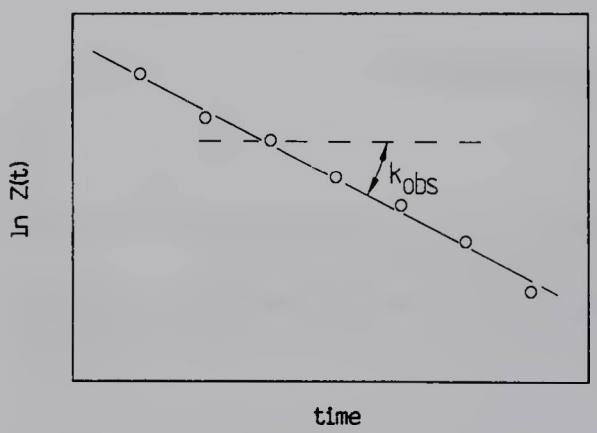


Fig. 3.32-4. Linearization of a first-order kinetic curve. Semi-log plot: $Z(t) = |y_t - y_\infty|$. Guggenheim plot: $Z(t) = |y_{t+\Delta} - y_t|$. In both cases, k_{obs} is calculated from the slope of the straight line.

Guggenheim's Method

This is quite similar to the semi-log plot, although the value of y_∞ is not required. Guggenheim's formula (Eq. 6) derives from the relationship in Eq. (1).

Thus, at any t:

$$y_t = (y_0 - y_\infty) \exp(-k_{obs} t) + y_\infty$$

and at $(t + \Delta)$:

$$y_{t+\Delta} = (y_0 - y_\infty) (\exp(-k_{obs} t)) (\exp(-k_{obs} \Delta)) + y_\infty \quad (4)$$

and

$$y_{t+\Delta} - y_t = (y_0 - y_\infty) (\exp(-k_{obs} t)) (\exp(-k_{obs} \Delta) - 1) \quad (5)$$

Taking the logarithm leads to Gugenheim's formula (6); see Figure 3.32-4.

$$\ln |y_{t+\Delta t} - y_t| = -k_{obs} t + (\exp(k_{obs} \Delta) - 1) \ln |y_0 - y_\infty| \quad (6)$$

R/R_Δ Method (Ratios of Rates)

This is a convenient alternative to Guggenheim's method which can be used directly on the recorded chart. The R/R_Δ relationship in Eq. (10) derives from the rates at t and $(t + \Delta)$.

At t:

$$R_t = (dy/dt)_t = -(y_0 - y_\infty) (\exp(-k_{obs} t)) k_{obs} \quad (7)$$

and at $(t + \Delta)$:

$$R_{t+\Delta} = (dy/dt)_{t+\Delta} = -(y_0 - y_\infty) \exp(-k_{obs} t) \exp(-k_{obs} \Delta) k_{obs} \quad (8)$$

Taking the ratio $R/R_{t+\Delta}$ and the ln reduces to Eq. (9).

$$k_{obs} = \ln [R_t / R_{t+\Delta}] / \Delta \quad (9)$$

With pure first-order decays, the successive ratio must remain constant.

$$k_{obs} = (\ln r_m) / \Delta \quad (10)$$

where r_m is the mean value of the successive ratios $R_t / R_{t+\Delta}$ along the whole kinetic curve.

Using a continuous recorded kinetic curve, it is quite easy to draw the tangents carefully by hand and estimate their respective slopes (dy/dt). As only the successive ratios of rates are needed, convenient arbitrary units can be used. This is shown in Figure 3.32-5.

When used in a comparative fashion, these four methods give sufficient accuracy to demonstrate first-order decay and detect the effects of the purity of the solvent (traces or acid, bases, free dithizone, photolysis products, water, etc.), which acceler-

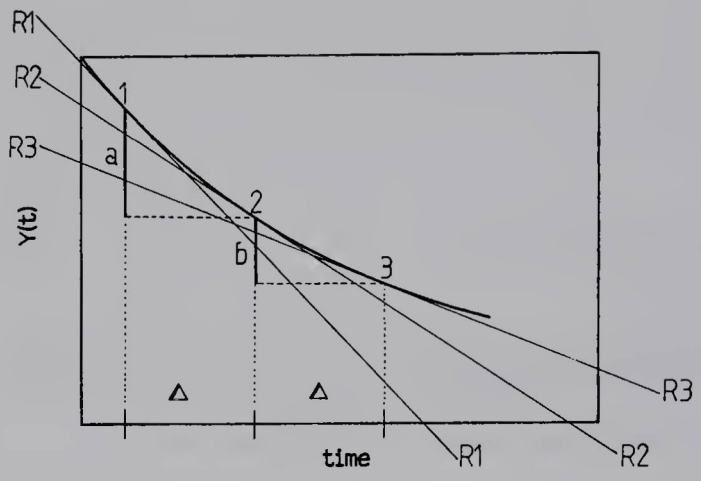


Fig. 3.32-5. First-order decay leading to a poor estimation of y_∞. Δ is the time-lag. *a* and *b* Guggenheim calculations of the successive steps $y_t - y_{t+\Delta}$. R_1, R_2, R_3: successive rates $(dy/dt)_t$, $(dy/dt)_{t+\Delta}$, $(dy/dt)_{t+2\Delta}$ for the R/R_Δ method. For the sake of clarity, only 2Δ intervals and 3 tangents are shown.

ate the thermal return rate constant. A spontaneous monomolecular isomerization and/or a catalyzed pseudo first-order bimolecular process with a large excess of a catalytic species ([cat]) could be deduced from the data obtained. Thus $k_{obs} = k_1 + k_2[\text{cat}]$, the usual range lies between $5 \times 10^{-3} < k_{obs} < 5 \times 10^{-2}\ s^{-1}$.

Further Reading

R. L. Petersen, G. L. Harris, *J. Chem. Educ.* **1985**, *62*, 802.
A. T. Hutton, *J. Chem. Educ.* **1986**, *63*, 888.
B. Borderie, D. Lavabre, G. Levy, J. C. Micheau, *J. Chem. Educ.* **1990**, *67*, 459.
See also: *J. Photochem. Photobiol. A*, **2000**, *134*, 163.

3.33
Molecular Orbital Calculations of Inorganic Compounds

Carole A. Morrison, Neil Robertson, Andrew Turner, Jano van Hemert, and Jos Koetsier

The structure and bonding of simple compounds can be reliably predicted by molecular orbital (MO) theory. The practical application of MO theory (called *ab initio* MO theory) allows us to run computer simulations that will reliably predict the sizes, shapes and properties of molecules and in this way we can interpret chemistry at the most fundamental of levels. In this practical, you will run some *ab initio* MO theory calculations to explore the bonding properties of some inorganic compounds. Before doing this, you will use valence shell electron pair repulsion (VSEPR) theory to make sensible predictions prior to running the calculations. Complete the preliminary VSEPR exercise on the worksheet.

At the heart of MO theory is obtaining an approximate solution to Schrödinger's equation:

$$\hat{H}\Psi = E\Psi$$

where $\hat{H}$ is the Hamiltonian operator (describing the kinetic and potential energies of the nuclei and electrons in the molecule). This we approximate using a specified *level of theory*, which in this practical will be done using *Hartree–Fock* theory. The symbol Ψ denotes the molecular wavefunction, which has the job of describing the sizes and shapes of the molecular orbitals for the molecule. In practical terms, this is done by defining a *basis set*, which is typically a collection of Gaussian functions that describe the atomic radial functions for each element present in the molecule. In this exercise you will use a medium-quality basis set called 6–31G*.

The computational chemistry program you will use is called *Gaussian* and you will submit your calculations and receive your results through a specially designed web portal. Properties that can be obtained from the calculation include the molecular geometry, atomic charges, bond energies and images of the electron density and shapes of orbitals, e.g. HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), etc. In addition to stating the level of theory and basis set, the input file for the calculation must also give an approximate starting geometry for the molecule of interest. For small molecules, this is most easily done using a Z-matrix, which defines the location of all atoms with respect to one another in

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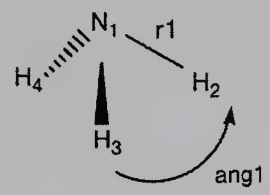


terms of bond lengths, bond angles and dihedral angles. For example, ammonia can be defined by the following:

```
N1                                          ← the first atom
H2   N1   r1                                ← H2 connects to N1 by distance r1
H3   N1   r1   H2   ang1                    ← H3 to N1 by r1 and H2 by angle ang1
H4   N1   r1   H3   ang1   H2   -ang1       ← H4 connects to N1 by r1, H3 by ang1 and
                                              H2 by -ang1 (i.e. anticlockwise)

r1 = 1.0                    ← starting values for parameters
ang1 = 109.0                defined in the Z-matrix (in ångstroms and degrees)
```

Most of the input files needed to run the *ab initio* MO calculations will be supplied for you through the web portal, but some you will be asked to modify for yourself.

3.33.1
Experimental

Note for Demonstrators

The web portal for the experiment and instructions for its use can be found at: http://www.chem.ed.ac.uk/undergrad/portal/comp_portal.html. The portal has been designed to submit jobs from the web to a separate workstation that runs the Gaussian calculations. The students should not need to download any of the output files to the local PCs as the portal has the Jmol molecular viewer directly embedded within it.

3.33.1.1
Exercise A: The Reaction Between NH_3 and BF_3

This exercise involves running *ab initio* MO theory calculations to follow the structural changes that take place to NH_3 and BF_3 when they combine to form NH_3BF_3. You will also be able to draw conclusions on the nature of the new chemical bond formed.

Part I. Geometry Optimisation of NH_3

Log into the web portal using the account name and password you have been given. Click on the first tab, labelled *Ammonia*, and display the input file, which will appear as shown below:

```
%chk=nh3.chk                          ← checkpoint file
# hf/6 31G* opt                       ← command line

Calculation on NH3                    ← comment line

0    1                                ← charge, multiplicity
N1
H2   N1   r1
H3   N1   r1   H2   ang1
H4   N1   r1   H3   ang1   H2   -ang1
r1=1.0
ang1=109.0
```

The checkpoint file <nh3.chk> stores results from the last calculation for the computer's benefit. The command line states the level of theory (hf = Hartree–Fock) and basis set (6–31G*) to be used. *Opt* denotes geometry optimisation. *Charge = 0* means the molecule is neutral; *multiplicity = 1* sets the electronic structure to be a singlet (there is an even number of electrons in ammonia and they are all arranged in pairs). Follow the instructions on the web portal on how to run this calculation and how to visualise the results.

On the worksheet (see p. 266/267), complete the relevant entries in the tables (given in question 1) for the bond lengths, angles and atomic charges for NH_3. Sketch and write a short description of the HOMO in the space provided in question 5. Try using several different values for the orbital cutoff and comment on the result.

Part II. Geometry Optimisation of BF_3

Click on the second tab on the web portal, labelled *Boron Trifluoride*. The original input file used for the NH_3 optimisation will be listed. You must edit this file to submit a new calculation to optimise the structure of BF_3. Change the 'N' labels to 'B' and the 'H' labels to 'F'. (Note there are four N and six H entries in the *Z*-matrix. Make sure you change them all!) Change the name of the checkpoint file to <bf3.chk>. You will also calculate the LUMO for BF_3. To do this, change the name of the cube file (from nh3.cube to bf3.cube) and the orbital identity from HOMO to LUMO. Follow the instructions on the web portal on how to run this calculation and how to visualise the results.

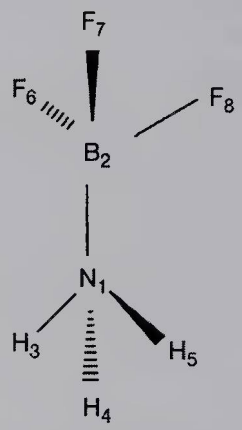
Note is BF_3 flat or pyramidal? Fill in the columns relating to BF_3 on the tables in question 1 on the worksheet. Sketch and write a short description of the LUMO in the space provided in question 5.

Part III. Geometry Optimisation of NH_3BF_3

Click on the third tab on the web portal, labelled *NH_3BF_3 optimisation*. The input file nh3bf3.com will be listed. Note that this file is incomplete – you have to provide sensible guess values for parameters r1, r2, r3, ang1 and ang2 by analysing the Z-matrix and the structure given below.

```
N1
B2  N1  r1
H3  N1  r2  B2  ang1
H4  N1  r2  B2  ang1  H3   120.0
H5  N1  r2  B2  ang1  H3  -120.0
F6  B2  r3  N1  ang2  H3    60.0
F7  B2  r3  N1  ang2  F6   120.0
F8  B2  r3  N1  ang2  F6  -120.0

r1=
r2=
r3=
ang1=
ang2=
```



Follow the instructions on the web portal on how to run this calculation and how to visualise the results. The calculation will take a couple of minutes to run. Complete the columns on NH_3BF_3 in the tables in question 1 on the worksheet and answer question 2. Now complete questions 3, 4 and 5 on the worksheet.

3.33.1.2

Exercise B: Hypervalent Compounds

Compounds of main group elements in the second row of the periodic table (such as C, N and O) have eight valence electrons. In contrast, main group elements from the third row (such as Cl, Si, P and S) may contain more than eight electrons in their valence shells. These are called hypervalent compounds and examples include ClF_3, SF_4, SF_6 and PF_5.

This exercise will focus on the pair of compounds SF_4 and SF_6 and discover that increasing the bond order of S from 4 to 6 comes at a price: the resulting S–F bonds are less strong. In order to calculate the bond strengths of the two different compounds you will need to know:

- the atomic energies of S and F (i.e. the energy of a single atom at infinity);
- the molecular energies for SF_4 and SF_6 (i.e. when the atoms are brought together and the bonds are formed).

We will give you the atomic energies and molecular energies for SF_4; you have to determine the molecular energy for SF_6 yourself.

Click on the final web portal tab, labelled *Sulphur Hexafluoride*. This file will perform a geometry optimisation assuming that the geometry of SF_6 is a perfect octahedron. Follow the instructions on the web portal on how to run this calculation. It will take a couple of minutes to run this calculation. The level of theory has been increased from HF to B3LYP – this means that the way in which electron interactions are modelled has been improved. *Note:* The energy of the optimised structure from the bottom-left corner of the Jmol window.

Enter the number given in the relevant place on your worksheet. Complete the calculation on the worksheet to determine the strength of the S–F bond in SF_4 and SF_6 and answer question 2.

Worksheet

Molecular Orbital Calculations of Inorganic Compounds

Name: _____ Bench: _____ Date: _____

Preliminary Exercise: Use VSEPR theory to predict the shapes of BF_3, NH_3, SF_4 and SF_6. Draw the structures below:

Exercise A: The Reaction Between NH_3 and BF_3

1. Complete the following tables with data obtained from the *ab initio* MO geometry optimisation calculations.

Parameter	NH_3	BF_3	NH_3BF_3
N–H bond length/Å			
H–N–H angle/degrees			
B–F bond length/Å			
F–B–F angle/degrees			

Atomic charge/ electron units	NH_3	BF_3	NH_3BF_3
N			
H			
B			
F			

2. Account for the changes in geometry in NH_3 and BF_3 observed upon formation of NH_3BF_3.

3. For the atomic charges you calculated for NH_3BF_3, sum the charges for the NH_3 and the BF_3 components. Hence deduce the amount of charge transferred from NH_3 to BF_3 by the formation of the chemical bond.

4. The bond formed between NH_3 and BF_3 is an example of a dative bond. Define a dative bond and how this differs from a standard covalent bond.

5. Sketch images of the HOMO on NH_3, the LUMO on BF_3 and the electron density in NH_3BF_3. Write a sentence to describe each of the two orbitals and the electron density image.

Exercise B: Hypervalent compounds

1. Below is a worked example to obtain the calculated enthalpy of the S–F bond in SF_4. Note that the hartree is the atomic unit of energy (1 hartree = 2625.5 kJ mol^{-1}). Read and understand the worked example then use the same method to calculate the S–F bond enthalpy in SF_6 using your computational results.

S–F bond strength in SF_4 – worked example

Calculated molecular energy of SF_4 = –797.45952 hartree
Atomic energy of S = –398.04257 hartree
Atomic energy of F = –99.71554 hartree
Binding energy = (atomic energy S + 4 × atomic energy F) – molecular energy SF_4
= –796.90473 – (–797.45952)
= 0.5548
Dividing by 4 (i.e. per bond) gives 0.139 hartree
Multiplying by 2625.5 (convert to kJ mol^{-1}) gives 364.1 kJ mol^{-1}

S-F bond strength in SF_6 – complete the calculation

Molecular energy of SF_6 = _____ hartree (enter from your calculation)
Binding energy = (atomic energy S + 6 × atomic energy F) – molecular energy SF_6
= _____
= _____
Dividing by 6 (i.e. per bond) gives _____ hartree
Multiplying by 2625.5 (convert to kJ mol^{-1}) gives _____ kJ mol^{-1}

2. Compare the calculated values of S–F bond enthalpy for SF_4 and SF_6 and comment on the values.
(*Note:* For comparison the values derived from experimental data are quoted in *Shriver and Atkins' Inorganic Chemistry*, 4th ed., p. 42 as 343 and 327 kJ mol^{-1} for SF_4 and SF_6, respectively).

4
Advanced Experiments

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4.1
2,2′:6′,2″-Terpyridine Complexes and Metal Directed Reactivity

Edwin C. Constable

Ligands such as 2,2′-bipyridine and 2,2′:6′,2″-terpyridine have been of great importance to coordination chemists over the past one hundred years. The photochemical and photophysical properties of their transition-metal complexes have been the subject of intense interest. Recently, derivatives of these ligands have been developed in which the photochemical and redox properties of the metal centre may be tuned by the nature of the peripheral substituents on the ligands. In modern coordination chemistry, it is usually necessary to prepare the organic ligands that you require. In this experiment, you will prepare 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine, and then make an iron complex and investigate its reaction with methyl iodide.

Special Safety Precautions

1. 2-Acetylpyridine and 4-pyridinecarboxaldehyde are toxic and irritants. They also smell very unpleasant. *Always* use these reagents in a fume cupboard, and perform part a) *entirely* in the fume cupboard. The residues from this preparation should be quenched in hydrochloric acid.
2. Tetrafluoroborate salts can hydrolyse in contact with water to give hydrofluoric acid. Do not allow either solid ammonium tetrafluoroborate or its solutions to come in contact with your skin. Do not keep solutions of ammonium tetrafluoroborate made up for long periods of time.
3. Methyl iodide is toxic and may be carcinogenic. Always use it in a fume cupboard. Remember that it is very volatile.
4. The health hazards of the 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine and its complexes are unknown. Like all chemicals, they should be treated with extreme caution.

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4.1.1 Experimental

a) 1,5-Bis(2-pyridyl)-3-(4-pyridyl)-1,5-pentanedione

2-Acetylpyridine (8.4 cm^3) and 4-pyridinecarboxaldehyde (3.0 cm^3) are dissolved in ethanol (35 cm^3) in a 100 cm^3 round-bottomed flask and a solution of sodium hydroxide (2.0 g) in water (25 ml) added. The mixture is stirred for one hour at room temperature, and then 30 ml of water added. This should give an off-white precipitate of 1,5-bis(2-pyridyl)-3-(4-pyridyl)-1,5-pentanedione. Collect this by filtration, wash well with water and a little *cold* ethanol, and dry in a desiccator.

Calculate the yield of your product and measure its IR spectrum.

b) 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine (pytpy)

Heat a solution of 1,5-bis(2-pyridyl)-3-(4-pyridyl)-1,5-pentanedione (0.40 g) and ammonium acetate (5.0 g) in 50 cm^3 of ethanol to reflux for two hours. Allow the solution to cool and add 50 cm^3 of water to precipitate the product. Recrystallise the product from a small amount of ethanol.

Calculate the yield of your product and measure its IR spectrum as a Nujol mull and, if possible, its ^1H NMR spectrum in $CDCl_3$ or CCl_4.

c) $[Fe(pytpy)_2][BF_4]_2$

Add 0.366 g of pytpy to 50 cm^3 of methanol in a 100 cm^3 twin-necked round-bottomed flask, attach a water condenser and a small dropping funnel containing a solution of $[Fe(H_2O)_6][BF_4]_2$ (0.1 g) in 10 cm^3 of methanol to the flask, and then heat the pytpy solution to boiling. Add the solution of the iron salt dropwise over 10 minutes, and then continue heating for another 10 minutes. Cool the dark purple solution and add to it a solution of $[NH_4][BF_4]$ (0.5 g) in 5 cm^3 of methanol. Collect the purple solid and dry it.

Calculate the yield of your product and measure its IR spectrum as a Nujol mull and, if possible, its ^1H NMR spectrum in CD_3COCD_3. Record the electronic spectrum (250–700 nm) of your product in acetonitrile solution. You should accurately weigh your sample so that you can report extinction coefficients. As a guide to the concentration required, the bands have ε values between 10000 and 40000 $dm^3\ mol^{-1}\ cm^{-1}$.

d) $[Fe(Mepytpy)_2]_2[BF_4]_2$

Fit a 100 cm^3 round-bottomed flask with a double surface reflux condenser. Dissolve $[Fe(pytpy)_2][BF_4]_2$ (0.1 g) in 50 cm^3 of acetonitrile and add the solution to the flask. Add 2 cm^3 of methyl iodide and heat to reflux for one hour. Add a solution of $[NH_4][BF_4]$ (0.5 g) in 5 cm^3 of methanol and concentrate the dark blue solution on a rotary evaporator to about 10 ml volume and allow to cool. Collect and dry the blue-black solid.

Calculate the yield of your product and measure its IR spectrum as a Nujol mull and, if possible, its ^{1}H NMR spectrum in CD_3COCD_3. Record the electronic spectrum (250–700 nm) of your product in acetonitrile solution. You should accurately weigh your sample so that you can report extinction coefficients. As a guide to the concentration required, the bands have ε values between 20 000 and 65 000 $dm^3\ mol^{-1}\ cm^{-1}$.

You will find additional details about these reactions in the references.

Further Reading

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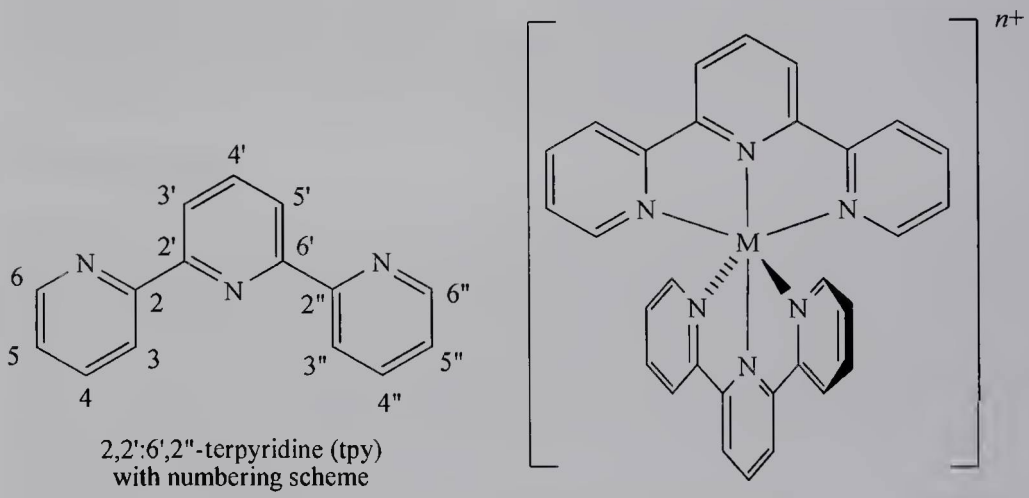
4.2
4′-(4-Pyridyl)-2,2′:6′,2″-terpyridine: Coordination to Iron(II) and Protonation Studies

Catherine E. Housecroft, Edwin C. Constable, and Emma L. Dunphy

The 2,2′:6′,2″-terpyridine (tpy) ligand has a well-established coordination chemistry, with functionalized $[M(tpy)_2]^{n+}$ units being attractive supramolecular building blocks [1, 2]. The free ligand adopts a *trans,trans*-configuration and must rearrange to a *cis,cis*-configuration upon binding in a tridentate mode to a metal ion (Scheme 4.2-1).



Scheme 4.2-1 Change in conformation of tpy upon coordination to M^{n+}.

The bis(tpy) motif has an advantage over the ubiquitous tris(bpy) (bpy = 2,2′-bipyridine) unit in that the former is achiral (unless asymmetrically substituted or functionalized with a chiral auxiliary), whereas the latter is complicated by the presence of Δ- and Λ-enantiomers (Scheme 4.2-2). Stability constants for $[Fe(tpy)_2]^{2+}$ (kinetically labile metal ion) and $[Ru(tpy)_2]^{2+}$ (kinetically inert metal centre) complexes are high, making manipulation of these complexes and their derivatives straightforward in an undergraduate laboratory.

Substituents in the 4′-position of tpy are readily incorporated, allowing the introduction of functionalities with a wide range of applications. For example, carboxylate groups provide an anchoring point for complexes on metal oxide surfaces, and this is of current interest in the development of dye-sensitized solar cells (DSCs) [3–5].

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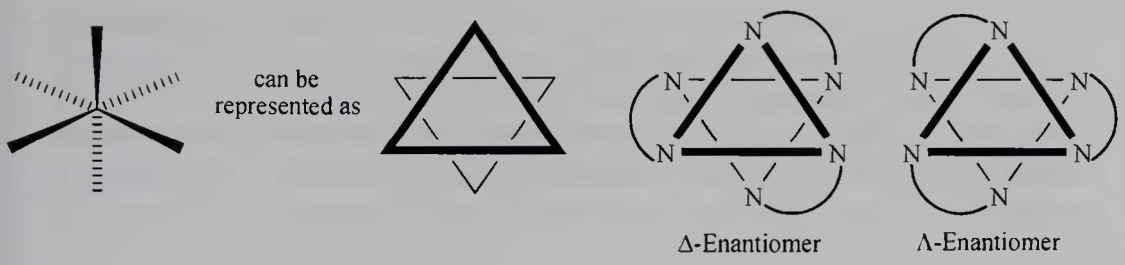
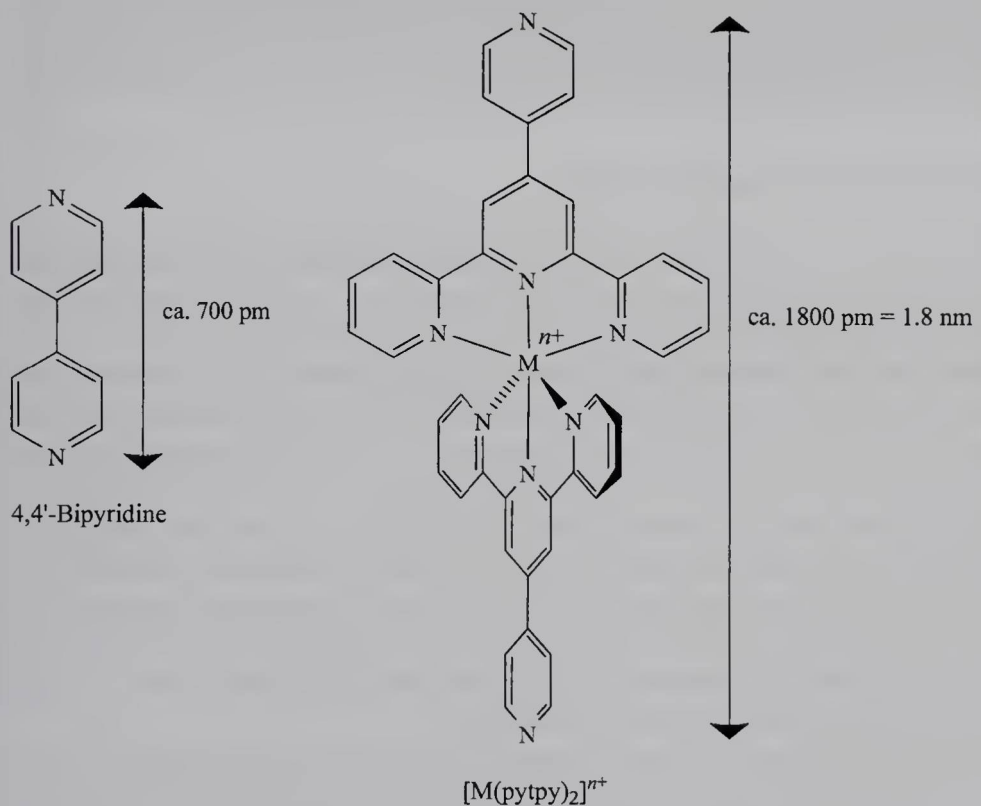


Scheme 4.2-2 The formation of enantiomers in a tris(chelate) complex.

The introduction of a donor group such as pyridine into the 4′-site of tpy to give 4′-(4-pyridyl-2,2′:6′,2″-terpyridine (pytpy) converts the $[M(tpy)_2]^{n+}$ unit into an 'expanded ligand' [6], and takes the ligand into the nanoscale domain (Scheme 4.2-3).

4,4′-Bipyridine has long been utilized as a building block in the construction of coordination polymers, and similarly $[M(pytpy)_2]^{2+}$ (M = Fe, Ru) is an ideal construct for one-dimensional coordination polymers [7]. Salts of both $[Fe(pytpy)_2]^{2+}$ and $[Ru(pytpy)_2]^{2+}$ are highly coloured (purple and orange–red, respectively) and the observed colour can be tuned by protonation of the pendant pyridine ring [8]. The colour arises from a metal-to-ligand charge-transfer band (MLCT) [9] that appears at 569 and 488 nm for MeCN solutions of hexafluoridophosphate salts of $[Fe(pytpy)_2]^{2+}$ and $[Ru(pytpy)_2]^{2+}$, respectively.



Scheme 4.2-3 The concept of the expanded ligand: a comparison of 4,4′-bipyridine with $[M(pytpy)_2]^{n+}$.

In the practical assignment described below, students prepare the pytpy ligand and the iron(II) complex $[Fe(pytpy)_2][PF_6]_2$. Investigation of the ^1H NMR spectra of the ligand and complex provides an exercise in NMR spectral assignment using 2D techniques. UV–VIS spectroscopy is used to investigate the effects of protonation, in addition to illustrating the types of absorption band that arise in complexes of this type.

4.2.1 Experimental

All reactions can be carried out open to the atmosphere, but must be in a fume cupboard.

Special Safety Precautions

Wear disposable gloves for handling chemicals. Solid KOH is caustic and skin contact must be avoided. 2-Acetylpyridine, pyridine-4-carbaldehyde and 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine may cause skin irritation and should not be inhaled. Ammonium hexafluoridophosphate is hygroscopic and may cause skin or eye burns; it must not be inhaled. Trifluoroacetic acid is volatile and must be opened in a fume cupboard; both liquid and vapour can cause severe burns to all parts of the body, and must not be inhaled.

a) 4′-(4-Pyridyl)-2,2′:6′,2″-terpyridine (pytpy)

4′-(4-Pyridyl)-2,2′:6′,2″-terpyridine is prepared by the one-pot method of Wang and Hanan [10]. Add 2-acetylpyridine (4.84 g, 40.0 mmol) to a solution of pyridine-4-carbaldehyde (2.18 g, 20.4 mmol) in ethanol (100 cm^3) contained in a 250 cm^3 round-bottomed flask equipped with a stir-bar. Add solid KOH pellets (2.7 g, 50 mmol) and aqueous NH_3 (60 cm^3, 25%, 0.85 mol) to the ethanol solution. Using a magnetic stirrer, stir the reaction mixture at room temperature for 4 hours. An off-white solid forms during this period. Filter the mixture through a frit using vacuum/water pump and collect the solid product. Wash it with H_2O (3 × 15 cm^3) and EtOH (3 × 15 cm^3). The pytpy ligand is isolated as a white crystalline solid after recrystallization from $CHCl_3$–MeOH: add the solid pytpy to ~100 cm^3 of methanol contained in a 250 cm^3 conical flask equipped with a stir-bar. Heat to boiling point while continuously stirring. Add $CHCl_3$ dropwise until the solid has just dissolved. Allow the mixture to cool to yield crystalline solid; yield ~40%.

Record the melting point, the IR spectrum and the $CDCl_3$ solution ^1H and $^{13}C\{^1H\}$ NMR spectra of your product and compare with the literature data [11]. Assignment of the ^1H NMR spectrum and interpretation of mass spectrometric and UV–VIS spectroscopic data are discussed below.

b) $[Fe(pytpy)_2][PF_6]_2$

Dissolve 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine (0.20 g, 0.64 mmol) and $FeCl_2 \cdot 4H_2O$ (0.064 g, 0.32 mmol) in methanol (30 cm^3) in a 50 cm^3 conical flask equipped with a stir-bar. Using a magnetic stirrer, stir the reaction mixture at room temperature for 30 minutes. Add an excess (1.2 equiv.) of aqueous NH_4PF_6. This results in the precipitation of purple $[Fe(pytpy)_2][PF_6]_2$. Filter the mixture through Celite contained in a frit and wash the purple solid that collects on the Celite with H_2O, EtOH and Et_2O. Remove the collecting flask, dispose of the washings and clean the flask. Reassemble the filtration apparatus. Redissolve the solid in a minimum amount of acetonitrile to remove it from the Celite and wash it through the Celite into the collecting flask. Transfer the filtrate to a small round-bottomed flask and remove the solvent under reduced pressure. $[Fe(pytpy)_2][PF_6]_2$ is isolated as a purple microcrystalline solid; typical yield ~90%.

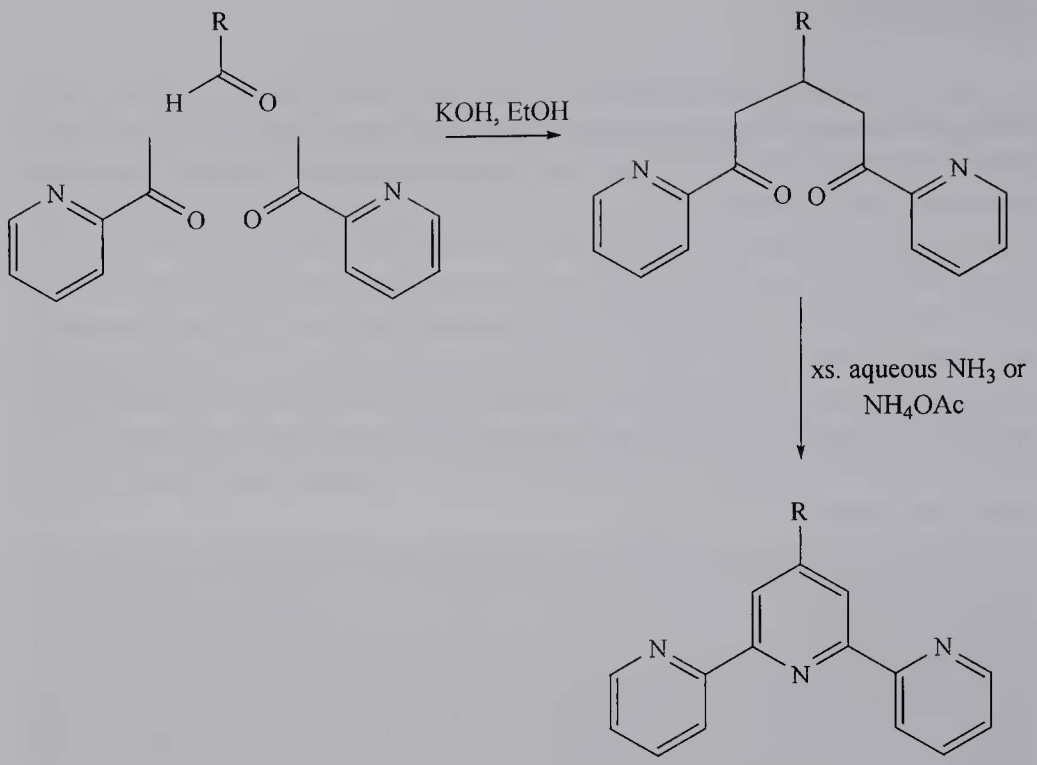
Record the IR spectrum (solid sample) and look for the characteristic absorption of the $[PF_6]^-$ ion at 840 cm^{-1}. Compare the IR spectrum of the free pytpy ligand with that of the complex.

Record the CD_3CN solution ^1H NMR spectrum of your product and compare with the data in the table on page 279 and Figure 4.2-2. Measure the coupling constants (in hertz) for each signal. With only this information, how far can you go in assigning the spectrum? Full assignment of the ^1H NMR spectrum and interpretation of mass spectrometric and UV–VIS spectroscopic data are discussed below.

4.2.2 Discussion

4.2.2.1 Synthetic Route to 4′-(4-Pyridyl)-2,2′:6′,2″-terpyridine

The synthesis of 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine uses the one-pot method described by Wang and Hanan [10] and is based on the general method of Kröhnke [12] for the synthesis of tpy (R = H in Scheme 4.2-4) or 4′-substituted tpy ligands (R = various in Scheme 4.2-4).



Scheme 4.2-4 Kröhnke methodology for the formation of 4′-substituted tpy ligands.

4.2.2.2
Interpretation of Data

Mass Spectrometric Data

The electron ionisation (EI) mass spectrum of pytpy shows peaks at m/z 310 and 232. Assign these two peaks.

The electrospray ionisation (ESI) mass spectrum of $[Fe(pytpy)_2][PF_6]_2$ (Fig. 4.2-1) shows peak envelopes at m/z 821 and 338. In the higher mass envelope, the peaks are one mass unit apart, but in the lower mass envelope, the peaks are separated by half mass units. Rationalize these data.

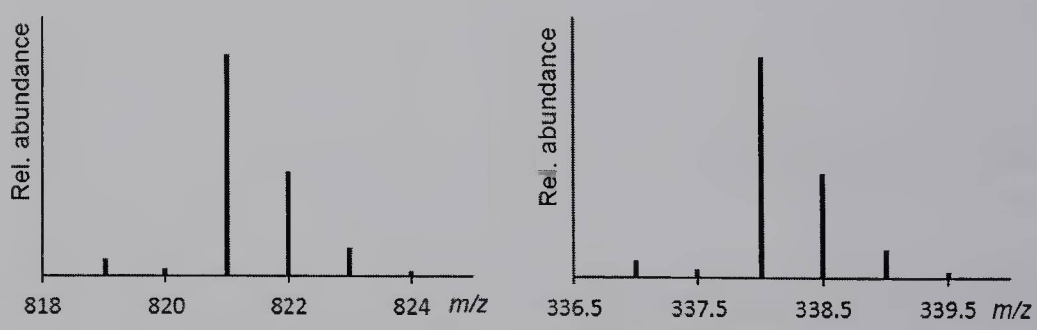
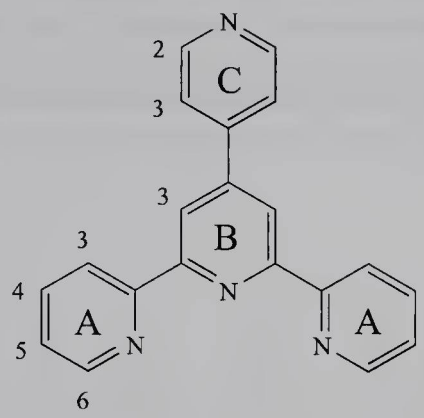


Fig. 4.2-1 Peak envelopes in the ESI mass spectrum of $[Fe(pytpy)_2][PF_6]_2$.

^{1}H NMR Spectroscopic Data

Using the ring labelling scheme shown below (both for the free ligand and metal complex), the ^{1}H NMR spectra of pytpy (in $CDCl_3$) [11] and $[Fe(pytpy)_2][PF_6]_2$ (in CD_3CN) [13] are assigned as follows (δ in ppm) (we return to how to assign the spectrum later):



	Species						
Proton	C2	B3	A6	A3	A4	C3	A5
pytpy	8.77	8.76	8.73	8.68	7.89	7.79	7.37
$[Fe(pytpy)_2]^{2+}$	9.02	9.23	7.18	8.63	7.93	8.23	7.10

The signal for proton H^{B3} appears as a singlet and typical ^{1}H–^{1}H spin–spin coupling constants within ring A are as follows:

$J(H^{A4}H^{A6}) \sim 1.8$ Hz
$J(H^{A5}H^{A6}) \sim 4.8$ Hz
$J(H^{A3}H^{A6}) \sim 0.8$ Hz
$J(H^{A4}H^{A5}) \sim 7.5$ Hz
$J(H^{A3}H^{A4}) \sim 7.5$ Hz
$J(H^{A3}H^{A5}) \sim 0.8$ Hz

Given the values above, predict the appearance of the signals for protons H^{A3}, H^{A4}, H^{A5} and H^{A6} and compare your predictions with the signals in your spectrum. The small couplings [e.g. $J(H^{A3}H^{A5})$] are not always resolved.

A significant change in chemical shift occurs for the signal assigned to proton H^{A6}. As the ligand coordinates, proton H^{A6} of one ligand is brought within the shielding region above the terminal pyridine ring of the second tpy ligand (see Scheme 4.2-1). This is a characteristic phenomenon when tpy ligands coordinate to a metal centre and can be used to confirm that complexation has occurred.

Figure 4.2-2 shows the ^{1}H NMR spectrum of a CD_3CN solution of $[Fe(pytpy)_2][PF_6]_2$. The ^{1}H–^{1}H spin–spin coupling patterns aid the assignment of the

spectrum. Proton H^{B3} is easily assigned because it appears as a singlet. The two doublets at δ 8.23 and 9.02 ppm have the same coupling constant (J = 6.0 Hz) and so arise from a coupled pair of protons. These are assigned as H^{C2} and H^{C3} and this is confirmed by looking at the NOESY spectrum (see below). The 2D COSY (**Correlation Spectroscopy**) spectrum is a routine means of assigning groups of coupled protons. In a COSY spectrum, you must look for pairs of cross peaks that lie across the diagonal (Fig. 4.2-3). Only protons that are coupled to one another give cross peaks. The spectrum is conventionally edited so that only ^2J and ^3J couplings are observed. Figure 4.2-3 shows the COSY spectrum for $[Fe(pytpy)_2][PF_6]_2$ and there are three pairs of cross peaks visible. One pair arises from H^{C2}–H^{C3} coupling and the origin of the cross peaks is highlighted in the figure. The other well-resolved pairs of cross

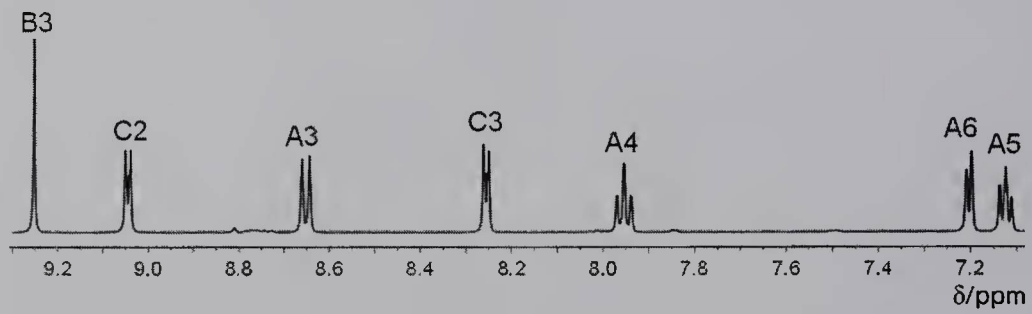


Fig. 4.2-2 500 MHz NMR spectrum of $[Fe(pytpy)_2][PF_6]_2$ (in CD_3CN) at 298 K.

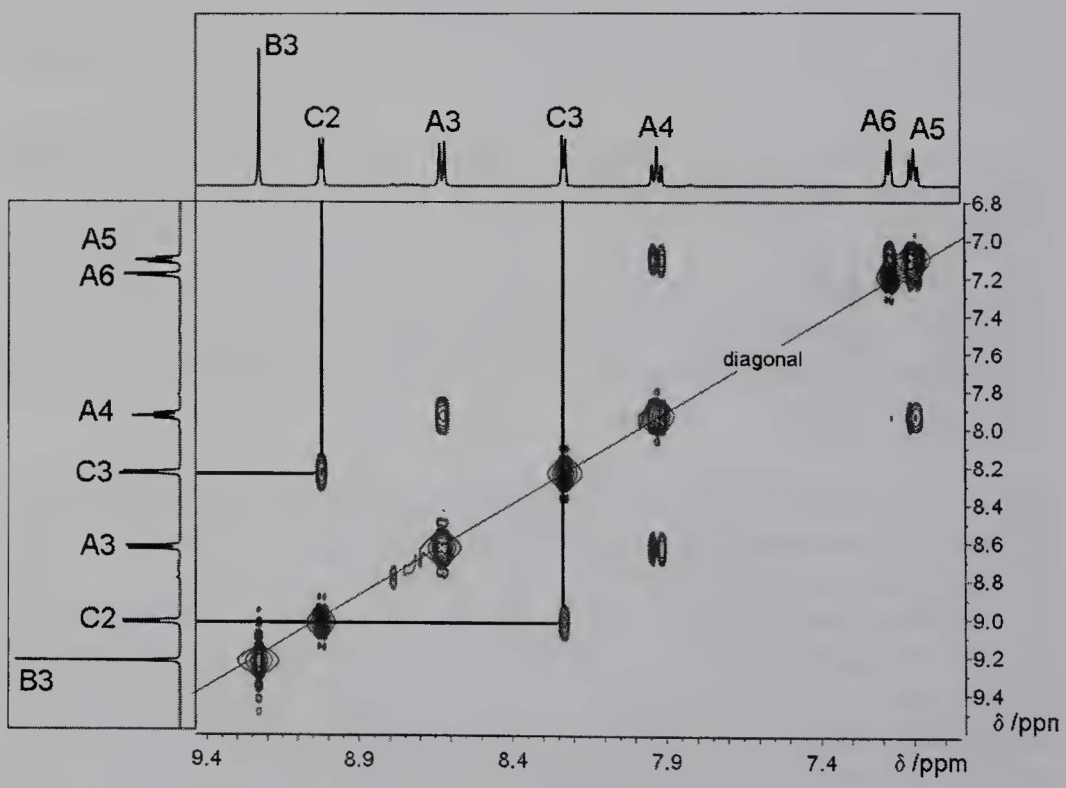


Fig. 4.2-3 500 MHz COSY NMR spectrum of $[Fe(pytpy)_2][PF_6]_2$ (in CD_3CN) at 298 K. The cross peaks that confirm spin-spin coupling between pyridyl protons H^{C2} and H^{C3} are highlighted.

peaks arise from H^{A3}–H^{A4} and H^{A4}–H^{A5} coupling. Cross peaks arising from coupling between H^{A5} and H^{A6} coincide with the diagonal and are difficult to resolve, but careful inspection of the spectrum in Figure 4.2-3 allows you to see the H^{A5}–H^{A6} cross peak.

How do we know which of the signals at δ 8.23 and 9.02 ppm belongs to H^{C2} and which arises from H^{C3}? The answer lies in the 2D NOESY (Nuclear Overhauser Effect Spectroscopy) spectrum, which records through-space spin–spin interactions, usually at distances 5 Å. Figure 4.2-4 shows the NOESY spectrum for $[Fe(pytpy)_2][PF_6]_2$. Cross peaks arise from interactions between protons H^{B3} and H^{C3} (but not H^{C2}) and this allows the pyridyl protons to be distinguished. Other NOESY cross peaks that are visible in Figure 4.2-4 are H^{C2}–H^{C3} and H^{A3}–H^{B3}.

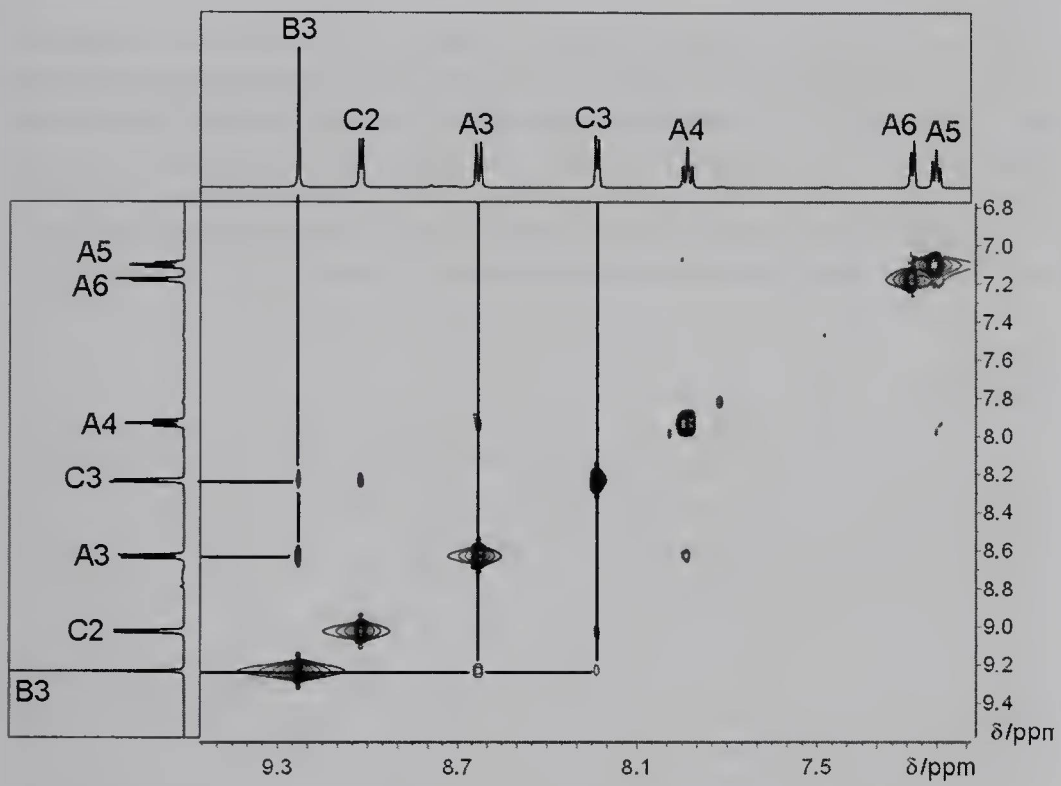


Fig. 4.2-4 500 MHz NOESY NMR spectrum of $[Fe(pytpy)_2][PF_6]_2$ (in CD_3CN) at 298 K.

UV–VIS Spectroscopic Data

The electronic absorption spectrum of an acetonitrile solution of $[Fe(pytpy)_2][PF_6]_2$ (1.87×10^{-5} mol dm^{-3}) shows the following bands:

λ_{max}/nm	569	324	284	276	245
ε/dm^3 mol^1 cm^1	25 000	45 100	81 700	74 100	48 200

The absorption at 569 nm arises from an MLCT transition, whereas the four lower wavelength bands are ligand-based, $\pi^* \leftarrow \pi$ transitions.

How does an MLCT band arise?
How do the $\pi^* \leftarrow \pi$ transitions arise?

This study can be extended (see below) by looking at the effect of adding CF_3CO_2H to an acetonitrile solution of $[Fe(pytpy)_2][PF_6]_2$. A change in visible colour is observed (purple to blue), and this can be correlated with a shift in the wavelength of the MLCT band in the UV–VIS spectrum.

Record the UV–VIS spectrum of $[Fe(pytpy)_2]^{2+}$ by making an acetonitrile solution of $[Fe(pytpy)_2][PF_6]_2$ with a concentration in the order of 10^{-5} mol dm^{-3}. Check that the spectrum corresponds to the data in the table above. Transfer the solution to a sample vial.

Take up a small amount of CF_3CO_2H into a glass Pasteur pipette and then transfer it back to the bottle. Pass the Pasteur pipette mouth back and forth over the vial containing $[Fe(pytpy)_2][PF_6]_2$ while swirling the mixture so that CF_3CO_2H vapour enters the solution. Observe the colour change from and re-record the UV–VIS spectrum. Does the MLCT band move to higher or lower energy upon protonation of the pendant pyridine nitrogen donor atoms? Confirm that the shift in wavelength corresponds to the change in the observed colour of the solution.

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4.3
Heteronuclear *d*–*f* Complexes Containing Binucleating Ligands

Francisco J. Arnáiz, Jean-Pierre Costes, and Javier García-Tojal

The synthesis of heteronuclear complexes containing both 3*d* and 4*f* ions is an emerging field due to the wide range of possible luminescent, magnetic and electronic properties of these complexes [1]. In this sense, discrete heterodinuclear compounds have attracted special attention because they represent the simplest models to understand how the mutual influences of two different metal centres modulate the physical and chemical properties of such compounds. In particular, the use of methoxy derivatives of salen [H_2salen = *N*,*N*′-bis(salicylidene)ethylenediamine] or closely related compartmental Schiff base ligands represents a useful preparative strategy due to their specific stereochemical preferences (Fig. 4.3-1). These ligands contain an inner site with four, two *N*- and two *O*-donor, chelating centres suitable for the linkage to *d*-block ions. The outer coordination site with its *O*-donor atoms is larger than the inner one and can incorporate larger ions, such as lanthanide ions. On the other hand, the preparation of such ligands through condensation of an aldehyde and a diamine can be achieved in a simple manner. Furthermore, the starting materials are often inexpensive.

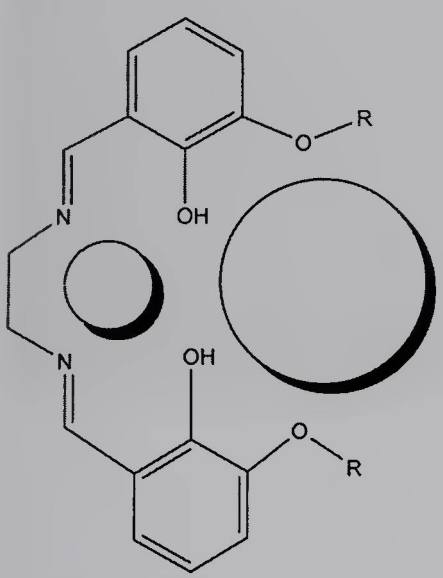

Fig. 4.3-1 Methoxy derivative of salen with the inner and outer coordination sites.

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The following experiments illustrate the preparation of the binucleating compartmental H_2L ligand {H_2L = 1,3-bis[(3-methoxysalicylidene)amino]-2,2-dimethylpropane}, along with two complexes containing 3*d* (M_d^{2+} = Cu^{2+}, VO^{2+}) and 4*f* (M_f^{3+} = Ce^{3+}, Gd^{3+}) ions (Fig. 4.3-2). They illustrate two different ways to achieve the synthesis of heterobinuclear compounds. The structures and properties of these complexes or their analogues have been described elsewhere [2]

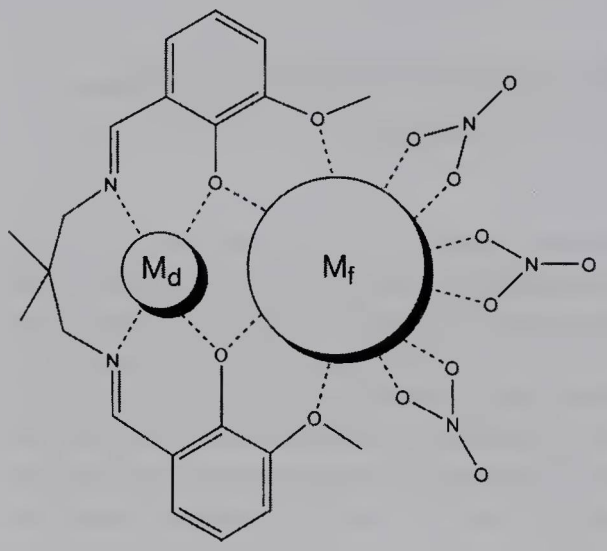

Fig. 4.3-2 $[M_dM_f(L)(NO_3)_3]$ compounds. It can be observed that nitrato groups coordinate to lanthanides as bidentate ligands.

Special Safety Precautions

Wear rubber gloves and eye protection during the experiment. Handling must be carried out in fume cupboard. Avoid inhalation of vapours and contact with the skin. Caution must be taken with all the starting materials: *o*-vanillin (= 2-hydroxy-methoxybenzaldehyde) is an irritant, 1,3-diamino-2,2-dimethylpropane is corrosive, lanthanide nitrates are irritants and oxidizing agents, copper(II) nitrate is an oxidizing agent and corrosive and oxovanadium(IV) sulfate is harmful. Acetone is highly flammable and an irritant, diethyl ether is extremely flammable and harmful and methanol is highly flammable and toxic. Be careful with the presence of heat sources when handling these solvents. As far as we are aware, biological activities of the synthesized compounds are not known, so they must be considered as highly toxic products.

4.3.1 Experimental

a) [CuCe(L)$(NO_3)_3$] Complex

Preparation of the H_2L Ligand

A solution of 1,3-diamino-2,2′ (PRIMA)-dimethylpropane (3.3 mmol, 0.337 g in 5 cm^3 methanol) is added dropwise to a solution of *o*-vanillin (6.6 mmol, 1.004 g) in 10 cm^3 of methanol placed in an Erlenmeyer flask. The addition must be very slow, requiring *ca.* 10 minutes while maintaining vigorous stirring, otherwise an oily product is usually obtained. Once the addition is completed, stirring must be maintained for 30 minutes. The yellow precipitate is filtered off in vacuum, washed with diethyl ether (30 cm^3) and dried in air for 30 minutes at room temperature. Calculate the yield for H_2L with MW = 370.44 g. Obtain the IR spectrum (KBr disc) and compare it with the following selected bands (cm^1): 2960, 2906, 2835, 1630, 1525, 1464, 1350, 1252, 1171, 1078, 1050, 972, 914, 874, 840, 779, 752, 733, 719. Record the ^1H NMR spectrum in DMSO-d_6 and compare it with the following (δ, ppm): 13.8 (s, 2H), 8.53 (s, 2H), 7.04 (d, J = 8 Hz, 2H), 7.03 (d, J = 8 Hz, 2H), 6.81 (t, J = 8 Hz, 2H), 3.78 (s, 6H), 3.49 (s, 4H), 0.99 (s, 6H) and two intense signals at 2.505 and 3.34 ppm.

Preparation of the [CuCe(L)$(NO_3)_3$] Complex

A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol, 0.242 g) in 10 cm^3 of methanol is added dropwise to a suspension containing H_2L (1 mmol, 0.370 g) in 10 cm^3 of methanol. Once the addition has finished, maintain stirring for 20 minutes. Subsequently, pour slowly a solution of $Ce(NO_3)_3 \cdot 6H_2O$ (1.5 mmol, 0.651 g in 10 cm^3 of methanol) on to the green solution previously obtained. Keep the reaction mixture stirring for 1.5 hours. Filter the light-green solid formed, wash with cold methanol (2 × 10 cm^3) and diethyl ether (10 cm^3) and dry in air at ambient temperature. Calculate the yield considering MW = 839.33 g, which corresponds to the formula $CuCe(L)(NO_3)_3(CH_3OH)_2$. Obtain the IR spectrum (KBr disc) and compare it with the following selected bands (cm^1): 3465, 2955, 2925, 1622, 1565, 1470, 1294, 1245, 1230, 1063, 1024, 999, 972, 933, 852, 815, 779, 736.

b) [VOGd(L)$(NO_3)_3$] Complex

Preparation of the [VO(L)] Precursor

Heat for 10 minutes an aqueous solution (20 cm^3) containing *o*-vanillin (20 mmol, 3.04 g) and 1,3-diamino-2,2′-dimethylpropane (10 mmol, 1.02 g). The solution turns orange. Add slowly a solution of $VOSO_4 \cdot xH_2O$ (10 mmol, 1.63 g) in water (20 cm^3). A light greenish brown precipitate appears, which is filtered off, washed with acetone (30 cm^3) and diethyl ether (30 cm^3) and dried in air. Calculate the yield for $VO(L)(H_2O)$ (MW = 453.39 g). Selected IR bands (cm^1): 3435, 2954, 1652, 1618, 1555, 1471, 1453, 1432, 1412, 1392, 1326, 1297, 1248, 1224, 1086, 1066, 958, 859, 733.

Preparation of the $[VOGd(L)(NO_3)_3]$ Complex

Solid $Gd(NO_3)_3 \cdot 6H_2O$ (1.55 mmol, 0.70 g) is added to a suspension of $VO(L)(H_2O)$ (1.00 mmol, 0.44 g) in 30 cm^3 of acetone. Keep the light green mixture boiling for 5 minutes and then maintain stirring without heating for 15 minutes. Filter off the solid, wash with acetone (20 cm^3) and diethyl ether (10 cm^3) and dry it in air. Calculate the yield for $VOGd(L)(NO_3)_3(C_3H_6O)$ (MW = 836.71 g). Selected IR bands (cm^1): 3391, 2962, 1703, 1630, 1609, 1567, 1521, 1489, 1473, 1435, 1311, 1283, 1245, 1230, 1064, 995, 857, 741, 735.

4.3.2 Exercises

1. Do the methyl groups in the diamine moiety play any role in the chemistry or physical properties of these complexes?
2. Think about the choice of solvents. Why is water used in the preparation of VO(L) but is not recommended in the step involving the addition of the lanthanide nitrate?
3. Assign the vibrations corresponding to the bidentate nitrato ligands in the IR spectra of the bimetallic compounds. Conductivity measurements have been carried out using both 10^3 M methanol and acetone solutions. The results are in good agreement with a 1 : 1 electrolyte and non-electrolytic behaviour, respectively. Propose an explanation for these differences considering the literature dealing with analogous complexes [3].
4. Taking into account the ^1H NMR signals given above, assign those corresponding to methyl (CH_3 and OCH_3), methylene, azomethine, phenoxy and aromatic protons. Deuterated DMSO contains traces of water.
5. Which of the two heterometallic compounds will give rise to intramolecular magnetic exchange interactions? Do you think that they are strong or weak? Which complex will exhibit spin–orbit coupling? Select two pairs of metal ions that allow *d–f* heterobimetallic compounds to be obtained with (a) paramagnetic and (b) diamagnetic behaviour.

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4.4
Electronic Characterisation of a Transition Metal Complex Using Electrochemical UV/Vis and EPR Techniques

Lesley J. Yellowlees

Many students will have encountered electroanalytical techniques where redox active species are detected both *qualitatively* and *quantitatively*. This experiment is designed to illustrate other uses of the technique – how electrochemistry can be used to probe the electronic characteristics of a redox active transition-metal complex and in the preparation and study of an air unstable species. In particular, you will investigate the frontier orbitals (HOMO and LUMO) of $[Fe(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine). UV/vis and EPR spectroscopies will also be employed in this study.

4.4.1
Experimental

a) $[Fe(bpy)_3][BF_4]_2$

$FeCl_2$ (0.1 g) is dissolved in a minimum amount of H_2O and bpy (0.4 g) is dissolved in a minimum amount of ethanol. The two solutions are mixed and a solution of $NaBF_4$ (0.2 g) in H_2O is added. The resulting deep red precipitate is filtered and washed with cold water and finally cold ethanol.

Record the UV/vis spectrum of the $[Fe(bpy)_3]^{2+}$ in CH_3CN from 850 to 250 nm. Calculate the maximum molar absorption coefficient, ε_{max}, for each of the absorption bands ($\varepsilon_{max} = Ac^{-1}l^{-1}$, where A = measured maximum absorption, c = concentration in mol dm^{-3} and l = pathlength of solution in cm). (*Note*: It will be necessary to record spectra of $[Fe(bpy)_3]^{2+}$ over a range of concentrations in order to observe all transitions).

Construct a qualitative molecular orbital diagram for $[Fe(bpy)_3]^{2+}$, remembering that bpy is a bidentate N-donor ligand and is a fairly good π-acceptor. Where are the HOMO and LUMOs *primarily* based? Which electronic transition is responsible for the deep red colour?

You should be able to probe the electronic character of the HOMO and LUMO electrochemically since an oxidation will involve removing an electron from the HOMO and a reduction involves adding an electron to the LUMO. Furthermore, if either of the redox processes is chemically reversible, i.e. the complex does *not* un-

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dergo a chemical raction following the electron transfer reaction, then the redox product may be studied in order to test the molecular orbital diagram derived qualitatively.

b) Electrochemical Studies

Initially, you will probe the redox behaviour of $[Fe(bpy)_3]^{2+}$. There are approximately 30 distinct perturbations of potential, current and charge which can be used in the study of electrode processes – however, only about 10 of these are widely used. In this experiment, you will consider three of the most common, namely *cyclic voltammetry* (CV), *stirred voltammetry* (SV) and *coulometry*.

Electrochemical experiments will be performed in a conventional three-electrode cell using a Pt micro-disc (diameter approximately 1 mm) electrode, an Ag/AgCl reference electrode and a Pt counter electrode. The solvent is acetonitrile and the supporting electrolyte is tetraethylammonium tetrafluoroborate ($TEABF_4$) (0.1 M). Coulometric experiments will use an H-type cell in which the counter electrode compartment is separated by a frit from the working electrode compartment so as to avoid product contamination.

Make up 50 cm^3 CH_3CN/0.1 M $TEABF_4$, set up the electrochemical cell and bubble the solution with Ar or N_2 for approximately 20 minutes. Why is it necessary to bubble the gas through the solution prior to experimentation? Check that the background solvent is free of any redox processes by running positive and negative CV's. Add approximately 20 mg of compound. Set the starting potential to 0 V and scan rate to 100 mV s^{-1}, sweep to +1.5 V and –2.0 V. Do SV at 20 mV s^{-1} to confirm whether the observed redox processes are oxidations or reductions. Note that the energy gap between the first reduction process and the oxidation process is in fairly good agreement with the energy of the visible absorption maximum of $[Fe(bpy)_3]^{2+}$. Why should this be?

Concentrating on the oxidative process, do a reversibility study by varying the scan rate from 20 mV s^{-1} to 500 mV s^{-1}. A reversible redox process means that the electron transfer rate from/to the electrode to/from the complex is rapid and the complex is not undergoing a major geometric change on electron transfer. Furthermore, the complex is not undergoing a chemical reaction following the electron transfer step. If the redox couple is fully reversible, then the following criteria must hold:

1. 'E_p' is independent of v (scan rate) and $E_a - E_c = 59/n$ mV (n = no. of electrons involved in the electron transfer process) at 298K and $E_p = (E_a + E_c)/2$ where E_a = anodic peak potential and E_c = cathodic peak potential.

2. $i_a/i_c = 1.0$ and i_a vs. $v^{1/2}$ is a straight line through zero. i_a = anodic peak current, i_c = cathodic peak current.

Is the $[Fe(bpy)_3]^{2+}$ oxidation process reversible?

Next, set up the coulometric cell and bubble the solution with Ar or N_2 for 20 minutes. Run background CVs and then add an accurately weighed amount of complex (approximately 20 mg). Run CVs and SVs. Perform electrogeneration of oxidised spe-

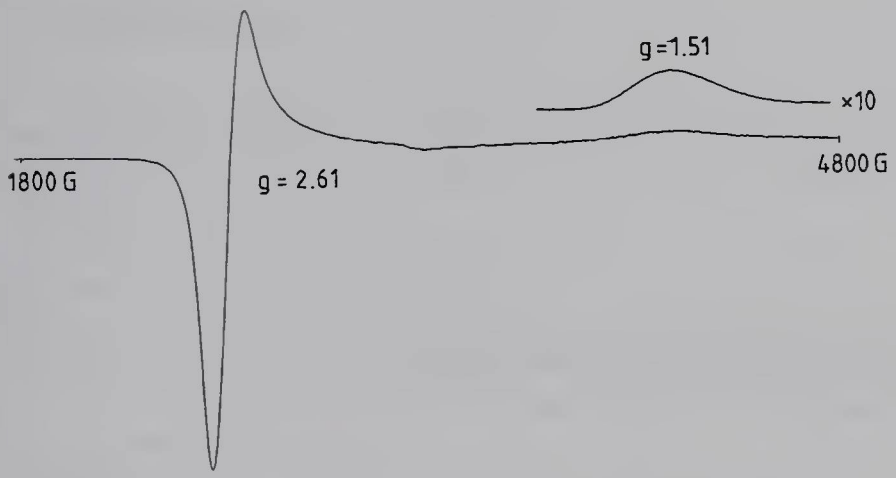

Fig. 4.4-1 EPR spectrum of $[Fe(bpy)_3]^{3+}$ in CH_3CN/0.1 M $TEABF_4$ at 77 K.

cies at relevant potential recording i vs. t curve throughout generation. After generation of oxidised product, calculate the number of moles of electrons passed. Repeat CVs and SVs. Note that CVs are identical before and after electrogeneration, but SVs are not. Why is this so?

Provided it is kept in an inert atmosphere, the oxidised product is relatively stable and may be studied using a variety of spectroscopic techniques. Record the UV/vis and EPR (Fig. 4.4-1) spectra of the oxidised species. Discuss them and decide whether they are in agreement with your qualitative molecular orbital diagram for $[Fe(bpy)_3]^{2+}$.

Comment on the electronic nature of the reductive processes and what you might expect to observe in the UV/vis and EPR spectra of the first reduction product.

4.5
Chlorotris(*tert*-butylimido)manganese(VII)

Andreas A. Danopoulos and Geoffrey Wilkinson

Although the manganese (VII) and (VI) compounds, Mn_2O_7, MnO_3X (X = F, Cl) salts of MnO_4^-, and MnO_4^{2-} have been known for over 140 years [1], no compounds without Mn=O bonds existed until the synthesis of $MnCl(NtBu)_3$ [2], which is the analogue to the explosive MnO_3Cl. Imido groups, $R\ddot{N}$ = (R = alkyl or aryl), are isoelectronic with $\ddot{O}$ = groups and can give similar compounds of transition metals in high oxidation states that are poorer oxidants than the corresponding oxides, cf. OsO_4 and $Os(NtBu)_4$.

$MnCl(NtBu)_3$ can be reduced, e.g. by Na/Hg to the manganese dimer $[(tBuN)_2Mn(\mu\text{-}NtBu)]_2$ and a variety of derivatives made by substitutions of Cl, e.g. by CH_3CO_2 [2].

Special Safety Precautions

1. Trimethylchlorosilane and *tert*-butylsilylamine hydrolyse and the products (HCl, and $tBuNH_2$) are harmful. A well ventilated fume cupboard should be used.
2. Acetonitrile and $tBuNH_2$ are toxic and should be handled using gloves in a fume cupboard.
3. The toxicity of $MnCl(NtBu)_3$, which has an appreciable vapour pressure at room temperature, is unknown. It is best kept in a sealed flask in a refrigerator.
4. Aqueous manganese residues should be safely disposed of.

4.5.1
Experimental

All glassware should be carefully dried to eliminate the possibility of hydrolysis. Although $MnCl(NtBu)_3$ can be handled in air, the following syntheses must be carried out under dry, oxygen-free N_2 or Ar.

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a) Tert-butylsilylamine [3]

In a 3 l 3-neck round-bottomed flask fitted with mechanical stirrer, a 1000 cm^3 pressure equalising dropping funnel and coil condenser connected to an N_2 line are placed 1.5 l of Et_2O (Note 1) and 315 cm^3 (3 mol) of tBuNH$_2$ (Note 2). The flask is cooled in an ice bath.

From the dropping funnel is added a solution of Me_3SiCl (190 cm^3, 1.5 mol) in 200–300 cm^3 Et_2O (made up under dry N_2). The rate of addition is adjusted so that refluxing of Et_2O is avoided. A white precipitate of tBuNH$_3$Cl is formed and the final thick white slurry is allowed to warm to ambient temperature and stirred for 3–4 hours. The liquid is then sucked off using a ground-joint filter stick. The residue is washed with Et_2O (3 × 300 cm^3) and the combined liquids distilled under N_2 at atmospheric pressure using a short (ca. 30 cm) column. After removal of Et_2O, the tBuNH(SiMe$_3$) is collected at 118–120 °C in yields ca. 50–60%.

b) Chlorotris(*tert*-butylimido)manganese (VII)

In a 1 l 3-neck flask with N_2 inlet, mechanical stirrer and dropping funnel as above is placed $Mn_{12}O_{12}(CO_2Me)_{16}\cdot(H_2O)_4\cdot CH_3CO_2H$ [4] (12.5 g, 6.5 mmol) and 450 cm^3 acetonitrile (Note 3) and the flask cooled to ca. –35 °C to –40 °C in a dry-ice/acetone or /isopropanol bath. At this temperature (Note 4), an excess of neat Me_3SiCl (40 cm^3, 315 mmol) is added dropwise (Note 5) with stirring. The initial dark brown solution (which may contain some unreacted acetate) becomes dark red and finally shows the dark red-purple colour of $MnCl_3$. After stirring for 0.5 hour, neat tBuNH(SiMe$_3$) (50 cm^3, 370 mmol) is added dropwise from the dropping funnel. The reaction mixture becomes orange-brown in colour. After stirring for ca. 12 hours whilst allowing to warm to ambient temperature, the colour changes to dark green. At this point, the mixture is very moisture sensitive and failure to work under N_2 results in low yields. The green solution is filtered under N_2 using a G3 glass frit covered with a Celite 521 pad (3–4 cm) and the filtrate evaporated in a rotary evaporator (water bath temperature should not exceed 50 °C) connected to a conventional vacuum/N_2 manifold. A liquid N_2 trap is used to collect volatiles and prevent them entering the vacuum line. After removal of volatiles, the green residue (which can now be handled in air if necessary) is shaken thoroughly with petroleum (40 °C–60 °C, 200 cm^3) and water (200 cm^3). The green organic phase is separated, the aqueous phase (also yellow-green due to formation of the $MnCl_4^{2-}$ ion) is extracted with petroleum (3 × 100 cm^3) and the combined solvent dried over anhydrous Na_2SO_4 for 2 hours. After filtration and removal of petroleum on a rotating evaporator, the green crystalline MnCl(NtBu)$_3$ is collected and recrystallised from petroleum. Yield (2 crops): 1.6–1.9 g; m.p.: 92–93 °C. For spectroscopic data, refer to the literature [2]. Since the complex is air and moisture stable, no special handling precautions are necessary.

4.5.2 Notes

1. Et_2O dried over Na wire can be used without further treatment.
2. $tBuNH_2$ is dried with solid KOH or with Na wire and preferably distilled under N_2.
3. Acetonitrile is dried over CaH_2 and distilled under N_2.
4. The temperature is not critical for the formation of the puple solution of $MnCl_3$ in MeCN, but it is important to keep the temperature ca. –40 °C during addition of $tBuNH(SiMe_3)$.
5. Excess Me_3SiCl is used to ensure removal of H_2O and CH_3CO_2H, which will solvate the oxoacetate.
6. Excess $tBuNH(SiMe_3)$ is used to scavenge any acidic compounds formed by hydrolysis in solution.

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4.6
Tetrakisphosphorane Iminato Complexes of Transition Metals

Kurt Dehnicke

Phosphorane iminato complexes of transition metals and main group elements contain the ligand group $(NPR_3)^-$ (R = organic residue, halogen or amido groups). Depending on the oxidation states of the counter cations, the bonding situation and rate of association change from ionic to covalent and from oligomeric to monomeric species, respectively (Table 4.6-1).

Table 4.6-1

$[K(NPPh_3)]_6$	$[ClFe^{II}(NPEt_3)]_4$	$[Cl_2Fe^{III}(NPEt_3)]_2$	$[Cl_3Ti^{IV}(NPPh_3)]$
Double cube with shared K_2N_2 plane	Heterocubane with Fe_4N_4 skeleton	Dimeric structure with planar Fe_2N_2 ring	Monomeric with linear $Ti{\equiv}N{-}PPh_3$ moiety

Linear bonding modes of the type $M{\equiv}N{-}PR_3$ are also present in the homoleptic tetrakis-phosphorane iminato complexes $[M(NPR_3)_4]^n$ with $n = 2+, +1, 0, -1$ of transition metals M = Mo, W, V, Ta, Ti, Hf, Yb, forming a series of valence-isoelectronic species with MNP angles from 145 to 165°:

$[W(NPR_3)_4]Cl_2$ $[Ta(NPR_3)_4][TaCl_6]$ $[Hf(NPR_3)_4]$ $Cs[Yb(NPR_3)_4]$

The MN bond lengths depend on the increase in the atomic radius of the metal atom, which is accompanied by a decrease in the oxidation state on going from tungsten to ytterbium (Table 4.6-2).

Table 4.6-2

Compound	MN separation/pm (average values)
$[W(NPPh_3)_4]^{2+}$	180.9
$[Ta(NPPh_3)_4]^+$	185.0
$Hf(NPPh_3)_4]$	200.9
$[Yb(NPPh_3)_4]^-$	214.6

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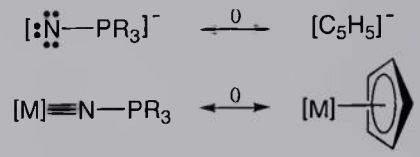
The bonding mode of complexes with a linear M≡N–P arrangement can best be described as pseudo-isolobal with the η^5-bonded cyclopentadienyl group; both ligands formally exist as a (σ,2π)-donor set of six electrons with the same charge:



Indeed, quantum chemical calculations show a striking analogy in the bonding behaviour of these two complex species, even on closer inspection of the real interaction and of their σ and π components. The different demands of the bulky Cp^- ligand and the 'slim' $[NPR_3]^-$ ligand cause high reactivity of the phosphorane iminato complexes, which makes them promising candidates as catalysts for the polymerization of olefins and lactones.

Synthetic routes to prepare homoleptic phosphorane iminato complexes of tungsten, tantalum, hafnium and ytterbium are shown in Eqs. (1) to (4).

$$WO_2Cl_2 + 4\,Me_3SiNPPh_3 \xrightarrow{CH_3CN} [W(NPPh_3)_4]Cl_2 + 2\,O(SiMe_3)_2 \quad (1)$$

$$[TaCl_5]_2 + 4\,Me_3SiNPPh_3 \xrightarrow{CH_3CN} [Ta(NPPh_3)_4][TaCl_6] + 4\,ClSiMe_3 \quad (2)$$

$$HfCl_4 + 4\,Cs(NPPh_3) \xrightarrow{thf} [Hf(NPPh_3)_4] + 4\,CsCl \quad (3)$$

$$[Yb(NPPh_3)_3]_2 + 2\,Cs(NPPh_3) \xrightarrow{thf} 2\,Cs[Yb(NPPh_3)_4] \quad (4)$$

$$2\,YbCl_3 + 6\,NaNPPh_3 \xrightarrow{thf} [Yb(NPPh_3)_3]_2 + 6\,NaCl \quad (5)$$

The preparation of $Cs[Yb(NPPh_3)_4]$ requires the dimeric complex $[Yb(NPPh_3)_3]_2$ as starting material (Eq. 4), which is easily available by reaction of $YbCl_3$ or $Y(O_3S\text{-}CF_3)_3$ with $NaNPPh_3$ (Eq. 5).

In some cases, metal nitrido complexes are also suitable to give phosphorane iminato derivatives (Eq. 6).

$$Mo(N)Cl_3 + 4\,Me_3SiNPMe_3 \xrightarrow{CH_2Cl_2} [Mo(NPMe_3)_4]Cl_2 + ClSiMe_3 + N(SiMe_3)_3 \quad (6)$$

Special Safety Precautions

1. Tungsten hexachloride (WCl_6), tungsten dioxodichloride (WO_2Cl_2) and tantalum pentachloride ($TaCl_5$) are moisture sensitive and therefore likely to hydrolyse to give HCl (which is toxic by inhalation), $WO_3 \cdot nH_2O$ and $Ta_2O_5 \cdot nH_2O$, respectively.

2. The preparation of silylated phosphanimines (Me_3SiNPR_3) requires the corresponding phosphanes (PR_3) and trimethylsilylazide (Me_3SiN_3), which are available from Aldrich or Merck. Always use an inert solvent (e.g. toluene) for PR_3 and add a solution of Me_3SiN_3 in toluene dropwise at boiling tempera-

ture. Make sure that dinitrogen as a result of the Staudinger reaction can leave the reaction apparatus. Never distil trimethylsilylazide prior to use!

3. Grease all joints carefully with silicone. All procedures must be carried out under dry nitrogen. Use dried solvents only.
4. The solvents dichloromethane, acetonitrile and tetrahydrofuran are toxic by inhalation or contact. Use a fume cupboard.

4.6.1 Experimental

a) $[W(NPPh_3)_4]^{2+}\ 2\,Cl^-$

Tungsten dioxodichloride (1.0 g, 3.5 mmol) and acetonitrile (20 cm^3) are placed in a 100 ml two-necked flask. To this suspension, a solution of trimethylsilyltriphenylphosphoranimine, $Me_3SiNPPh_3$ (2.75 g, 7.0 mmol), in acetonitrile (20 cm^3) is slowly added dropwise while stirring (magnetic stirrer). The reaction mixture is now refluxed until a clear yellow solution is obtained. After cooling to room temperature, 1 cm^3 of diethyl ether is added and the reaction tube is separated for 2 days. White single crystals are filtered off, washed with 3 ml of diethyl ether and dried in vacuum.

The yield can be increased by evaporating the filtrate (use a magnetic stirrer!) to a volume of 20 cm^3. The remaining crystal powder is filtered off and worked up as above.

Calculate the yield, measure its IR spectrum (KBr plates, Nujol mull) and give an explanation for the relative broadness of the absorption bands. Compare the results with literature data. The progress of slow hydrolysis on exposing the sample to humid air can be observed by IR spectroscopy. The following reaction sequence occurs step by step:

$$[W(NPPh_3)_4]Cl_2 + H_2O \rightarrow [WO(NPPh_3)_3]Cl + [Ph_3PNH_2]^+\ Cl^- \quad (7)$$

$$[WO(NPPh_3)_3]Cl + H_2O \rightarrow [WO_2(NPPh_3)_2] + [Ph_3PNH_2]^+\ Cl^- \quad (8)$$

$$[WO_2(NPPh_3)_2] + H_2O \rightarrow WO_3 + 2HNPPh_3 \quad (9)$$

$$HNPPh_3 + H_2O \rightarrow NH_3 + OPPh_3 \quad (10)$$

$$[Ph_3PNH_2]^+Cl^- + H_2O \rightarrow NH_4Cl + OPPh_3 \quad (11)$$

Take samples for measuring the IR spectrum at regular intervals (e.g. every 5 minutes) and identify the resulting species by assignment of NH, WO and PO stretching vibrations.

b) $[Ta(NPPh_3)_4]^+ Cl^-$

Tantalum pentachloride (4.7 g, 13.1 mmol) and acetonitrile (70 cm^3) are placed in a 250 cm^3 two-necked flask. $Me_3SiNPPh_3$ (10.3 g, 29.5 mmol) is added with stirring (magnetic stirrer) and refluxed until a clear solution occurs. After cooling to room temperature, the white crystalline solid is filtered off, washed with 10 cm^3 of diethyl ether and dried in vacuum. The filtrate is separated for 2 days to give single crystals.

Calculate the yield, measure the IR spectrum (CsI plates, Nujol mull) and compare it with literature data. Identify the $[TaCl_6]^-$ anion by assignment of the triply degenerate antisymmetric stretching vibration (F_{1u}).

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4.7
Magnetochemistry Experiments: Exchange Coupling in Copper(II)-Nickel(II) Bimetallic Complexes and Spin Transition in Iron Complexes

Eugenio Coronado and J. J. Borrás-Almenar

The aim of this experiment is to illustrate two phenomena of current interest in molecular magnetism, namely magnetic exchange interaction in bimetallic complexes and spin transition[1)], both of which can easily be detected by means of magnetic susceptibility measurements at variable temperatures. In the former case, two bimetallic coordination isomers of the *trans*-cyclohexane-1,2-diamine-*N,N,N′,N′*-tetraacetate (CDTA) containing Cu(II)-Ni(II) pairs are prepared and magnetically characterised. These compounds belong to an extensive series of bimetallic materials, the so-called EDTA family, in which the ability of the EDTA-like ligands to selectively coordinate to metal ion while still providing carboxylate bridges to link a second metal provides the possibility of preparing a wide variety of ferrimagnetic systems of variable dimensionality. Furthermore, the inertness of these CDTA complexes in solution makes these systems of particular interst to illustrate the possibility of kinetic control of their syntheses.

In the second case, the compound di-*iso*thiocyanatobis(1,10-phenanthroline) iron(II), $Fe(phen)_2(NCS)_2$, is particularly suitable since it shows an abrupt $S = 0 \Leftrightarrow S = 2$ spin transition at a critical temperature close to 175 K, which may be detected by magnetic measurements.

4.7.1
Experimental

a) The Bimetallic Complexes NiCu(cdta) · $6H_2O$ (1) and CuNi(cdta) · $7H_2O$ (2)

Both compounds are prepared following the same general procedure. To 2 mmol of H_4CDTA acid (Titriplex IV), a concentrated solution containing 8 mmol of NaOH is added dropwise with stirring until complete deprotonation of the acid is effected (final pH ca. 11.7). To this solution, an equimolar solution of the relevant metal nitrate (Cu or Ni respectively) is added. After allowing a short period (ca. 15 minutes)

1) Equivalent terms found in the literature are spin crossover, magnetic crossover or spin equilibrium. For a review see P. Gütlich, *Struct. Bonding (Berlin)*, **1981**, *44*, 83; see also E. König, G. Ritter, S. K. Kalshreshtha, *Chem. Rev.* **1985**, *85*, 219.

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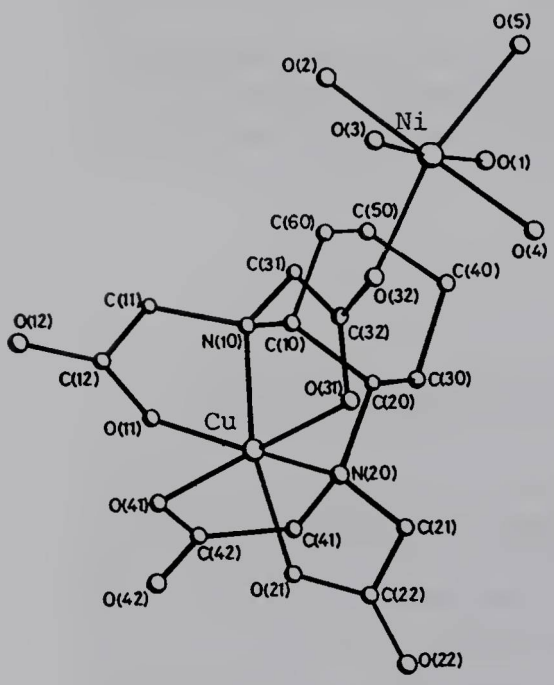
to ensure complexation of this metal ion, an equimolar aqueous solution of the second metal nitrate is added. Then, acetone is added dropwise with stirring until incipient turbidity. The resultant solutions are filtered and stored at ca. 5 °C. Blue crystalline solids of **1** and **2** appear after a few hours.

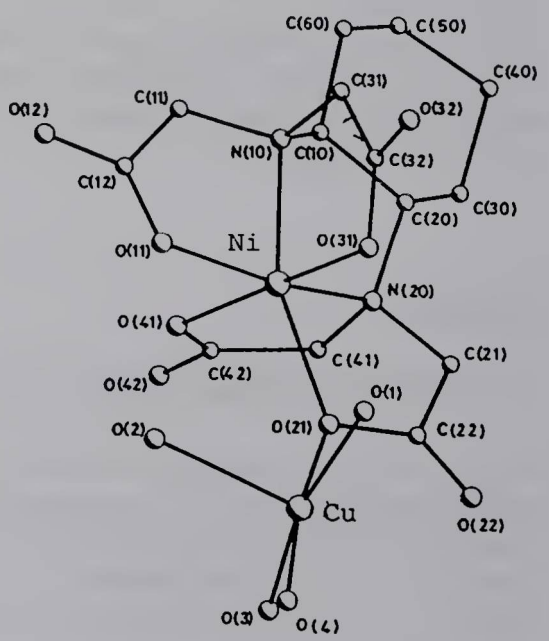
Caution: In the preparation of **2** small modifications of the experimental conditions (for example, heating the solutions) and allowing long periods of time for crystallization (slow evaporation of the solution at room temperature with no addition of acetone) can lead to a different compound formulated as $Cu_3Ni_2(cdta)_2(NO_3)_2 \cdot 15H_2O$. This compound can easily be identified by the presence of nitrates in its IR spectrum (sharp absorption at ca. 1390 cm^{-1}). Record the IR spectra of the obtained compounds as KBr pellets in order to verify this point.

The structures of **1** and **2** (see Fig. 4.7-1) show the presence of bimetallic dimers with two different coordination sites in which the two metal atoms are linked through a carboxylate bridge. In **1**, the CDTA hexacoordinates the Cu^{II} ion while the Ni^{II} ion is in an octahedral site formed by five water molecules and an oxygen atom from the carboxylate bridge. In **2**, the CDTA site is occupied by Ni^{II}, while Cu^{II} is now occupying a square pyramidal site with four water molecules and an oxygen atom.

Determine the magnetic susceptibilities of the two products as a function of the temperature with a Faraday balance equipped with a helium or nitrogen cryostat. Correct the experimental data for the diamagmetic contributions of the constituent atoms using the Pascal tables and from T.I.P. contributions of the metal ions. Plot the product magnetic susceptibility times the temperature (proportional to μ^2_{eff}), vs. the temperature.



1



2

Fig. 4.7-1 Structures of **1** and **2**.

The magnetic behaviour of 1 follows a Curie law with a constant value of the product χT (≈ 1.6 emu K mol^{-1}) over the temperature range 4–300 K. Conversely, as the temperature is lowered, 2 exhibits a continuous decrease of χT down to 15 K. Below this temperature a constant value of χT (≈ 0.4 emu K mol^{-1}) is observed.

Derive the susceptibility expression for an exchange-coupled pair with spins 1/2–1 in terms of the exchange coupling, J, and the Landé factor, g. Use this expression to fit the magnetic data of 2. Explain the different behaviours of the two compounds on the basis of the presence or absence of magnetic exchange interactions between the Cu^{II}-Ni^{II} pairs. Correlate this result with the structural differences in the bridging network and in the two coordination sites of the two complexes. For a general discussion see Fuertes *et al.*

b) $Fe(phen)_2(NCS)_2$

This is one of the spin-crossover systems that have been most investigated through various techniques including magnetic and calorimetric measurements, Mossbauer, IR, UV-visible, NMR and XPS spectrometries, and X-ray diffraction and absorption. Depending on the method of synthesis, two different polymorphs can be prepared.

Method A: All operations are carried out under inert atmosphere. A suspension of potassium thiocyanate K(SCN) (8 mmol) and hydrated iron(II) sulfate, $Fe(SO_4) \cdot 6H_2O$, (4 mmol) in methanol is stirred until the reaction is complete. The colourless solution containing Fe^{2+} and SCN^- is separated from the white precipitate of potassium sulfate by filtration. The eventual colouring of the solution indicates the presence of traces of Fe^{3+}, and can be eliminated by addition of some crystals of ascorbic acid. A stoichiometric amount of 1,10-phenanthroline (phen) in methanol is added dropwise to the above stirred solution. The pink-violet precipitate of $Fe(phen)_2(NCS)_2$ is filtered off, washed several times with methanol and dried in an argon stream. The purity of the compound can be checked by IR (the presence of a broad band at 1100 cm^{-1} is indicative of sulfate impurities).

Method B: In this case $Fe(phen)_2(NCS)_2$ is prepared by extracting a phenanthroline group from $Fe(phen)_3(NCS)_2 \cdot H_2O$ in a Soxhlet apparatus using acetone. The extraction is carried out for a period of 3 weeks under argon atmosphere. $Fe(phen)_3(NCS)_2 \cdot H_2O$ can be prepared by adding the stoichiometric amount of phen to a solution of Fe^{2+} and SCN^- prepared as described in method A. A more simple method for preparing $Fe(phen)_3(NCS)_2 \cdot H_2O$ consists of adding a saturated aqueous solution of K(SCN) to a mixture of $Fe(SO_4) \cdot 6H_2O$ and phen (in stoichiometric amounts) dissolved in the minimum quantity of water. The precipitate is washed with acetone and ether. In such a case the use of an inert atmosphere is not necessary.

c) Magnetic Properties of $Fe(phen)_2(NCS)_2$

Determine the magnetic susceptibilities on the polycrystalline samples in the temperature range 77–300 K. Correct the molar susceptibilities for diamagnetism and plot the χT product vs. T. An abrupt increase associated to the singlet ⇔ quintet spin

transition should be observed around $T_c \approx 176$ K; such a transition is much sharper in sample B than in sample A. Determine the relative amounts of high- and low-spin isomers above and below T_c in sample A. For a general discussion see Gallois *et al.* and Ganguli *et al.*

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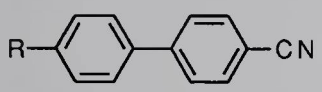
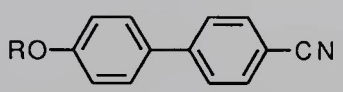
4.8
Metal-Containing Liquid Crystals. The Synthesis of *trans*-bis(4-Alkyl-4′-cyano-1,1′-biphenyl)dichloroplatinum(II) and Related Species – The Use of Melt Syntheses

Duncan W. Bruce

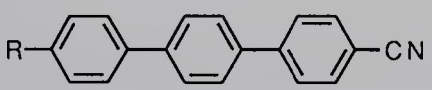
Almost everyone will now own some device or other containing a liquid crystal display (LCD), be it a flat-panel television, a calculator, a lap-top computer or even the display on the washing machine. The wholesale commercialisation of LCDs began in the early 1970s following the synthesis of the alkylcyanobiphenyls, alkoxycyanobiphenyls and alkycyanoterphenyls (shown below) by Gray and coworkers at the University of Hull.



Alkylcyanobiphenyls



Alkoxycyanobiphenyls



Alkylcyanoterphenyls

These materials were important as they had the correct combination of physical properties and chemical inertness for exploitation. Research on liquid crystals has boomed since that time and groups are internationally active in all areas of the subject from biology (cell membranes are liquid crystals) to device engineering, from the applied to the pure and from the experimental to the theoretical.

One of the more recent areas to come to prominence involves the design and synthesis of metal complexes which are liquid crystalline and these are discussed in several review review articles. The area is of considerable fundamental interest, but one of the driving forces is the fact that certain properties of metals can be incorporated into liquid-crystalline media in this way, for example paramagnetism, polarisability or even colour.

The complexes described in this synthesis are platinum(II) complexes of the original cyanobiphenyls, being readily prepared from $PtCl_2$ and the ligand directly.

The liquid-crystalline state is a true state of matter which exists between the liquid and the solid state and as such, has properties reminiscent of each. Thus, in common with a liquid it is fluid, while in common with a solid, it possess order – a useful way to think about these systems is as ordered liquids. There are several different

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classifications of liquid crystals of which the broadest are *thermotropic*, in which the solid-liquid crystal-liquid transitions are thermally induced, and *lyotropic*, where they are solvent induced. We will concentrate solely on thermotropic systems.

Thermotropic liquid crystals can be further classified as polymeric, discotic (i.e. disc-shaped), bent-core and calamitic (or rod-shaped). This experimenta deals only with the last of these. The point about rod-like molecules is that they are structurally anisotropic and hence there are anisotropic dispersion forces existing between molecules. It is these rather weak forces which stabilise liquid crystal phases. This is not the place to discuss the various structural criteria which will promote the formation of liquid crystalline behaviour, but for our purposes, it is sufficient to say that rods built up of a rigid core (usually aromatic with at least two rings either linked directly or *via* groups such as ester, imine or vinyl) and terminated at one end by a flexible alkyl (or alkoxy) chain and at the other either by the same or by a small polar group (*e.g.* –CN, $-NO_2$, –OMe) are often liquid crystalline.

Such molecules generally form two general types of liquid crystal phase, *nematic* and *smectic*. If our rods were in a fluid state with one-dimensional orientational order and no positional order, then they would describe the nematic phase (N) (Fig. 4.8-1). The nematic phase is the most disordered type of mesophase and is the one used in most display applications.

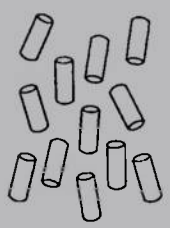


Fig. 4.8-1 Schematic picture of a nematic phase (from *Inorganic Materials* by permission of John Wiley & Sons).

If we then introduce partial positional order in addition to the orientational order, a family of smetic phases is generated, which are characterised by having some layering of the molecules. In the smectic A (SmA) phase (Fig. 4.8-2a), the molecules are loosely associated within layers and point on average in a direction perpendicular to the layers. In the smectic C phase (SmC), the situation is similar (Fig. 4.8-2b), except that the molecules now make some angle, θ, to the layers. There is, however, no positional correlation between molecules within the SmA or SmC layers and there is considerable fluidity within, and easy diffusion between, the layers. Other types of smectic phase exist but will not be described here.

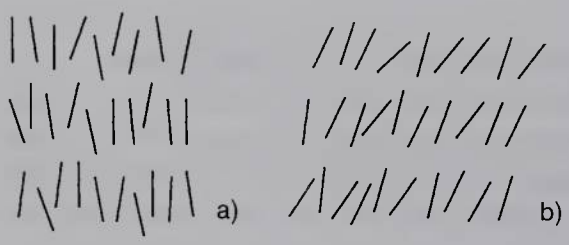


Fig. 4.8-2 Schematic representation of a) the S_A and b) the S_C phases (from *Inorganic Materials* by permission of John Wiley & Sons).

Special Safety Precautions

Cyanobiphenyls:	Are effectively non-toxic and non-irritants.
Platinum(II) chloride:	Is an eye and skin irritant, but should prevent no hazard in the quantities to be used. Gloves should be worn as a precaution.
Chloroform:	Handle in a ventilated area and avoid exposure to skin.
Diethylether:	Flammable. Use in ventilated area and avoid skin contact.
Celite:	Is a silica dust and so inhalation should be avoided.

4.8.1 Experimental

This is a very general procedure which is applicable to a whole host of cyanobiphenyl-type liquid crystals. It is described in detail here for 4-octyl-4-cyanobiphenyl.

An oil bath is heated to 140 °C. On reaching the temperature, a round-bottomed flask (capacity 25 or 50 cm^3 and preferably with a B24 socket) equipped with a small magnetic stir bar and containing 4-octyl-4-cyanobiphenyl (873 mg, 3 molar equivalents; abbreviated 8CB) is placed in the oil. Stirring is commenced and $PtCl_2$ (269 mg, 1 molar equivalent) is added. The temperature is maintained for about 30 minutes during which time the mixture solidifies, turning a dirty yellow. After cooling to room temperature, the solid mixture is dissolved in chloroform (~15–20 cm^3) and filtered twice through celite to remove unreacted $PtCl_2$. A large excess of diethyl ether is added to precipitate the complex. Ideally, the precipitated solid is recovered by centrifugation (as the precipitate tends to be quite fine), but it can be obtained by decanting off the mother liquor after standing (don't let all the ether evaporate off!). A small amount of residual solvent is not too important at this stage. The precipitate is then crystallised from hot chloroform/diethyl ether to give yellow crystals, which are recovered by filtration, washed with diethyl ether and air dried.

Obtain the ^1H NMR spectrum in CD_2Cl_2 at 250 MHz and the infrared spectrum (4000–200 cm^{-1}) as a Nujol mull between CsI plates. The 250 MHz ^1H NMR spectrum of *trans*-$[PtCl_2(8CB)_2]$ is shown in Figure 4.8-3 for reference. Analyse the spectrum.

In the ^{13}C NMR spectrum, the cyanide carbon is seen at δ 117, but coupling to ^{195}Pt ($^2J_{Pt-C}$ = 289 Hz) is seen at 80 MHz with a little difficulty. There is no advantage in going to higher field. Why?

The infrared spectrum can be used to confirm the geometry of the complex and to say something about its purity. Consult the literature, identify ν_{CN} for the bound ligand in your spectrum and determine whether your sample contains any free ligand. Similarly, confirm the *trans* geometry of the complex by locating ν_{Pt-Cl} and

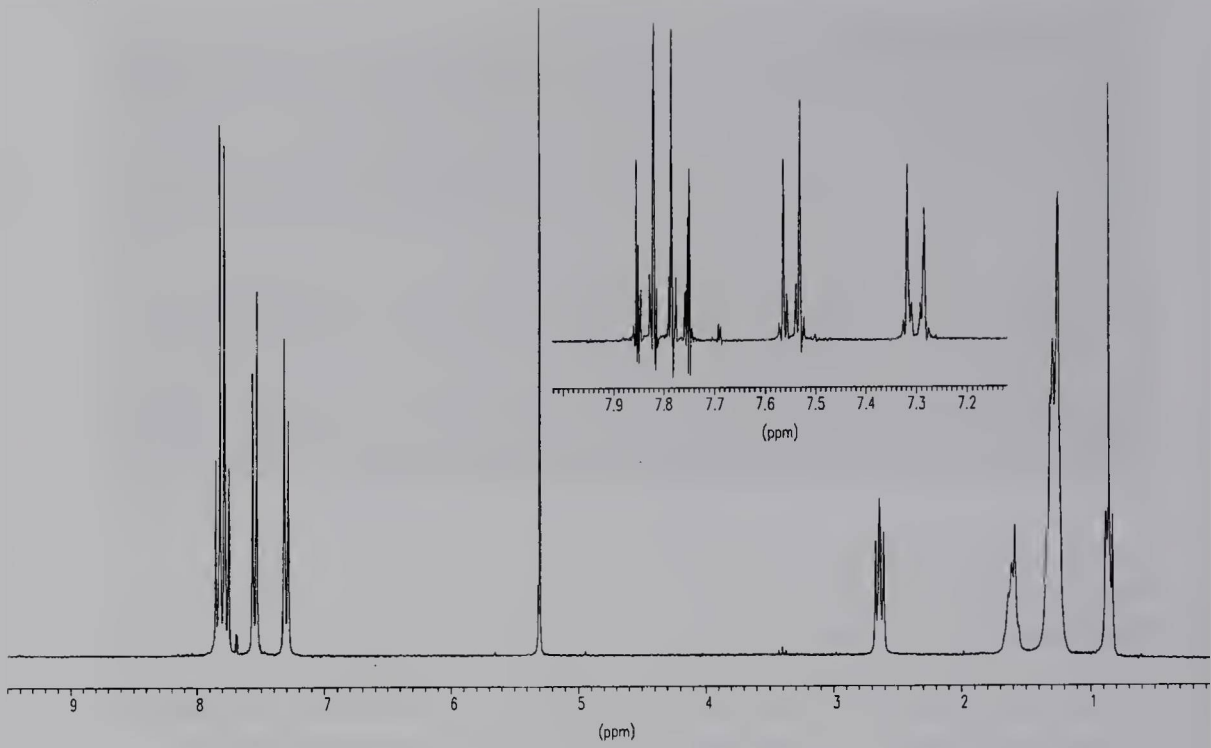


Fig. 4.8-3 250 MHz ^{1}H NMR spectrum of $[PtCl_2(8CB)_2]$.

identifying the number of stretching vibrations. If you are familiar with the use of group theory, then identify the points groups for *cis*-and *trans*-$[PtCl_2(8CB)_2]$ and determine the predicted number of Pt-Cl stretching vibrations which are active in the infra-red and Raman spectra. Compare these predictions with the spectrum you obtained.

Ideally, liquid crystal phase characterisation is carried out by a combination of techniques, namely polarising optical microscopy, differential scanning calorimetry and X-ray scattering. The most immediately useful of these is microscopy which is described below.

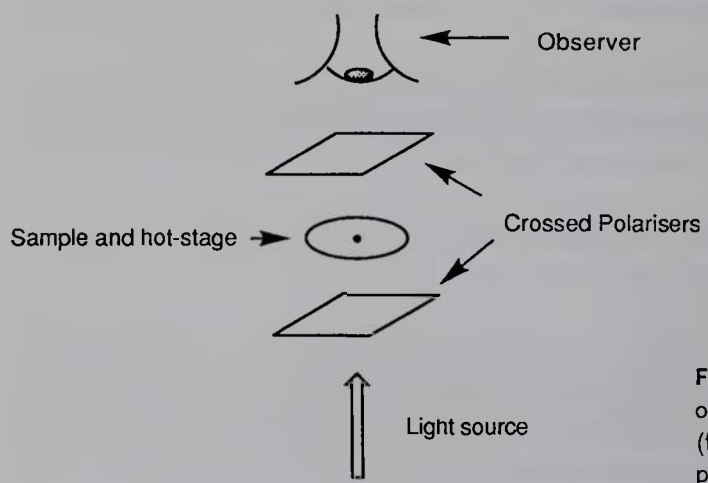


Fig. 4.8-4 Schematic diagram of a polarising microscope (from *Inorganic Materials* by permission of John Wiley & Sons).

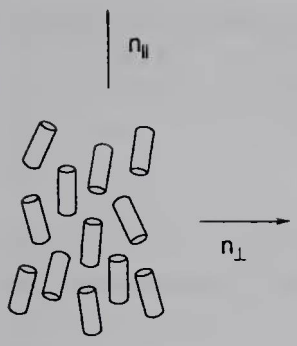


Fig. 4.8-5 Representation of the molecular organisation in a nematic phase showing the origin of the two refractive indices.

A sample is placed between two glass slides which are then placed on a hot stage, mounted on a microscope stage. The light which falls on the sample is plane polarised. Between the sample and the objective lens, there is another piece of polaroid whose polarisation direction is at right angles to that of the first polariser (Fig. 4.8-4). In the absence of any sample, or in the presence of a 'normal' liquid such as water, the observer would see nothing as no light would pass through. However, when a material is in a liquid crystal phase, its physical parameters become anisotropic (i.e. different in different directions). One of these anisotropic properties is refractive index and nematic liquid-crystalline phases have two of these as shown in Figure 4.8-5.

Thus, it is convenient to think that two refracted rays are produced when light is incident on the sample in its liquid crystal phase. These two rays can then interfere with one another to produce an interference pattern which is now not absorbed by the polariser. These patterns, known as *textures*, are characteristic of individual liquid crystal phases, although in certain circumstances a given liquid crystal phase can exhibit more than one type of texture. A characteristic texture of the nematic phase is shown in Figure 4.8-6. The fluid nature of these phases can be demonstrated by the

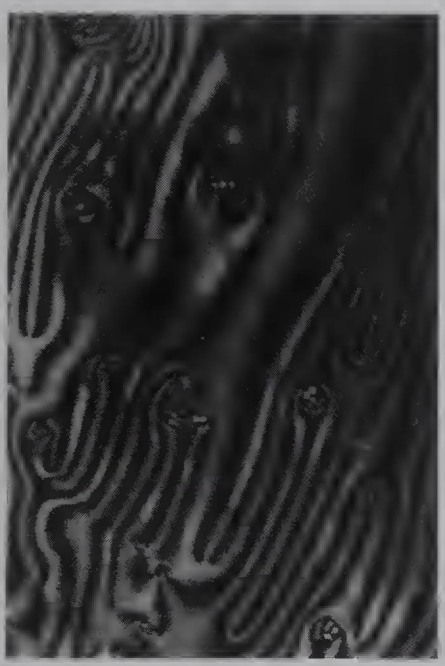


Fig. 4.8-6 Characteristic optical texture of the nematic phase (from *J. Chem. Soc., Chem. Commun.*, **1994**, *729*, by permission of the Royal Society of Chemistry).

application of mechanical stress (i.e. tap the cover slip); this can result in characteristic optical 'flashing' for the nematic phase.

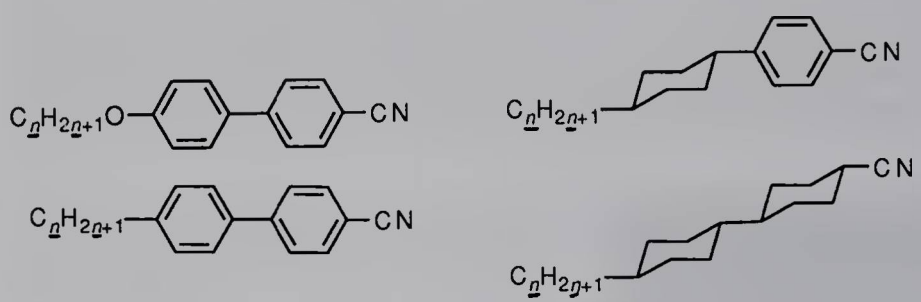
The complex you have just made has the following phase behaviour:

$$K \xrightarrow{166} N \xrightarrow{176} I$$

This means that the complex melts from the crystal phase (Crys) into the nematic phase at 166 °C. The nematic phase then persists until 176 °C, when the fluid becomes isotropic (Iso – i.e. a 'normal' liquid). If held in this latter state for any length of time, the material will decompose.

Although you may not have access to the correct equipment to see this properly, a standard melting point experiment should show the crystals melt to a turbid fluid at 166 °C.

The synthetic method described above has been used for compounds with the structures shown below, with *n* varying typically between 1–12 when there is no cyclohexyl ring present, and taking the values 2, 3, 5 and 7 when there is a cyclohexyl ring. Not all of these results are published as yet, but interested parties are invited to contact the author for advice if they wish to look at other derivatives. All of these materials are commercially available. The method also works with $PtBr_2$, although the yields are smaller unless the conditions are modified slightly. PtI_2 does not work with these ligands. Further, this method works with other ligands and readers are directed to the literature for further details.



It is also possible to make palladium equivalents of these platinum systems, although there are drawbacks. They are synthesised by stirring two equivalents of the desired ligand for three hours at room temperature with $[PdCl_2(PhCN)_2]$ in acetone, removing the solvent on a rotary evaporator, chilling the residue in the freezer for two hours, and then triturating with ethanol to leave the pure, solid product after drying; yields are in the range 50–90%. This route is superior and generally more reliable than that published by Adams, *et. al.* Unfortunately, these complexes are labile in solution and so cannot be readily crystallised, which is why the 'melt' route is inappropriate. However, the melt route can be used with palladium if more inert complexes are to be synthesised.

The palladium complexes are also liquid crystalline and at lower temperatures than the platinum homologues. However, for complexes with alkylcyanobiphenyls, the nematic phase is monotropic, meaning that it is less stable that the crystal phase

and so is found on supercooling the complex from its isotropic state (i.e. crystals melt straight to 'normal' liquid and the liquid crystal phase is found on supercooling). Therefore, it is suggested that alkoxycyanobiphenyls be used with palladium for convenience; all complexes with ligand chains up to and including octyloxy show only a nematic phase.

It would be possible to construct two general types of phase diagrams from the materials obtained above. In one scenario, the experiment could be made into a class experiment with different groups using ligands of different chain lengths. Thus, for one particular series, a phase diagram with chain length plotted on the x axis and temperature plotted on the y axis could be constructed, which would show the limits of liquid crystal phase stability.

In another scenario, it would be possible to construct binary phase diagrams at different percentage compositions. The clearing point of a mixture consisting of complexes with similar shape and type is simply expressed as:

$$T_c = \sum_i a_i T_i$$

where T_m = clearing point of the mixture; a_i is the percentage of component i in the mixture and T_i is its clearing point, i.e. it is a linear function of composition. A typical phase diagram for a mixture of two nematic compounds is shown in Figure 4.8-7.

This shows the linear behaviour of the clearing point and the eutectic behaviour of the melting point. Such phase diagrams can typically be constructed at compositional increments of 10%. Further, they can be used to effect if one or both of the components has a monotropic phase as the drop in melting point can lead to an enantiotropic phase (*i.e.* observed on heating *and* cooling) for the mixture within a particular composition range. An example of this is the binary phase diagram constructed for the Pd complexes of propyl- and pentyl-bicyclohexylcarbonitrile (abbreviated CCH3 and CCH5 respectively), although in this case the lability of the palla-

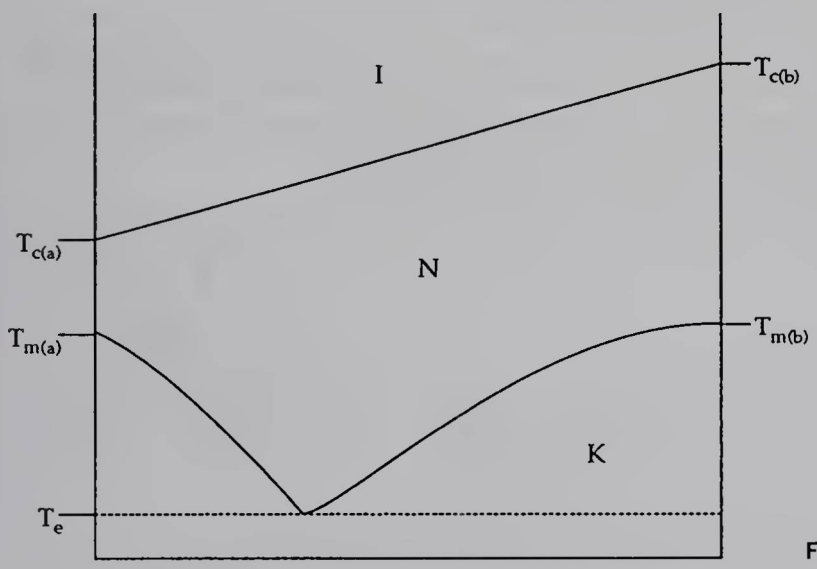


Fig. 4.8-7

dium complexes meant that all three possible complexes (i.e. $[PdCl_2(CCH3)_2]$, $[PdCl_2(CCH5)_2]$ and $[PdCl_2(CCH3)(CCH5)]$ were present in statistical proportions. In our experience, mixtures for binary phase diagram studies are best made by mixing the two components in the correct proportion in solution (e.g. $CHCl_3$) and then removing the solvent.

4.8.2 Note

The idea for this synthesis came from examination of the synthesis of $[PtCl_2(NCPh)_2]$. This complex can be made in its *cis* form by reaction of aqueous $K_2[PtCl_4]$ with PhCN at room temperature. Mixtures of *cis*- and *trans*-$[PtCl_2(NCPh)_2]$ can be made by direct reaction of $PtCl_2$ with PhCN and the *trans/cis* ratio increases with the increased temperature of the reaction, although in this method, pure *trans* isomer is never recovered and the mixture must be separated by chromatography. See also Fanizzi *et al.* for a discussion of the formation of *cis*- and *trans*-$[PtCl_2(NCMe)_2]$. This melt synthesis produces exclusively the *trans* isomer in good yield, although with different ligand types (*e.g.* phosphines), exclusively *cis* complexes can be similarly obtained.

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4.9
Structural, Electrical and Magnetic Properties of Perovskite Ceramics

Colin Greaves

The perovskite structure (Fig. 4.9-1), which is adopted by many oxides with formula ABO_3, is very versatile, and many perovskites have useful technological applications (e.g. as ferroelectrics, catalysts, sensors and superconductors). In this structure, the A and O ions together form a cubic close-packed array, and the B ions occupy 1/4 of the octahedral holes. This experiment involves the synthesis of four compounds which are structurally closely related to perovskite, but have very different physical properties. Control of the types of cations in the large sites (A) allows some variation of the oxidation state of the smaller octahedral cations (B), and this confers the variable physical characteristics.

Transition metal ions with unpaired electrons are paramagnetic, provided interactions between neighbouring ions are weak; this "magnetically dilute" situation occurs in solutions and many solids. The perovskite structure allows quite strong interactions to occure *via* covalence in the M–O–M bonds, and this may result in ordering of the magnetic moments to give "ferromagnetic" or "antiferromagnetic" materials. At elevated temperatures, both classes are paramagnetic (random arrangement of magnetic moments), but below a critical temperature, the moments order in a parallel (ferromagnetic) or anti-parallel (antiferromagnetic) fashion. This temperature is known as the Curie temperature (T_c) for ferromagnets and the Néel temperature (T_N) for antiferromagnets.

The synthesis of solid state ceramic samples may be achieved by a variety of techniques. The simplest exploits the finite ionic or atomic diffusion processes which

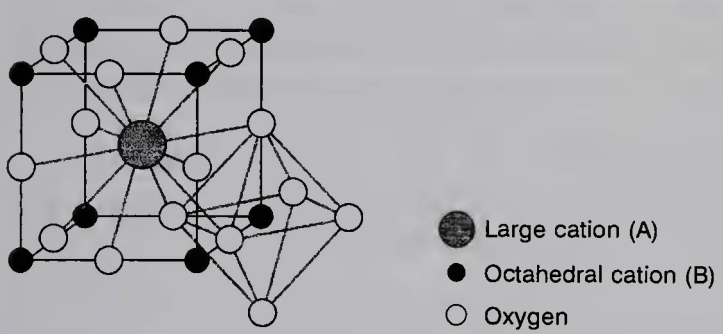

Fig. 4.9-1 The perovskite structure adopted by many ABO_3 compounds.

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occur in mechanically mixed reactants at elevated temperatures and, in general, this allows precise control of the product's stoichiometry. An alternative approach involves the precipitation of a precursor, which can easily be converted to the final product by heating. This method assures intimate cation mixing prior to heating such that lower temperature my often be used for the final heating stage. In this experiment, both methods are used.

$CaMnO_3$, $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ are prepared from precipitated precursors, whereas $YBa_2Cu_3O_7$ is prepared from a mechanical mixture of Y_2O_3, $BaCO_3$ and CuO. For $YBa_2Cu_3O_7$, it is not easy to ensure the correct cation ration by simple precipitation methods, and a ceramic grinding and sintering technique is preferred. $CaMnO_3$ is a paramagnetic insulator at room temperature, whereas $La_{0.85}Sr_{0.15}MnO_3$ is paramagnetic but electrically conducting, and $La_{0.7}Sr_{0.3}MnO_3$ is both electrically conducting and ferromagnetic. $YBa_2Cu_3O_7$ is metallic at room temperature, but becomes a superconductor with zero resistance to d.c. currents below 93K. Superconductors are perfectly diamagnetic, and it is this property which is examined in this experiment.

Special Safety Precautions

Barium salts are very toxic. Due to the involatile nature of the barium compounds studied in this experiment, the use of a fume cupboard is unnecessary, but care should be taken to avoid ingestion during all handling operations.

4.9.1 Experimental

a) $YBa_2Cu_3O_7$

If is preferable to use reagents (Y_2O_3, CuO, $BaCO_3$) which have been dried (e.g. 2 hours at 400 °C in a muffle furnace). Accurately weigh out about 0.5 g of $BaCO_3$ and the corresponding amounts of Y_2O_3 an CuO to give a Y:Ba:Cu ratio of 1:2:3 (0.1430 g and 0.3023 g respectively for 0.5000 g of $BaCO_3$). Grind the materials together in a clean pestle and mortar until no white steaks are observed on grinding (ca. 10 min). Press 1 or 2 pellets (1–2 mm thick, 13 mm diameter) of the mixture at ca. 5000 kg and place the pellets in an alumina boat. Using a furnace with a programmable controller, subject the pellects to the following thermal programme in air:

1. Heat to 930 °C and hold for 12 hours
2. Cool to 500 °C and hold for 1 hour
3. Cool to 400 °C at 50 °C h^{-1}
4. Cool to room temperature

When the furnace temperature is below 400 °C, the samples may be removed using tongs and placed on an insulating board until cold.

b) $CaMnO_3$

Dissolve 2.36 g of $Ca(NO_3)_2 \cdot 4H_2O$ and 2.87 g of $Mn(NO_3)_2 \cdot 6H_2O$ in 50 cm^3 of distilled water. Whilst stirring the solution (magnetic stirrer), slowly add 100 cm^3 of 1 M KOH using a separating funnel (about 3 min). After standing for 15 minutes, the brown precipitate should be filtered using a large Büchner funnel and washed thoroughly with distilled water (to remove excess KOH and KNO_3). Pump the sample as dry as possible, transfer to a watch glass and dry at 200 °C in a drying oven (ca. 1 hour). Grind the sample and press two pellets 1–2 mm thick. The pellets should be placed in a porcelain or alumina boat and heated at 1000 °C for about 12 hours. When the furnace has cooled to below 400 °C, the boat may be removed using tongs and placed on an insulating board until cold.

c) $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$

Repeat the procedure described for $CaMnO_3$, but use the following reagents:

$La_{0.85}Sr_{0.15}MnO_3$: 3.68 g of $La(NO_3)_3 \cdot 6H_2O$; 0.32 g of $Sr(NO_3)_2$;
2.87 g of $Mn(NO_3)_2 \cdot 6H_2O$

$La_{0.7}Sr_{0.3}MnO_3$: 3.03 g of $La(NO_3)_3 \cdot 6H_2O$; 0.63 g of $Sr(NO_3)_2$;
2.87 g of $Mn(NO_3)_2 \cdot 6H_2O$.

d) Physical Properties

Place one of the pellets of each oxide in turn on a piece of paper and note its behaviour when a bar magnet is placed under the paper. Cool the pellet of $La_{0.85}Sr_{0.15}MnO_3$ in liquid nitrogen using nylon forceps and re-examine its response to the magnet. If necessary, the pellets may be ground in order to examine the magnetic properties. Grind one of the pellets of $CaMnO_3$ using a clean pestle and mortar. Determine the magnetic susceptibility and effective magnetic moment of Mn^{4+} using any suitable method (e.g. a Johnson Matthey magnetic balance).

Cool one of the pellets of $YBa_2Cu_3O_7$ in liquid nitrogen, and quickly place a small magnet (Nd-Fe-B or Sm-Co) above it. The diamagnetic properties of a superconductor should allow you to float the magnet above the sample.

For each sample, measure the electrical resistance of one of the pellets using a suitable method (qualitatively, differences should be observable using a simple DVM in resistance mode, but quantitative measurements will require the use of a conventional 4-probe dc method, if available).

$CaMnO_3$ gives an X-ray powder diffraction trace with the first six reflections at 2υ values of 23.85°, 34.00°, 41.93°, 48.83°, 55.06° and 60.82° (wavelength 1.542 Å). If X-ray diffraction facilities are available, the pattern can be recorded for the $CaMnO_3$ sample prepared. Confirm the primitive cubic structure of perovskite and determine the unit cell size.

4.9.2 Exercises

The structures of all four compounds are related to perovskite (Fig. 4.9-1). If available, a model of the structure should be examined. There are two independent cation arrays: the first consists of octahedrally coordinated ions, which are Ti^{4+} in the parent $CaTiO_3$ and Mn/Cu ions in the compounds synthesised; the second array has 12-coordinate ions which are Ca^{2+} in $CaTiO_3$, La/Sr in $La_{0.85}Sr_{0.15}MnO_3$, etc. In fact, the Mn perovskites prepared all show minor deviations from the ideal cubic structure, due to size and electronic effects.

For an ideal, undistorted perovskite ABO_3 in which each cation (ionic radii r_A and r_B) contacts the coordinating O^{2-} ions (radius r_O), show that

$$r_A + r_B = \sqrt{2}\,(r_B + r_O)$$

Generally, some tolerance is allowed such that

$$r_A + r_B = t\sqrt{2}\,(r_B + r_O)$$

where the tolerance factor t is 0.8–1. For undistorted perovskites, t is high, e.g. 0.99 for $SrTiO_3$. From a table of ionic radii, determine t for $CaMnO_3$.

Mn^{3+} has the electron configuration $t_{2g}^3\, e_g^1$ and is therefore likely to show a substantial Jahn-Teller distortion. In fact, the distortion is cooperative as shown in Figure 4.9-2. In the layer shown, for example, each Mn has 2 short Mn-O bonds and 2 long bonds. If the O ions above and below the Mn ions have short bonds, all the Mn ions can achieve a similar distorted stereochemistry. Explain why the distortion shown in Figure 4.9-2 should stabilise the structure.

The electrical and magnetic properties of Mn perovskites are critically dependent on the Mn oxidation state. What is the formal oxidation state of Mn in $CaMnO_3$, $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$? The conductivity of many transition metal oxides may be related to a simple mechanism involving the hopping of electrons between two

$$\chi_a = \mu^2/8T$$

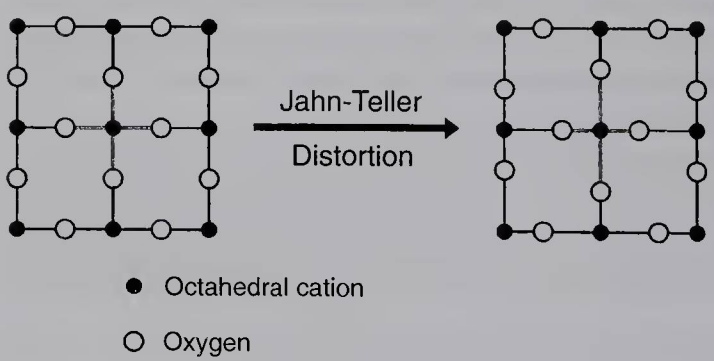

Fig. 4.9-2 Cooperative Jahn-Teller distortions in a layer of the perovskite structure.

transition metal ions. Using such a mechanism and considering the energy involved when an electron hops from one Mn ion to a neighbouring Mn ion, explain the difference in conductivity between $CaMnO_3$, $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$. In the determination of the effective magnetic moment, μ_{eff}, for Mn^{4+}, the Curie Law is used:

$$\chi_a = \mu^2/8T$$

Compare your value μ_{eff} with μ_{so}, the spin-only moment, which is the magnetic moment expected if only electron spins contribute to μ_{eff}. The main reason for the disagreement is that $CaMnO_3$ is antiferromagnetic at low temperatures (T_N *ca.* 120 K). Interactions between magnetic moments are still apparent at higher temperatures and result in an apparent reduction in μ_{eff} due to a deviation from the Curie Law:

$$\chi_a = \mu_{so}^2/8(T + \theta)$$

Using your value of χ_a and the formula above, determine a value for θ.

Notice that whereas $CaMnO_3$ is antiferromagnetic, $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ are ferromagnetic. What do your measurements on $La_{0.85}Sr_{0.15}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ tell you about the change in Curie temperature (associated with the onset of ferromagnetic behaviour) with Mn oxidation state in this system?

Superconductors are materials which lose all electrical resistivity below a certain temperature, the critical temperature, T_c; above T_c, they are generally metallic in nature. Until 1986, when "high temperature superconductors" were discovered, the highest T_c was 23 K for Nb_3Ge. $YBa_2Cu_3O_7$ was the first material discovered with T_c above the temperature of liquid nitrogen, 77 K. When pure, and having its maximum possible oxygen content, this material becomes superconducting at 93 K. An important property of superconductors is that below T_c, magnetic fields are expelled from within the material – it becomes a perfect diamagnet. This is achieved by

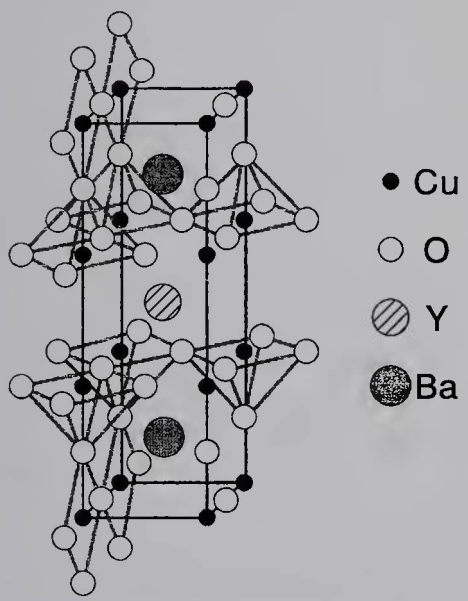

Fig. 4.9-3 The unit cell of $YBa_2Cu_3O_7$ highlighting the Cu stereochemistry.

setting up currents on the surface of the bulk material to oppose the applied magnetic field. In this way, it is possible to float a superconductor above strong magnets, using the induced opposing field for levitation.

The structure of $YBa_2Cu_3O_7$ (Fig. 4.9-3 and model if available) comprises three perovskite-like unit cells in a row; the Y and Ba ions occupy the large cation positions but in this material, not all the oxygen sites are occupied, which reduces the coordination numbers for all the cations. Layers of 5-coordinate (square pyramidal) and chains of 4-coordinate (coplanar) Cu ions are formed. What is the ratio of 5-coordinate Cu to 4-coordinate Cu in the structure (remember that certain sites in the unit cell are shared with other unit cells)? What is the ratio of Cu^{2+} to Cu^{3+} ions in $YBa_2Cu_3O_7$? A square pyramidal crystal field influences the *d*-orbital energies of a transition-metal ion in the same way as an elongated octahedral (tetragonal) field, which is common for Jahn-Teller distorted ions. On the basis of Crystal Field Theory, discuss the preferred distribution of the Cu^{2+} and Cu^{3+} ions between the available sites in $YBa_2Cu_3O_7$.

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4.10
Polyoxomolybdate Clusters: Nanoscopic Wheels and Balls

Leroy Cronin, Ekkehard Diemann, and Achim Müller

Inorganic metal-oxygen cluster anions form a class of compounds that is unique in its topological and electronic versatility and is important in several disciplines. Names such as Carl Wilhelm Scheele, Jöns Jakob Berzelius, Alfred Werner and Linus Pauling appear in the early literature of this field. These clusters, so-called isopoly- and heteropolyanions, contain highly symmetric core assemblies (coordination polyhedra) of MO_x units (M = V, Mo, W) and often adopt spherical structures based on Achimedean and Platonic solids of considerable topological interest. Understanding the driving force for the formation of high-nuclearity clusters is still a formidable challenge.

Polyoxometallates are especially common amongst the group VIA metals. In aqueous solution they have a rich pH dependent chemistry where the ions are able to polymerise through sharing of edges and/or corners of the metal oxygen polyhedra. For example, the acidification of a solution of molybdate gives rise to fragments which increase in nuclearity as the pH of the solution decreases (Scheme 4.10-1).

$$7\ [MoO_4]^{2-} + 8\ H^+ \rightleftharpoons [Mo_7O_{24}]^{6-} + 4H_2O$$

$$8\ [MoO_4]^{2-} + 12\ H^+ \rightleftharpoons [Mo_8O_{26}]^{4-} + 6\ H_2O$$

$$36\ [MoO_4]^{2-} + 64\ H^+ \rightleftharpoons [Mo_{36}O_{112}]^{8-} + 32\ H_2O$$

Scheme 4.10-1 Formation of polyoxomolybdates at low pH in aqueous solution.

The molybdenum polyoxometallates (polyoxomolybdates) are particularly interesting because they exhibit a vast number of structures due to the various sharing and linking of co-ordination polyhedra. This is especially the case under reducing conditions as these support protonation due to related increase of higher electron density at the O atoms. Note: The largest polymolybdate under non-reducing conditions is $[Mo_{36}\ O_{112}]^{8-}$.

Figure 4.10-1 depicts a set of polyhedra or related building groups like $\{Mo_8\}$ present in the $[Mo_{36}O_{112}]^{8-}$ anion. The central polyhedron is a pentagonal bipyramid which is linked via edges with five octahedral polyhedra.

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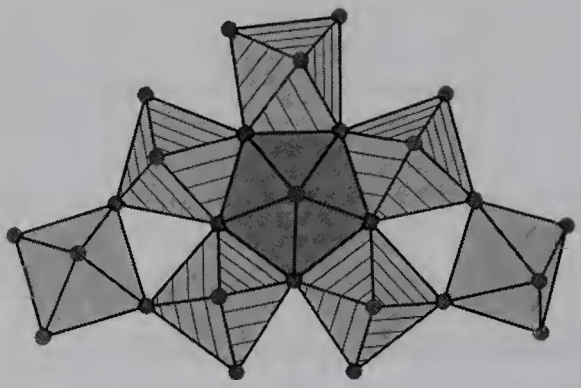

Fig. 4.10-1 A polyhedral representation of a section of aggregated polyhedra found in the $[Mo_{36}O_{112}]^{8-}$ anion while the $\{Mo_8\}$ building group shown is also present in the larger wheel system. The Mo(VI) ions (not shown) are at the centres of the polyhedra with the oxygen ligands at the corners, represented by black spheres.

Considering the number of potential combinations of polyhedra it is not surprising that such systems form a bewildering number of anions (Mathematicians would call it combinatorial explosion). The main control parameters in the synthesis of such anions appear to be pH, ionic strength, molybdate concentration, type of electrolyte, and, particularly important for the compounds reported here, the concentration and type of the reducing agent. By reduction the overall negative charge of the anion is increased which results in an increase of the charge density mainly on some of periphery type oxygen atoms which might then be protonated and thus get susceptible for a further condensation step. Another choice could be spin-pairing between two reduced, neighboured metal atoms, thus forming a metal-metal bond. It can be imagined that the situation opens a vast number of possibilities for linking and growing new exciting structures and even more if hetero atoms are included. Carl Wilhelm Scheele first documented solutions of strongly acidified reduced molybdate, so called *molybdenum blue* solutions, already in 1783. However the true nature of the system eluded scientists for well over two hundred years. In one of the following two experiments material will be crystallised from a *molybdenum blue* solution – this was first achieved in experiments by the group in Bielefeld in 1995. In the second experiment a giant polyoxomolybdate is obtained on the base of a higher pH value.

We report here the syntheses of two aesthetically beautiful nanoscale polyoxomolybdates of the type $\{Mo_{11}\}_n$ which have spherical (n = 12) or circular (n = 14) shape, i.e. molybdenum blue type which were highlighted worldwide in newspapers and magazines. In spite of their completely different structure (see Fig. 4.10-2), they have similar $\{Mo_{11}\}$ type building blocks which results in an almost equivalent stoichiometry. In the ball type cluster the $\{Mo_{11}\}$ group has necessarily the high C_5-symmetry, as 12 of these span an icosahedron. It should be mentioned that it is a difficult task to determine the complete formula of a compound like the wheel type species with a protonated, mixed-valence anionic species of the class II or III type (classification according to Robin and Day) with rather high molar masses, mainly if a very low concentration of (crystallographically) disordered cations in the lattice complicates additionally the determination of the correct anion charge. The accuracy of the usual analytical determinations often does not suffice to answer this question directly.

In the case of the circular 'molybdenum blue' compound the general synthetic strategy involves the strong acidification (pH~1) of an aqueous molybdate(VI) solu-

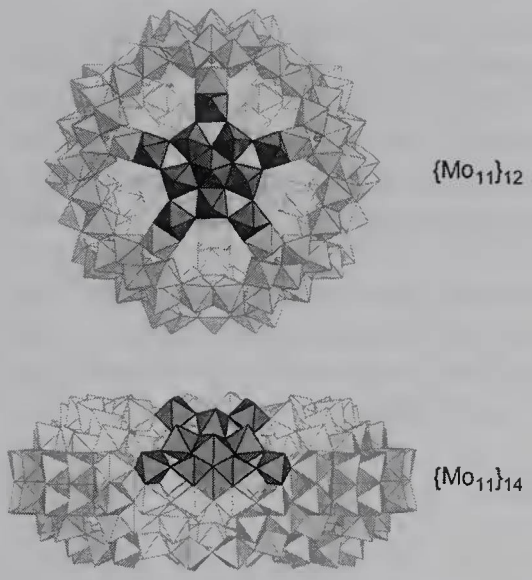

Fig. 4.10-2 Comparison of the $\{Mo_{11}\}_{14}$-type "Giant Wheel" (side view) with the $\{Mo_{11}\}_{12}$-type "Giant Ball" cluster.

tion and its subsequent treatment with an reducing agent like iron powder, tin(II) chloride, molybdenum(V) chloride, ascorbic acid, cysteine, hydroxylamine, hydrazine, hypophosphite, dithionite etc.. On the other hand, an icosahedral ball-shaped cluster can be formed in an aqueous molybdate(VI) solution at higher pH values ranging from 2–4 in the presence of an appropriate bridging ligand, e. g., acetate which in effect stabilises the dinuclear $\{Mo_2^V\}$ units (see below) formed upon reduction.

Special Safety Precautions

1. Sodium molybdate salts: irritant.
2. Sodium dithionite: irritant, can liberate toxic gas (handle in fume hood).
3. $Ce(IV)(SO_4)_2$: corrosive (handle with gloves).
4. Hydrochloric and sulfuric acid: toxic, corrosive (handle with gloves in fume hood).
5. Hydrazinium sulfate is assumed to be carcinogenic (handle with gloves in fume hood).

4.10.1 Experimental

a) Preparation of the "Giant Wheel" Type Compound

Dissolve 3.0 g (12.4 mmol) of $Na_2MoO_4 \cdot 2H_2O$ in 13 ml water (use 100 ml Erlenmeyer flask) and then add *freshly powdered* $Na_2S_2O_4$ (0.2 g, 1.15 mmol) to the solu-

tion under continuous stirring (hint: be sure to use fresh $Na_2S_2O_4$). The colour changes to light yellow. Under continuous stirring 30 ml of hydrochloric acid (1 M) are added dropwise (use a burette). The resulting solution should turn to dark blue colour. After stirring for 10 more minutes flush the flask through with either nitrogen or argon for 5 minutes before removing the stirrer and closing the flask with an airtight stopper. Be sure to leave the flask in a place undisturbed at ca. room temperature for a minimum of 24 hours. After this time the solution should have precipitated a quantity (ca. 1 g) of blue, slightly oblique, rectangular crystals. Carefully isolate the crystalline material by filtration and wash the crystals with a small amount of cold water (care, these crystals are highly soluble in water!). Note the yield and store the crystals in a closed flask under nitrogen or argon.

Analysis of the "Giant Wheel" Type Compound

Deduction of the unit cell of the crystals gives the space group P-1 with $a = 30.785(2)$, $b = 32.958(2)$, $c = 47.318(3)$ Å, $\alpha = 90.53(1)$, $\beta = 89.86(1)$, $\gamma = 96.85(1)$, $V = 47665(6)$ Å^3. Determination of the structure of the crystals reveals that the unit cell comprises two non-equivalent cluster rings with 154 and 152 Mo atoms (Fig. 4.10-3). (The last one has a defect, with one $\{Mo_2\}$ group less, while the minor difference between both species will not be considered here.) The giant anion ring is *ca.* 34 Å wide (outer width) with an inner cavity of *ca.* 20 Å and is *ca.* 15 Å thick, being mostly composed by octahedrally coordinated Mo centres with Mo in either the VI or V metal oxidation state and different functionalities of the oxygen atoms. The formal aggregation of these units can be rationalised by dividing the system into repeating building blocks as shown in Figure 4.10-3. The building block principle adopted in Figure 4.10-3 means that the overall anion can be described as being composed of fourteen $\{Mo_8\}$,

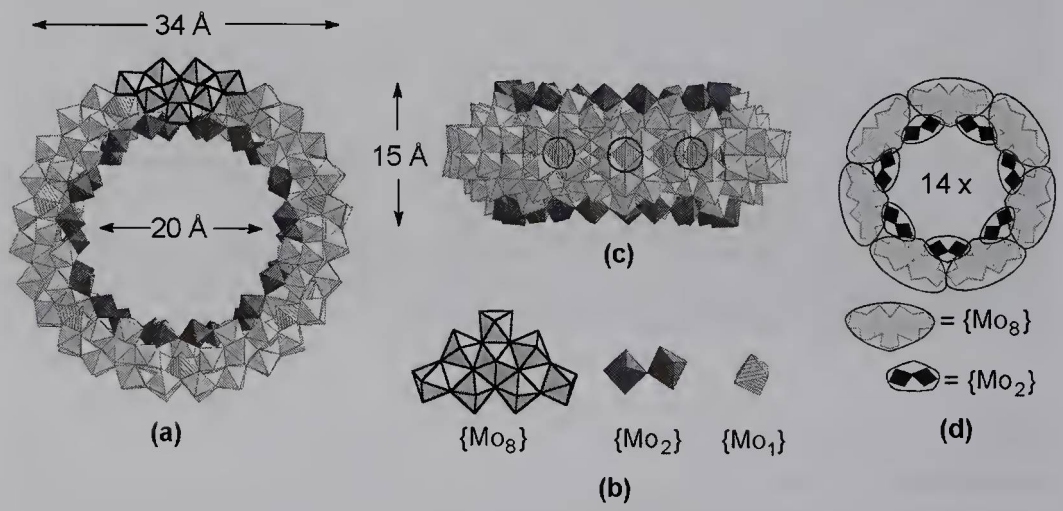

Fig. 4.10-3 Top and side views of the giant-ring shaped anion with the metal coordination sphere drawn as polyhedra (a), while the $\{Mo_8\}$, $\{Mo_2\}$ and $\{Mo_1\}$ building blocks are shown separately for clarity (b). The positions of the $\{Mo_1\}$ building blocks in the equator of the ring are highlighted with circles in the side view (c). A cartoon representation of the top half of the ring showing how the $\{Mo_8\}$ and $\{Mo_2\}$ building blocks are connected (d).

$\{Mo_2\}$ and $\{Mo_1\}$ fragments. The top half of the ring is shown as a cartoon (right-hand-side) and can be clearly seen to comprise seven $\{Mo_8\}$ and $\{Mo_2\}$ groups on the top side with the fourteen $\{Mo_1\}$ groups (not shown in the cartoon) occupying the equator of the ring. The complete ring is constructed when the bottom half (also comprising seven $\{Mo_8\}$ and $\{Mo_2\}$ groups) is rotated around 360/14° relative to the first and fused to it through the fourteen $\{Mo_1\}$ groups. The formula of the compound is: $Na_{15}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]_{0.5}$ $[Mo^{VI}_{124}Mo^{V}_{28}O_{457}H_{14}(H_2O)_{68}]_{0.5}$ · ca. 400 H_2O. The positions of the coordinated water molecules and bridging hydroxides can be determined from a single-crystal X-ray structure analysis especially by bond-valence calculations, but it is not possible to determine the number of sodium ions present in the cell due to disorder of these ions.

The IR spectrum shows peaks (in cm^{-1}) at 1616 (m) ($d(H_2O)$), 975 (m), 913 (w-m) (ν(Mo=O)), 820 (sh), 750 (s), 630 (s), 555 (s) (s = strong, m = medium and w = weak intensity; sh = shoulder). The electronic absorption spectrum is dominated by two bands characteristic for all *molybdenum blue* species (in H_2O/HCl, pH = 1): λ_{max} [nm] $\varepsilon_{max}[M^{-1}cm^{-1}]$ = 745 ($1.8 \cdot 10^5$), 1070 ($1.4 \cdot 10^5$). These bands have to be assigned to intervalence Mo^V/Mo^{VI} charge transfer transitions (IVCT). The second ε value corresponds because of a linearity relation to the abundance of altogether 28 Mo^V centres. Using an excitation within the contour of the 1070 nm band gives rise to a *Resonance Raman Spectrum*. It shows five bands at 802 (s), 535 (m), 462 (s), 326 (s) and 215 (s) cm^{-1} and is also characteristic for all *molybdenum blue* species.

Analytical Exercises

Although a reasonable formula for the anion may be determined using the crystallographic data, the number of sodium ions and the number of Mo(VI)/Mo(V) centres cannot.

1. Determine, if possible, the number of water solvent molecules present in the sample using thermogravimetric analysis to confirm or adjust the number of water solvent molecules deduced using crystallography. Keep a part of the sample open on your desk for two hours and a second part for four hours. Repeat the thermogravimetry on these samples. From the results try to extrapolate approximately the loss of water due to weathering to t = 0.
2. Determine the number of sodium ions per cluster by performing a sodium analysis using a suitable method (e.g. by flame photometry or potentiometrically with a sodium selective electrode).
3. Determine the number of Mo(V) ions per ring by conducting several redox titrations. This can be achieved by dissolving between 50 and 100 mg of the material in ca. 50 ml of water (flushed with nitrogen or argon for some minutes). Then by monitoring the solution with a redox electrode, titrate the blue solution with a 0.01 M solution of $Ce(IV)(SO_4)_2$ in 0.5 M of H_2SO_4. By carefully recording the voltage (this should be of the order of 400 mV) as a function of volume of Ce(IV) solution added it should be possible to determine the total number of Mo(V) centres present. The

end-point of the titration is characterised by a potential jump (e.g. from around 400 mV to 1100 mV) at the point when all the Mo(V) centres present have been oxidised (the solution will also no longer be blue!). Record the volume of Ce(IV) added at this point and continue adding past this point whilst still recording the voltage to ensure that all the Mo(V) is oxidised (if the potential jump continues adjust the end point accordingly). Analyse these data graphically to confirm the end point position and determine the volume of the Ce(IV) solution added at the end point.

Using the above results, including the crystallographically deduced formula as a basis, to calculate the number of Mo(V) centres per formula unit and the charge of the ring-cluster anion. Discuss the significance of any possible errors or discrepancies in the results you have obtained and possible approaches to overcoming them.

b) Preparation of the "Giant Ball" Type Compound

0.8 g (6.1 mmol) hydrazinium sulfate is added to a solution of 5.6 g (4.5 mmol) ammonium heptamolybdate tetrahydrate and 12.5 g (162 mmol) ammonium acetate in 250 ml water under stirring, and finally after stirring for 10 min 83 ml of 50% (v/v) acetic acid (use a 500 ml Erlenmeyer flask). The deep green reaction mixture is then kept at room temperature without further stirring for four days (colour change to dark brown) and then filtered through a glass frit (pore size G2). The reddish-brown crystalline residue is washed with 90% ethanol, then with a 1:1 mixture of ethanol/diethyl ether and finally dried in air. The yield is about 3 g.

Analysis of the "Giant Ball" Compound

The formula determined for this product is $(NH_4)_{42}[\{Mo^{VI}(Mo^{VI}{}_5O_{21})(H_2O)_6\}_{12}\{(Mo^{V}{}_2O_4)(CH_3COO)\}_{30}] \cdot$ ca. 300 $H_2O \cdot$ ca. 10 CH_3COONH_4 (The anion has the general formula $[\{pentagon\}_{12}\{linker\}_{30}]^{42-}$). It forms octahedral and truncated octahedral crystals which crystallize cubic (space group Fm-3) with a = 46.0576(14) Å. The IR spectrum (Nujol suspension) shows peaks (in cm^{-1}) at 1626 (m) ($\delta(H_2O)$), 1546 (m) ($\nu_{as}(COO)$), 1440 (sh), 1407 (m) ($\delta(CH_3)$, $\nu_s(COO)$, $\delta_{as}(NH_4^+)$), 969 (m), 936 (w-m) ($\nu(Mo{=}O)$), 853 (m), 792 (s), 723 (s)and 567 (s). Due to the very high symmetry of the cluster anion only very few Raman bands are observed (may be assigned to symmetric vibrations): 953 (m), 935 (m), 875 (s) ($\nu(Mo{=}O)$, ca. 845 (sh), 374 (m-s), 314 (m) and 212 (w) cm^{-1}. The electronic absorption spectrum (H_2O/CH_3COOH, pH=4) shows only one intense band at 450 nm.

Analytical Exercises

1. Determine the number of ammonium cations per formula unit (you may either use a classical Kjeldahl setup without employing Devarda's alloy (why not?) or an ammonium sensitive electrode).
2. Determine the number of reduced Mo centres per formula unit using the cerimetric procedure as explained above.

3. If possible, obtain a X-ray powder pattern from the finely ground sample (which is not easy because this may lead to loss of crystal water and crystallinity). Try to index the pattern on the basis of the unit cell dimensions given above. What is the effect of *large* and *symmetric* cells on the appearance of such patterns. – The lattice is made up from almost perfect spherical entities. What kinds of packing would be possible? (hint: compare with close packing of metals). Could you relate the crystal symmetry to its morphology?
4. If possible, measure the magnetic susceptibility of the finely ground sample at room temperature (either with a magnetometer or even with a simple magnetic balance of the Evans type). Can you give an explanation for your findings?

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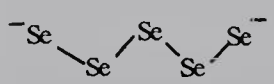
4.11
Reaction of Alkali Metal Polyselenides and Polytellurides with Group 6 Metal Carbonyls

Joseph W. Kolis

The polyatomic dianions of the group 16 elements selenium and tellurium have been known for a very long time. These highly coloured compounds can be made easily by the reduction of the elements with alkali metals in liquid ammonia, or by direct reaction of the elements at high temperatures. Once prepared, these salts are quite soluble and stable in a number of polar solvents including water, alcohols, acetonitrile and dimethylformamide (DMF). However, they are extremely sensitive to oxidation and should be protected from air at all times, especially in solution. In solution, a number of extremely complex and poorly understood equilibria dominate the chemistry of these species. In general, any solution of these anions is best thought of as a mixture of the various possible chain lengths (E_n^{2-}) where E is S, Se, Te and $n = 2–8$) like



These anions can be readily crystallised as pure salts by the addition of large organic counterions such as $[Ph_4P]^+$ and $[Et_4N]^+$. The chain length of the anions in the salts are much more dependent upon the counterion and solvents than the nominal identity of the alkali metal salt used as starting material.

Despite the ancient lineage and ease of preparation of these unusual polyatomic anions, their chemistry has been very poorly developed until recently. However, the last eight years has seen an explosive growth of the complexation chemistry of these anions with transition metals in particular. In fact their chemistry is often substantially different than that of the better known polysulfides. One specific class of transition metal complexes which have a very rich and diverse coordination chemistry with the polychalcogenides is the simple metal carbonyls. In this experiment, the preparation of a salt of each of the polychalcogenides will be carried out, and their reactions with $Mo(CO)_6$ and $W(CO)_6$ investigated. The resultant products will be characterized by IR and visible spectroscopy. It will be seen that polyselenides readily oxidise the metal centre to its highest oxidation state, leading to complete loss of all CO ligands and formation of the well known tetrathio and tetraseleno-metalates.

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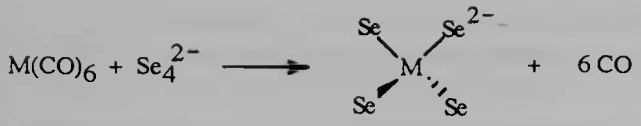
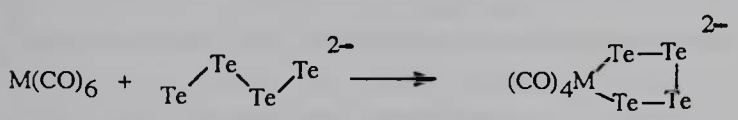


In contrast, the polytellurides do not oxidise the metal centre, but merely replace two CO ligands forming a chelating complex.



Special Safety Precautions

1. Alkali metals are very strong reducing agents and can burn in the presence of protic solvents such as water or alcohols.
2. Ammonia is a gas at room temperature with a vapor pressure of approximetely 10 atmospheres. Thus, is closed systems, it should be handled with extreme care. Any glass vessel containing liquid ammonia should always be kept below the boiling point of ammonia (–33 °C)
3. Ammonia solutions containing dissolved alkali metals are unstable and slowly decompose to form the alkali metal amide and H_2. Thus, care should always be taken to adequately vent any closed system from time to time to prevent H_2 buildup. The decomposition reaction is catalysed by trace amounts of water or other basic impurities. If clean, dry glassware is used initially, the H_2 buildup should be quite slow.
4. Transition metal carbonyls are quite toxic and should always be handled in a well vented fume cupboard. Also, CO will be produced in the experiment so flasks and vacuum pumps should also be in well vented areas or in a fume cupboard.
5. Any time vacuum and Schlenk lines are used, there is a finite possibility of breakage so eye protection should be worn at all times.

4.11.1 Experimental

a) Na_2E_4 (E = Se, Te)

All the alkali metal polychalcogenides can be prepared in the same manner and the preparation of Na_2Se_4 is detailed here. Two clean, dry flasks are attached to the vacuum line, one containing a small pellet of Na and the other containing 0.145 g (6.3 mmol) Na, 1.0 g (12.6 mmol) selenium powder and a magnetic stir bar. Both

flasks are evacuated and the second flask sealed off temporarily. Approximately 15 ml of ammonia from a storage cylinder is distilled into the first flask using an acetone slush bath. The storage cylinder is closed off. The ammonia solution is allowed to warm slightly to form the inky blue solution characteristic of solvated electrons. The second flask is now opened to the line and the ammonia is transferred into it again using an acetone slush bath. WARNING: This is a closed system and the pressure should constantly be monitored using a Hg manometer or other pressure sensing device. If the pressure begins to approach one atmosphere, both flasks should be cooled and the vacuum line manifold evacuated before more ammonia is distilled. Once all the ammonia is transferred, the second flask is evacuated one more time, sealed and placed on a magnetic stirrer in a low Dewar flask with an isopropanol or acetone slush. The reaction is stirred for 45 minutes, with care being taken to replenish the slush in the cooling bath. The reaction should probably be done behind a blast shield or in a fume cupboard, although there is little danger of breakage if the flask is kept cool by the bath. After a while, the solution should begin to assume a characteristic colour, reddish orange for polysulfide, dark greenish red for polyselenide and deep purple for polytelluride. After 45 minutes to 1 hour, the flask is placed back on the vacuum line and the ammonia evacuated into the first flask which is removed to a fume cupboard where it is vented to the air and the ammonia allowed to evaporate. The second flask is subjected to dynamic vacuum for 10 minutes to remove the last traces of ammonia. Remaining in the flask should be a dry powder of the appropriate sodium polychalogenide (yellow-orange for Na_2S_4 and dark grey for Na_2Se_4 and Na_2Te_4). If an adequate glove box is available, the solids can be transferred to clean, dry storage ampoules and stored under nitrogen for use at a later time. If this is not convenient, the powder can be stored in the closed flask under N_2 until it is used for further reactions.

b) $[PPh_4]_2[MSe_4]$ (M = Mo, W)

The student can choose between any combination of $Mo(CO)_6$ or $W(CO)_6$ and polyselenide. If desired, the same chemistry takes place with polysulfides and these could be used in a similar fashion. The reactions are performed in exactly the same way in each case. A detailed procedure is given for the preparation of a $MoSe_4^{2-}$ salt.

In a glove bag, a 100 ml Schlenk flask is charged with 200 mg (0.76 mmol) $Mo(CO)_6$, 274 mg (0.76 mmol) Na_2Se_4 and stir bar. The flask is attached to a Schlenk line and evacuated and purged with N_2 several times. Using a cannula or gas tight syringe, 12–15 ml DMF is added to the flask. The DMF should have previously been dried and de-airated by storage for 24 hours over activated sieves and bubbled for 30 minutes with N_2. After the DMF is added, the flask should be evacuated (very important!) and sealed off. The flask is transferred to an oil bath or heating mantle and heated at 90 °C for 1 hour. Although you are heating a closed system, the boiling point of DMF is 153 °C so if the flask is evacuated properly, little pressure is generated within. Also, the small amount of CO produced will not be sufficient to strain the glass flask. However, to be safe, the flask can be reattached to the Schlenk line once or twice during heating and carefully evacuated before returning it to the heat.

If desired, the reaction can also be monitored during this time by withdrawing a small aliquot and obtaining an IR spectrum to watch the disappearance of bands in the CO stretching region (2100–1700 cm^{-1}).

After some heating, the reaction mixture will begin to undergo a noticable colour change. A combination of $Mo(CO)_6$ and polysulfide will change from greenish blue to orange, while the corresponding reaction with polyselenide changes from brown-green to blue. The tungsten analogues are yellow and cherry red for sulfide and selenide respectively. Once the reaction is complete, the flask is removed from the heat and allowed to cool. The flask is repurged with N_2 and, against the flow of N_2, 650 mg (1.50 mmol) PPh_4Br is added to the mixture. The solution is stirred for 5 minutes to allow the counterion salt to dissolve, then filtered into a clean Schlenk flask under N_2 using a fritted Schlenk filter. De-aerated THF (10 ml) is added to the mixture to cause slow precipitation of the metal chalcogenide complex. To prevent the product from forming an oil, the THF is added via syringe and allowed to roll very *slowly* down the inside of the flask so as to form a second layer of THF on the DMF solution. The flask is placed in a refrigerator overnight, taking care not to disturb the two layers. The layers will slowly mix and the THF will cause precipitation of well formed crystals of the product. Occasionally, white crystals of NaBr will precipitate first and contaminate some of the product. These can be removed by Schlenk filtration and discarded. A fresh 10 ml layer of THF and storage overnight will lead to formation of a new crop of the desired product. The crystals are isolated by Schlenk filtration of the solution, which can then be discarded. The product is washed with a 3 ml aliquot of THF and dried by pumping on the Schlenk line. The compounds $[PPh_4]_2[ME_4]$ can be handled in the air for short periods of time but any prolonged manipulation should be done under a protective nitrogen atmosphere. The salts can be characterised by IR and visible spectroscopy, and the results compared to the values in Table 4.11-1. The compounds are quite stable as their salts if stored under a protective atmosphere of N_2.

Table 4.11-1 Spectroscopic data.

	IR (cm^{-1})	UV-Vis (nm)
MoS_4^{2-}	458	467, 317
$MoSe_4^{2-}$	255	555, 359
WS_4^{2-}	480	392, 277
WSe_4^{2-}	281	463, 316
$[Cr(CO)_4Te_4]^{2-}$	1951, 1850, 1821, 1778	
$[Mo(CO)_4Te_4]^{2-}$	1971, 1950, 1821, 1780	
$[W(CO)_4Te_4]^{2-}$	1971, 1950, 1821, 1780	

c) $[PPh_4]_2[M(CO)_4Te_4]$ (M = Cr, Mo, W)

These chelate complexes can be prepared using a procedure exactly analogous to that for the formation of the ME{th,4,2-} salts prepared above. However, the polytelluride does not induce oxidative decarbonylation of the metal centre, but merely sub-

stitutes two *cis* CO ligands. In this case, $Cr(CO)_6$ can also be chosen as a starting material. ($Mo(CO)_6$ can be used but the Mo containing product often does not crystallise well.) The synthesis and workup occurs exactly as described above except that the solution colour changes from dark purple to dark brown. Also, two 10 ml layerings of THF are usually needed to induce crystallisation. The product can be isolated as described above, but it is more air sensitive than the ME_4^{2-} salts, so it should be handled under N_2 at all times. The IR spectrum in the CO stretching reagion is quite distinctive and contains the four bands predicted for a molecule with C_{2v} symmetry.

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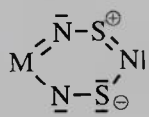
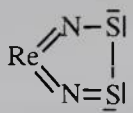
4.12
Chlorothionitrene and Cyclothiazeno Complexes of Tungsten

Kurt Dehnicke

Chlorothionitrene complexes are compounds with the $\left[\underline{\overline{N}}=S^{/Cl}\right]^{2-}$ ligand, which is unknown as a free ion. Examples are prepared from molybdenum, tungsten, rhenium, ruthenium and osmium. They can easily be prepared by reaction of metal chlorides like $MoCl_5$ or WCl_6 with $(NSCl)_3$, which is in equilibrium with its monomer in solution. The reactions with metal chlorides are thus accompanied by the redox reaction $NSCl + 2e^- \rightarrow [NSCl]^{2-}$. Chlorothionitrene complexes are useful precursors for the syntheses of nitrido complexes, thionitrosyl complexes as well as of cyclothiazeno complexes.

Metallacyclothiazeno complexes are heterocycles of the type  with planar six-membered rings, delocalised N-S bonds and metal-nitrogen double bonds. Examples are known from vanadium, molybdenum and tungsten, whilst with rhenium the heterocycle  is formed.

Special Safety Precautions

1. Tungsten hexachloride (WCl_6) and tungsten oxotetrachloride ($WOCl_4$) should be regarded as air and moisture sensitive and thus likely to hydrolyse to HCl (which is toxic by inhalation) and $WO_3 \cdot nH_2O$.
2. Chlorothionitrene tungsten tetrachloride ($[Cl_4W(NSCl)]_2$) and cyclothiazeno tungsten trichloride $[Cl_3W(N_3S_2)]_2$ are also moisture sensitive and thus likely to hydrolyse to NH_4Cl, $WO_3 \cdot nH_2O$ and sulfur chlorides. The latter are toxic by inhalation or contact.
3. Dichloromethane is toxic by inhalation or contact, just as the thionyl chloride formed by the reaction of $WOCl_4$ with $(NSCl)_3$. The solution of $SOCl_2$ in CH_2Cl_2, which remains after filtration of the $WCl_3(N_3S_2)$ sample, must be destroyed by adding an aqueous suspension of sodium bicarbonate in a fume cupboard. After separating the aqueous phase by means of a dropping funnel, the dichloromethane is regained by distillation.

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4. Make sure that you carefully grease all joints with silicone. All procedures must be carried out under dry nitrogen.

4.12.1 Experimental

a) $[Cl_4W(NSCl)]_2$

Tungsten hexachloride (10.7 g) and dichloromethane (50 cm^3) are placed in a dry 100 cm^3 Schlenk tube. To this suspension, a solution of $(NSCl)_3$ (2.20 g) in CH_2Cl_2 (20 cm^3) is slowly added dropwise with stirring (magnetic stirrer). The preparation is stirred for altogether 48 h at room temparature; the reddish brown precipitate is filtered under inert gas through a sintered glass frit, then washed with 10 ml CH_2Cl_2 and dried *in vacuo* (yield: 77%). Single crystals can be prepared by cooling a saturated solution of the sample in CH_2Cl_2 to –18 °C, or by subliming *in vacuo* at 145 °C.

Calculate the yield of the dry precipitate, measure its IR spectrum (glove bag, Nujol mull, KBr plates) and compare it with the literature data. Seal up a small sample in an ampoule.

b) $[Cl_3W(N_3S_2)]_2$

This complex can be synthesised by reaction of the chlorothionitreno derivative described above with excess $(NSCl)_3$ according to Eq. (1). In this reaction, by-products are also formed, which reduce the yield.

$$Cl_4W(NSCl) + 2/3\ (NSCl)_3 \rightarrow Cl_3W(N_3S_2) + SCl_2 + Cl_2 \qquad (1)$$

The complete conversion to the cyclothiazeno complex can be induced when tungsten oxotetrachloride (Eq. 2) is the starting reactant.

$$WOCl_4 + (NSCl)_3 \rightarrow Cl_3W(N_3S_2) + SOCl_2 + Cl_2 \qquad (2)$$

For this route, $WOCl_4$ (6.24 g) is suspended in dichloromethane (50 cm^3) and mixed with $(NSCl)_3$ (4.60 g) with stirring at 20 °C; $(NSCl)_3$ must be dissolved in dichloromethane (40 cm^3). After only a few minutes, a change of colour can be observed from red-orange to brown. To complete the reaction, the preparation is stirred for a further 48 hours. Thereafter, the dark brown precipitate is filtered under dry nitrogen, washed with 20 cm^3 CH_2Cl_2 and dried *in vacuo*. 4.56 g of the product can be isolated (yield 63%). The yield can be increased by reducing the solvent of the filtrate.

Calculate the yield of the dry precipitate, measure its IR spectrum (glove box, Nujol mull, KBr plates) and compare it with the literature data. Seal up a small sample in an ampoule.

$[Cl_3W(N_3S_2)]_2$ reacts with PPh_4Cl in CH_2Cl_2, forming a red solution, from which $PPh_4[Cl_4W(N_3S_2)]$ can be precipitated by adding CCl_4. The cyclothiazeno complex also reacts with Lewis bases like THF or pyridine, forming the donor-acceptor complexes $[(THF)Cl_3W(N_3S_2)]$ and $[(Py)Cl_3W(N_3S_2)]$ respectively.

The crystal structure of $[Cl_3W(N_3S_2)]_2$ was solved in 1997, forming centrosymmetric molecules with W_2N_2 four-membered rings and planar WN_3S_2 units.

c) $WOCl_4$

$WOCl_4$, which is needed for the synthesis of $[Cl_3W(N_3S_2)]_2$, can easily be prepared by reaction of tungsten hexachloride with hexamethyldisiloxane or with trichloronitromethane.

For the synthesis from WCl_6 and $(Me_3Si)_2O$, add a dichloromethane (15 cm^3) solution of $(Me_3Si)_2O$ (2.05 g) dropwise to a suspension of WCl_6 (5.0 g) in CH_2Cl_2 (20 cm^3) at room temperature over a period of 75 minutes. The red solid is collected by removing the supernatant liquor by filtration, washed with petroleum ether (b.p.: 40–60 °C, 2 × 20 cm^3) and dried *in vacuo*. The yield is nearly complete. The reaction follows Eq. (3).

$$WCl_6 + (Me_3Si)_2O \rightarrow WOCl_4 + 2\,ClSiMe_3 \quad (3)$$

Cl_3SiMe_3, which is contained in the filtrate, can be transformed into hexamethyldisiloxane again by its reaction with the calculated amount of water in the presence of such bases as triethylamine (Eq. 4). After filtration of triethyl ammonium chloride, the solution can be used anew for the synthesis of $WOCl_4$.

$$2\,ClSiMe_3 + H_2O + 2\,Et_3N \rightarrow (Me_3Si)_2O + 2[Et_3NH]Cl \quad (4)$$

The synthesis of $WOCl_4$ from trichloronitromethane proceeds according to Eq. (5). The emerging nitrosyl chloride is very toxic and must be destroyed by leading it into a NaOH solution.

$$WCl_6 + CCl_3NO_2 \rightarrow WOCl_4 + NOCl + CCl_4 \quad (5)$$

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4.13
Sulfur-Rich Homocycles and Heterocycles: Titanocene Pentasulfide, *cyclo*-Heptasulfur and 1,2,3,4,5,6,7-Heptathionane

Jörg Albertsen and Ralf Steudel

Elemental sulfur occurs naturally as a mineral but is commercially produced in huge amounts from hydrogen sulfide (H_2S), which is a constituent of natural gas ("sour gas") and a product of the desulfurization of crude oil performed in refineries.

Natural and commercial sulfurs consist mainly of S_8 molecules but, in addition, they always contain traces of S_7 as a solid solution in the S_8 matrix. In this experiment, you will prepare pure, crystalline S_7 using the titanocene complex $(C_5H_5)_2TiS_5$ as a sulfur transfer reagent. This reagent is useful also to prepare sulfur-rich organic polysulfanes (R_2S_n, $n \geq 5$) like the cyclic $C_2H_4S_7$ which forms a nine-membered ring. Organic polysulfanes are intermediates in the industrial vulcanization of caoutchouc by elemental sulfur to procduce rubber on a huge scale.

Special Safety Precautions

1. Chloroform ($CHCl_3$): observe the general precautions for the handling of chlorinated hydrocarbons, wear gloves, do not inhale, longer exposition may result in health problems.
2. Carbon disulfide (CS_2): very toxic on inhalation and on skin contact, very flammable; always wear gloves; make sure that all glass joints are secured by springs.
3. Dichlorodisulfane (S_2Cl_2) and sulfuryl chloride (SO_2Cl_2): very cauterising, react with water to produce acid. Residues may be carefully added (dropwise) to ice-cooled aqueous sodium hydroxide (10%).
4. Bismercaptoethane: flammable, toxic, residues may be oxidised by stirring in aqueous sodium hypochlorite (NaClO) for 12 hours.

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4.13.1 Experimental

a) Titanocene Pentasulfide

$$NH_3 + NH_4(HS) + 1/2\ S_8 \rightarrow (NH_4)_2S_5$$
$$(C_5H_5)_2TiCl_2 + (NH_4)_2S_5 \rightarrow (C_5H_5)_2TiS_5 + 2NH_4Cl$$

Sublimed sulfur (4.7 g) is placed in a 500 ml round-bottomed vessel and 36.8 ml of an aqueous ammonium sulfide solution (1 M) are added. The mixture is stirred until all the sulfur has dissolved (ca. 20 min). Then 300 ml $CHCl_3$ and 9.2 g $(C_5H_5)_2TiCl_2$ dissolved in $CHCl_3$ (300 ml) is added, resulting in two liquid phases which are stirred for at least 3 h. After transfer of the mixture into a separatory funnel (volume 500 ml), the lower $CHCl_3$ phase is separated and then washed with several portions of distilled water (total volume 1000 ml). The combined aqueous phases are extracted with ca. 800 ml $CHCl_3$ until the red colour of the aqueous phase has faded. The combined $CHCl_3$ phases are evaporated to dryness in a vacuum.

The black-violet residue is the desired product, but still contains ca. 1% S_8 impurity, which can be removed by recrystallisation from CS_2 using a Soxhlet apparatus. The purification process may be checked by reversed-phase HPLC analysis (C18 stationary phase, methanol as eluent), the retention time of S_8 is larger that that of $(C_5H_5)_2TiS_5$ (detection by UV absorption).

Titanocene pentasulfide melts at 201 °C with decomposition, the ^1H NMR spectrum in CS_2 shows two singlets at $\delta = 6.10$ and 6.42 (30 °C). Calculate the yield of your product and explain why two NMR signals are observed. The structure of $(C_5H_5)_2TiS_5$ is given by Epstein *et al.*

b) Cyclo-heptasulfur

$$(C_5H_5)_2TiS_5 + S_2Cl_2 \rightarrow S_7 + (C_5H_5)_2TiCl_2$$

Titanocene pentasulfide (2.7 g) and carbon disulfide (90 ml) are stirred in a 100 ml round-bottomed vessel at 20 °C for 10 minutes. Then S_2Cl_2 (0.64 ml) is added from a pipette and the stirring is continued for 30 minutes. The now cherry red reaction mixture is filtered (folded filter) to remove the precipitated $(C_5H_5)_2TiCl_2$ and the volume is reduced to 45 ml in a vacuum evaporator (water bath temperature 70 °C). If necessary, the solution is filtered again, 70 ml of cold diethyl ether (–78 °C) are added and the mixture is rapidly cooled to –78 °C.

After 20 h, the precipitated crude S_7 is isolated by suction of the cold mixture through a paper filter. The crystals are rapidly transferred to a beaker and immediately dissolved in 80 ml of toluene. The golden yellow solution is dried with anhydrous $MgSO_4$ (ca. 5 g), filtered by suction and cooled to –78 °C. After 20 hours, the needle-like crystals of S_7 are filtered off at 20 °C, quickly washed with 5 ml toluene and 10 ml *n*-pentane followed by pumping off of the solvents in a vacuum for 15 minutes. Since solid S_7 fairly rapidly polymerises at 20 °C and is light sensitive, it is stored at –78 °C in the dark.

The HPLC retention time (see above) of S_7 is intermediate between those of $(C_5H_5)_2TiS_5$ and S_8. S_7 melts reversibly at 39 °C but prolonged heating to temperatures above the melting point results in exothermic polymerisation. Record the infra-red spectrum of S_7 dissolved in CS_2 and compare it with the published spectrum. How can the structure of S_7 be understood compared with the well-known crown structure of S_8?

c) 1,2,3,4,5,6,7-Heptathionane

$$1,2\text{-}C_2H_4(SH)_2 + 2\,HClSO_2Cl_2 \rightarrow C_2H_4(SCl)_2 + 2\,HClSO_2$$
$$1,2\text{-}C_2H_4(SCl)_2 + (C_5H_5)_2TiS_5 \rightarrow C_2H_4S_7 + (C_5H_5)_2TiCl_2$$

1,2-Bismercaptoethane (2.4 g) is placed in a well-dried Schlenk tube (50 ml) which is then filled with a protecting atmosphere of dry N_2. After addition of 10 ml of dry CH_2Cl_2 and cooling to 5 °C in an ice bath, the sulfuryl chloride (4.9 ml; dissolved in 10 ml CH_2Cl_2) is added dropwise within 90 minutes. Eventually, the solvent and dissolved SO_2 and HCl are removed by evaporating to dryness in a rotary evaporator. The orange solid residue of $C_2H_4(SCl)_2$ "melts away" when exposed to moist air due to hydrolysis.

1,2-Ethane-bis-sulfenyl chloride, $C_2H_4(SCl)_2$, (0.6 g), dissolved in 10 ml of dry methylene chloride, is placed in a 50 ml round-bottomed flask and 1.3 g of titanocene pentasulfide, dissolved in 10 ml CH_2Cl_2, are added at once. After stirring for 30 min, the precipitated titanocene dichloride is filtered off (paper filter) and the solution evaporated to dryness on a rotary evaporator. The residue is purified by extraction with *n*-pentane (100 ml) in a Soxhlet apparatus. The volume of the extract is reduced by 50% and the solution cooled to –78 °C. After 20 hours, the crystals of $C_2H_4S_7$ are isolated by rapid suction through a paper filter followed by washing with a little *n*-pentane. The product forms yellow crystals which are stable in air and having a m.p. of 62.5 °C. The HPLC retention time of $C_2H_4S_7$, using a C18 stationary phase and methanol as an eluent, is intermediate between those of $(C_5H_5)_2TiS_5$ and S_7.

Try to draw the molecules of $C_2H_4S_7$ three-dimensionally starting from S_8 and compare your result to the actual molecular structure as determined by X-ray crystallography.

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4.14
N-Ferrocenyl Amine and Some Reactive Derivatives

Max Herberhold, Heidi E. Maisel, and Bernd Wrackmeyer

The sandwich complex di(cyclopentadienyl) iron ("ferrocene", $Fe(\eta^5\text{-}C_5H_5)_2$ (**1**)), first described in 1951/52 [1], is still one of the most important organometallic compounds [2]. A major part of its rich chemistry is based on the facile substitution reactions at the cyclopentadienyl rings. In this context, N-ferrocenyl amine ($Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4\text{-}NH_2)$), $Fc\text{-}NH_2$ (**5**) [3], is of particular interest due to its formal analogy to N-phenyl amine ($Ph\text{-}NH_2$, aniline).

Several routes to **5** have been explored [4–6]. At present, the best method (cf. [6]) to synthesize **5** is the hydrolytic cleavage of the stable precursor N-ferrocenyl phthalimide (**4**) which is easily prepared from ferrocene via lithioferrocene (**2**) and iodoferrocene (**3**).

With respect to further reactions with $Fc\text{-}NH_2$ (**5**), the trimethylsilyl- and trimethylstannyl derivatives (**6** and **8**) are useful intermediates. In the presence of triethylamine, **5** reacts with trimethylsilyl chloride to give $Fc\text{-}N(H)SiMe_3$ (**6**) [7]. N-Lithiation of **5** using *n*BuLi and subsequent reaction of the N-lithio reagent with trimethylstannyl chloride leads to $Fc\text{-}N(H)SnMe_3$ (**7**). Similar to many secondary N-trimethylstannyl amines, **7** is unstable and slowly "disproportionates" into $Fc\text{-}NH_2$ (**5**) and $Fc\text{-}N(SnMe_3)_2$ (**8**).

In contrast to most other N-trimethylsilyl amines which can be conveniently N-lithiated using *n*BuLi, complex **6** has to be N-lithiated with *t*BuLi – otherwise the N-Si bond is cleaved. However, the N-lithiated derivative of **6** can conveniently be used for further transformations. For example, it readily reacts with trimethylstannyl choride to give N-ferrocenyl-N-trimethylsilyl-N-trimethylstannyl amine, $Fc\text{-}N(SiMe_3)(SnMe_3)$ (**9**).

The monosubstituted ferrocene derivatives **3–9** are best characterized by their ^1H and ^{13}C NMR spectra (Table 4.14-1, cf. Figure 4.14-1). In particular, the signal of the unsubstituted η^5-cyclopentadienyl ring is easily identified on the basis of its relatively high intensity. The α- and β protons (H(2,5) and H(3,4) give rise to pseudotriplets; the NH proton signals are broad due to the quadrupole moment of ^{14}N. The hetero NMR spectra ($^{14,15}N$, ^{29}Si, ^{119}Sn) of **5–9** have been described [8].

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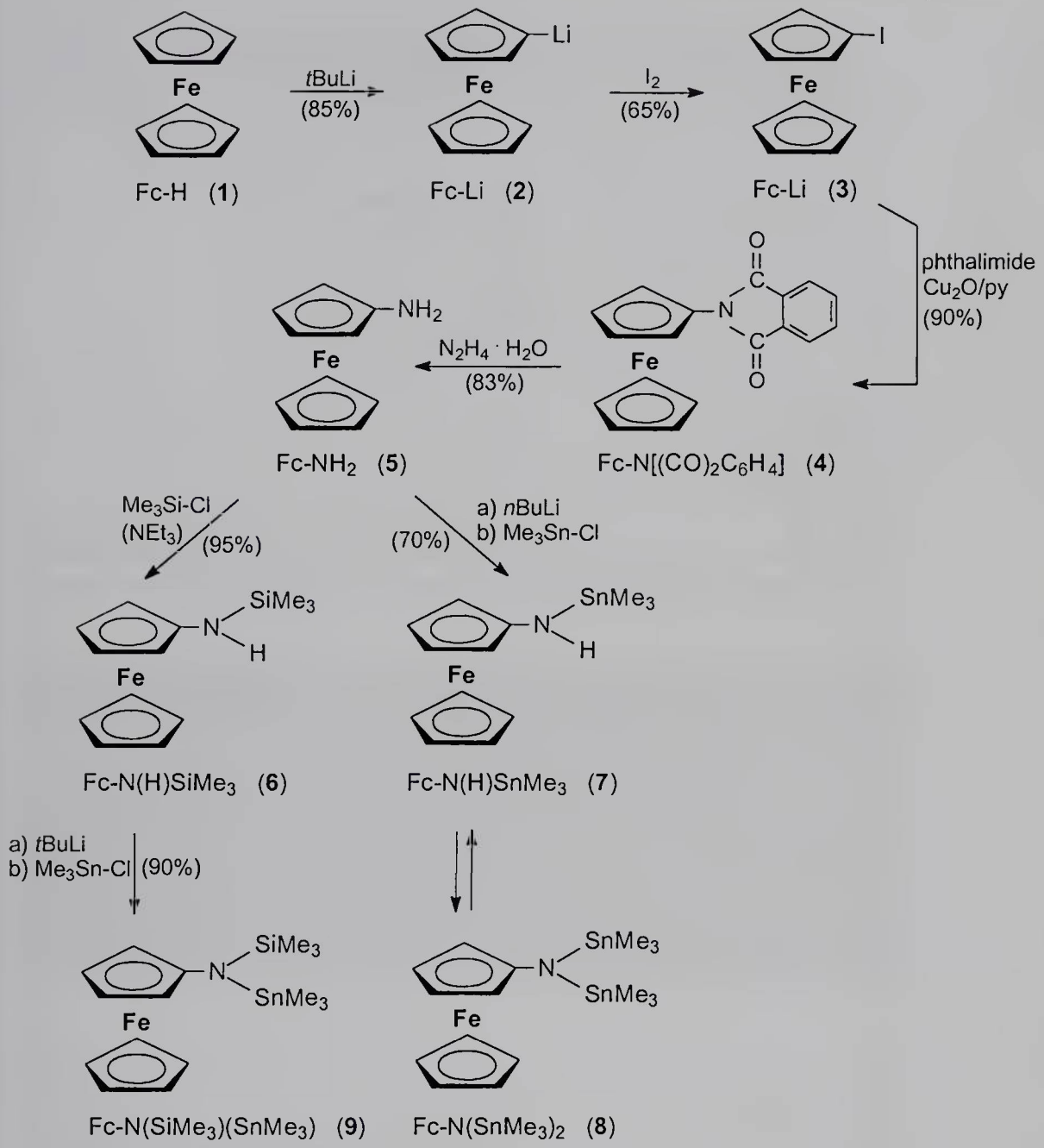
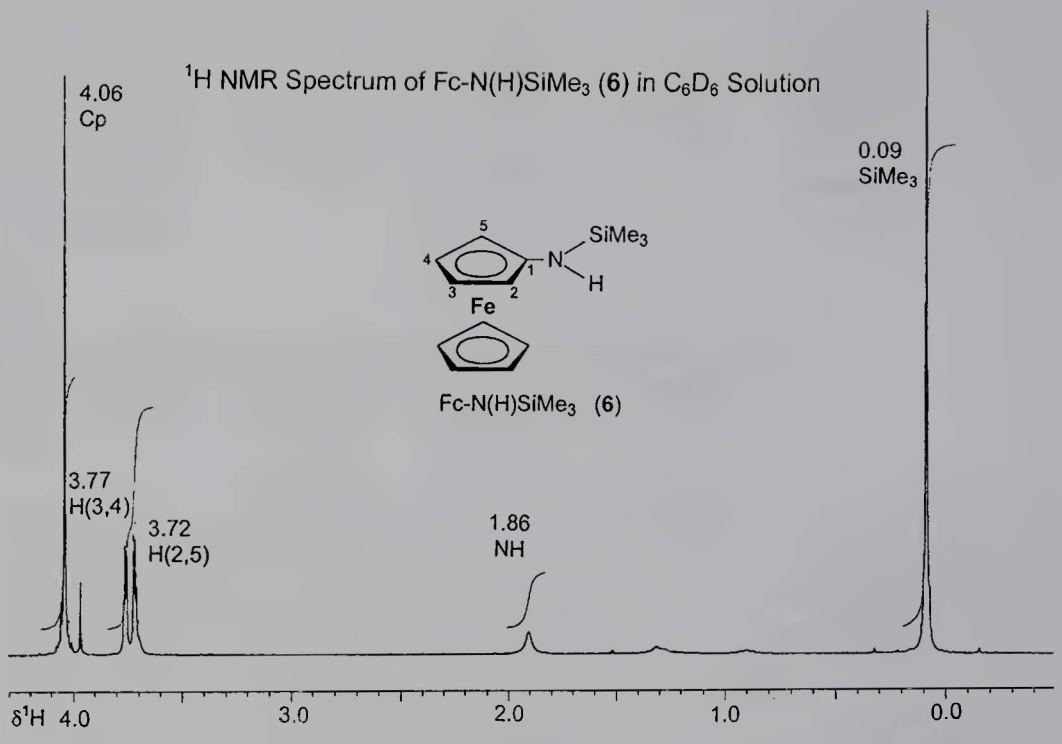

Fe
tBuLi
(85%)
Li
I2
(65%)
I
Fc-H (1)
Fc-Li (2)
Fc-Li (3)
phthalimide
Cu2O/py
(90%)
O
C
N
NH2
N2H4 · H2O
(83%)
Fc-NH2 (5)
Fc-N[(CO)2C6H4] (4)
Me3Si-Cl
(NEt3)
(95%)
(70%)
a) nBuLi
b) Me3Sn-Cl
SiMe3
SnMe3
H
Fc-N(H)SiMe3 (6)
Fc-N(H)SnMe3 (7)
a) tBuLi
b) Me3Sn-Cl
(90%)
Fc-N(SiMe3)(SnMe3) (9)
Fc-N(SnMe3)2 (8)

Scheme 4.14-1


^{1}H NMR Spectrum of Fc-N(H)SiMe$_3$ (6) in C_6D_6 Solution
4.06
Cp
0.09
SiMe$_3$
SiMe$_3$
N
H
Fe
Fc-N(H)SiMe$_3$ (6)
3.77
H(3,4)
3.72
H(2,5)
1.86
NH
δ^1H 4.0
3.0
2.0
1.0
0.0

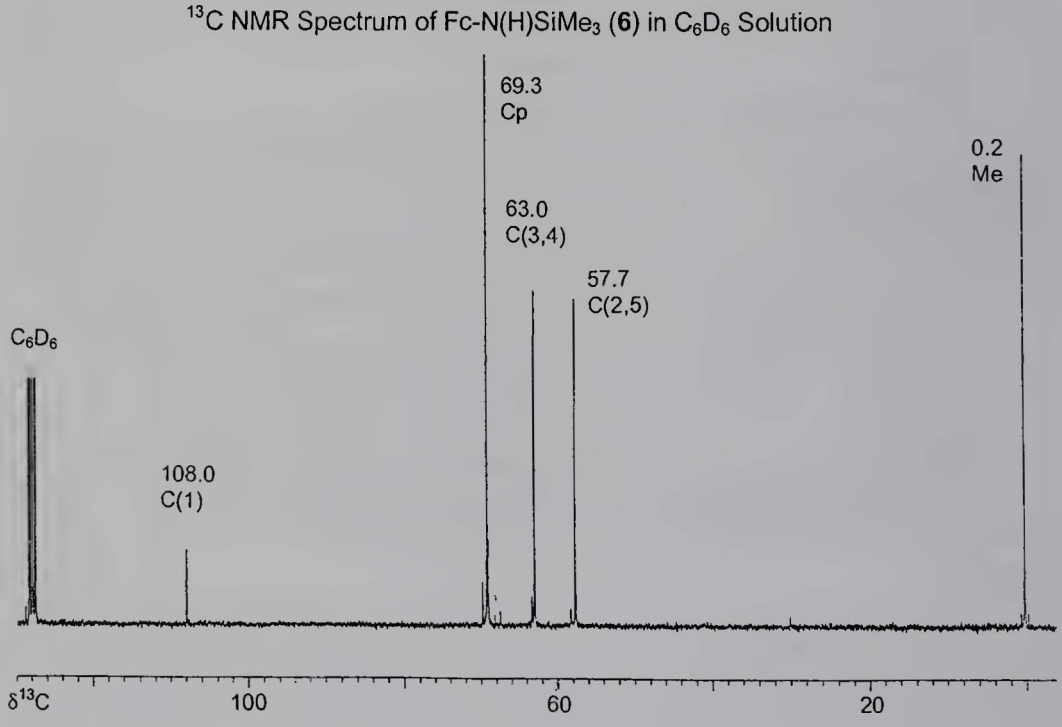

^{13}C NMR Spectrum of Fc-N(H)SiMe$_3$ (6) in C_6D_6 Solution
69.3
Cp
0.2
Me
63.0
C(3,4)
57.7
C(2,5)
C_6D_6
108.0
C(1)
δ^{13}C
100
60
20

Fig. 4.14-1

Table 4.14-1 ^{1}H and ^{13}C NMR Spectroscopic Data

Compound (Fc = CpFe(C_5H_4))		^{1}H NMR					^{13}C NMR					Solvent	[Ref.]
		Cp	H(2,5)/H(3,4)		Me	NH	Cp	C(1)	C(2,5)/C(3,4)		Me		
Fc-H	(1)	4.15					67.9					$CDCl_3$	
FC-I	(3)	4.18	4.40	4.14			71.0	72.3	68.8	74.4		$CDCl_3$	
Fc-N[$(CO)_2C_6H_4$]	(4)[a]	4.17	4.98	4.19			69.5	88.6	62.8	65.5		$CDCl_3$	[6]
Fc-NH_2	(5)	4.08	3.97	3.82		2.57	69.0	105.5	59.0	63.6		$CDCl_3$	[7]
		3.96	3.71	3.69		1.85	69.1	106.6	58.2	63.4		C_6D_6	
Fc-N(H)$SiMe_3$	(6)[b]	4.04	3.80	3.85	0.20	2.30	68.8	107.9	57.3	62.6	0.16	$CDCl_3$	[7]
		4.06	3.72	3.77	0.09	1.86	69.3	108.0	57.7	63.0	0.20	C_6D_6	
Fc-N(H)$SnMe_3$	(7)	4.07	3.79	3.64	0.13	1.54	69.2	116.0	56.8	62.5	−6.0	C_6D_6	[8]
Fc-N($SnMe_3$)$_2$	(8)	4.06	3.71	3.70	0.20		69.3	122.6	60.1	62.4	−2.6	C_6D_6	[8]
Fc-N($SiMe_3$)($SnMe_3$)	(9)	4.06	3.77	3.72	0.09 (Si)		69.2	114.3	62.5	62.9	3.1 (Si)	C_6D_6	[8]
					0.20 (Sn)						1.4 (Sn)		

[a] The phtalimido part gives ^{1}H NMR multiplets at 7.86 and 7.72 (phenylene) [6]; ^{13}C NMR signals are observed at 123.2, 131.9, 134.1 (phenylene) and 167.0 (CO).

[b] The correct assignment of the ^{1}H and ^{13}C NMR signals to the positions 2,5 and 3,4, respectively, has been confirmed for **6** by $^{1}H/^{1}H$ NOE difference spectra and 2D $^{13}C/^{1}H$ HETCOR experiments.

Special Safety Precautions

1. Handling of the commercially available (pyrophoric) solution of *tert*-butyl lithium (*t*BuLi) in pentane requires inert gas (argon or dinitrogen).
2. Solid lithioferrocene is extremely sensitive to air and pyrophoric.
3. Solids separated by filtration can be pyrophoric and should be allowed to hydrolyse and oxidise slowly on air in the fume cupboard.
4. All contacts of the products with the skin should be avoided.

4.14.1 Experimental

a) Synthesis of N-Ferrocenyl Amine, Fc-NH_2 (5)

Lithioferrocene (2)

$$\underset{\mathbf{1}}{\text{Fc-H}} + t\text{-BuLi} \rightarrow \underset{\mathbf{2}}{\text{Fc-Li}} + C_4H_{10}$$

All precautions to exclude oxygen and moisture must be strictly observed; instead of argon, dry and oxygen-free dinitrogen can be used as inert gas. In a 500 cm^3 two-necked flask, equipped with a dropping funnel and a magnetic stirring bar, flushed with argon, ferrocene (**1**) (20 g; 0.107 mol) is dissolved in THF (125 cm^3) and the so-

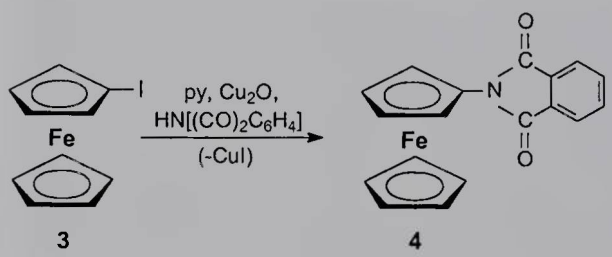
lution cooled to 0 °C in an ice bath. The resulting orange coloured suspension is vigorously stirred, and *t*BuLi (71 cm^3; 1.5 M in pentane) is added dropwise within 15 minutes. Then hexane (150 ml) is added, and the mixture is cooled at –78 °C (dry ice/isopropanol). The precipitate (**2**) is isolated by filtration, washed five times with hexane (30 ml each time) and finally dried in high vacuum; yield 17.5 g (85 %).

Iodoferrocene (3)

$$\underset{\mathbf{2}}{\text{Fc-Li}} + I_2 \rightarrow \underset{\mathbf{3}}{\text{Fc-I}} + \text{LiI}$$

In a 1-litre one-necked Schlenk vessel containing a magnetic stirring bar, flushed with argon, lithioferrocene (**2**) (17.5 g; 0.091 mol) is dissolved in THF (200 cm^3), and then the flask is cooled at –78 °C. Iodine (23.1 g; 0.091 mol) is added to the stirred mixture in one portion. The reaction mixture is allowed to warm up to ambient temperature. After adding ether (600 cm^3) and an aqueous solution of $Na_2S_2O_3$ (10 %; 150 ml), the organic phase is washed with water, dried with anhydrous Na_2SO_4, and the solvents are removed in vacuo. The raw product can be further purified by column chromatography on silica (15 cm column). Elution with hexane removes some ferrocene, whereas the product **3** is eluted with ether as a brown, oily substance; yield 18.5 g (65 %).

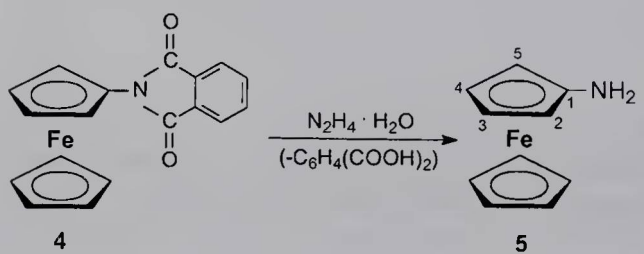
N-Ferrocenyl Phthalimide (4)



3 **4**

A mixture of iodoferrocene (**3**) (18.5 g; 0.06 mol), freshly distilled pyridine (100 cm^3), phthalimide (9.5 g; 0.096 mol), and Cu_2O (4.2 g; 0.029 mol) is prepared in a 250 cm^3 one-necked flask, equipped with a magnetic stirring bar and a reflux condenser, all flushed with argon. This mixture is heated under reflux for 2 days; during this time the colour changes from red to black. The pyridine is then removed in vacuo, and the black residue is extracted with ether in a Soxhlet apparatus. The ether is evaporated in vacuo, and the residue is recrystallized from hot ethanol to give the product **4** as orange-red crystals (m.p. 150 °C); yield 17.9 g (90 %).

N-Ferrocenyl Amine (5)



4 **5**

A suspension of N-ferrocenyl phthalimide (**4**) (5.0 g; 0.015 mol) in ethanol (100 cm^3; degassed) is prepared in a 250 cm^3 one-necked flask, equipped with a magnetic stirring bar and a reflux condenser, all flushed with argon. After addition of hydrazine hydrate (30 cm^3), the mixture is kept under reflux for 4 hours. Then the reaction mixture is cooled to 0 °C in an ice bath, and water (80 cm^3; degassed) is added. The aqueous phase is extracted several times with ether (under argon), until the ether extract is no longer yellow. The combined ether extracts are dried over anhydrous Na_2SO_4, and then the ether is removed in vacuo. The residue is purified by chromatography on silica (15 cm column). Elution with hexane/ether (10 : 2) gives **5** as a yellow solid (m.p. 157 °C); yield 2.5 g (83%).

b) Silylated and Stannylated Ferrocenyl Amines (Scheme 1)

N-Ferrocenyl-N-trimethylsilyl Amine, Fc-N(H)$SiMe_3$ (6)

A solution of N-ferrocenyl amine (**1**) (2.0 g; 0.010 mol) in hexane (200 cm^3) is prepared under argon atmosphere in a 300 cm^3 Schlenk-tube containing a magnetic stirring bar. Et_3N (1.5 cm^3; 0.011 mol) is added, followed by the dropwise addition of Me_3Si-Cl (1.12 g; 0.010 mol) through a syringe. The light-yellow suspension is stirred at room temperature for 12 h. All insoluble material is then filtered off, and the solvent hexane is removed from the filtrate in vacuo. The pure product **6** remains as orange plates (m.p. 66 °C); yield 2.58 g (95%).

N-Ferrocenyl-N-trimethylstannyl Amine, Fc-N(H)$SnMe_3$ (7), and N-Ferrocenyl-N,N-bis(trimethylstannyl) Amine, Fc-N($SnMe_3$)$_2$ (8)

A solution of *n*BuLi in hexane (1.3 cm^3, 1.6 M, 2.0 mmol) is further diluted with hexane (10 cm^3), transferred into a 100 cm^3 Schlenk tube under argon and cooled to –30 °C, before a solution of N-ferrocenyl amine (**5**) (0.40 g; 2.0 mmol) in hexane-ether (25 ml; 4 : 1) is slowly added dropwise. When the mixture has reached room temperature, the suspension is centrifuged, the liquid phase carefully decanted and the yellow solid (0.50 g), N-ferrocenyl-N-lithio amine (Fc-N(H)-Li), dried in high vacuum. A hexane (100 cm^3) suspension of Fc-N(H)-Li (0.50 g; 1.9 mmol) is prepared in a Schlenk tube under argon, and solid Me_3Sn-Cl (0.37 g; 1.9 mmol) is added in one portion at room temperature. The mixture is stirred for 12 hours and then filtered. The filtered solution is brought to dryness in vacuum to give a brown solid of almost pure **6**; yield 0.49 g (70%).

In solution (as well as in the solid state), **7** decomposes slowly into N-ferrocenyl amine (**5**) and N-ferrocenyl-N,N-bis(trimethylstannyl) amine (**8**). In hexane solution, **5** precipitates and can be separated, whereas the supernatant liquid becomes enriched in **8**.

N-Ferrocenyl-N-trimethylsilyl-N-trimethylstannyl Amine, Fc-N(SiMe$_3$)(SnMe$_3$) (9)

In a 100 cm^3 Schlenck tube, a solution of N-ferrocenyl-N-trimethylsilyl amine (**6**) (0.42 g; 1.5 mmol) in hexane (50 cm^3) is prepared under inert gas and cooled to −40 °C. *t*BuLi (1.5 cm^3; 1.5 M in pentane, 1.5 mmol) is slowly added through a syringe. The reaction mixture is allowed to reach room temperature and stirred for 1 hour. Solid Me$_3$Sn-Cl (0.30 g; 1.5 mmol) is then added in one portion, and the mixture is kept stirring at room temperature for 12 hours. After filtration, the solvents are removed in vacuo, and a brown solid is left as the raw product **9**; yield 0.58 g (90 %).

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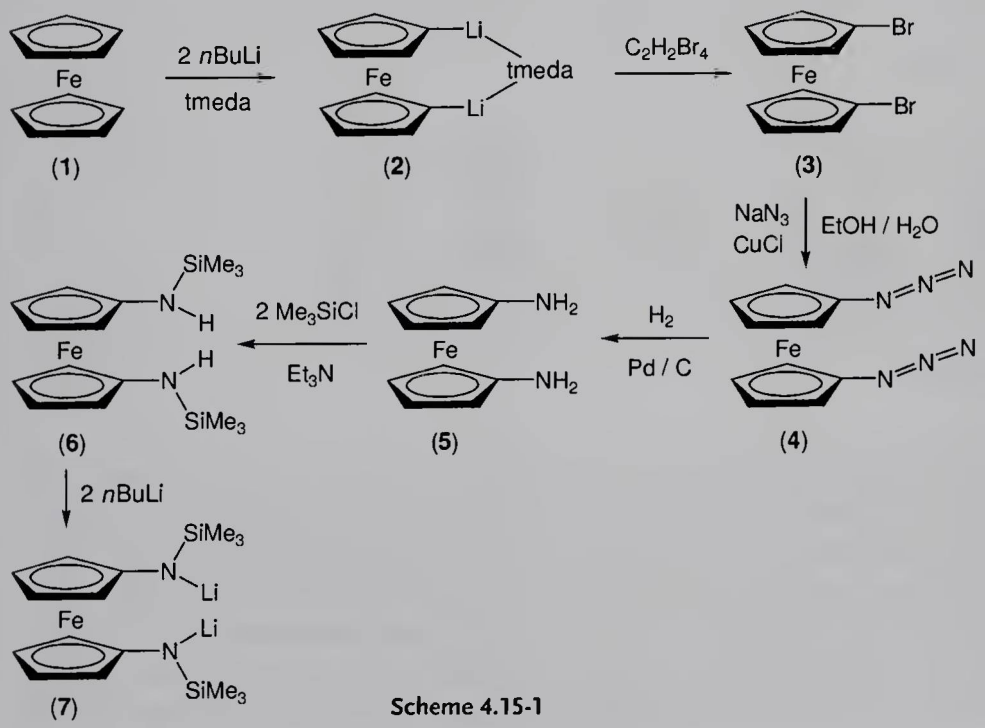
4.15
1,1′-Bis(trimethylsilylamino)ferrocene – A Useful Precursor to 1,*n*-Diaza-[*n*]ferrocenophanes

Max Herberhold, Elena V. Klimkina, and Bernd Wrackmeyer

Amido ligands, in particular those acting as chelate ligands, have contributed significantly to the multifaceted coordination chemistry of both main group [1] and transition metals [1, 2]. Considering the structural features of 1,1′-diaminoferrocene, $Fe(\eta^5\text{-}C_5H_4\text{-}NH_2)_2$, $fc(NH_2)_2$ (5), with its rigid and bulky backbone, (5) must be regarded as an attractive starting material for chelating diamido ligands with promising synthetic potential.

The synthesis of (5) has been reported previously [3]. At present, the best route to (5) [4] starts from ferrocene (1) and leads via 1,1′-dilithioferrocene (2) [5] and 1,1′-dibromoferrocene (3) [4] to 1,1′-diazidoferrocene (4) [3c, 4], which is then reduced with dihydrogen over Pd/C to give (5). The conversion of (5) into its bis(trimethylsilylamino) derivative (6) [6] is straightforward (Scheme 4.15.1) and (6) itself or its *N,N′*-dilithiated derivative (7) [6, 7] can be used for numerous further transformations.



Scheme 4.15-1

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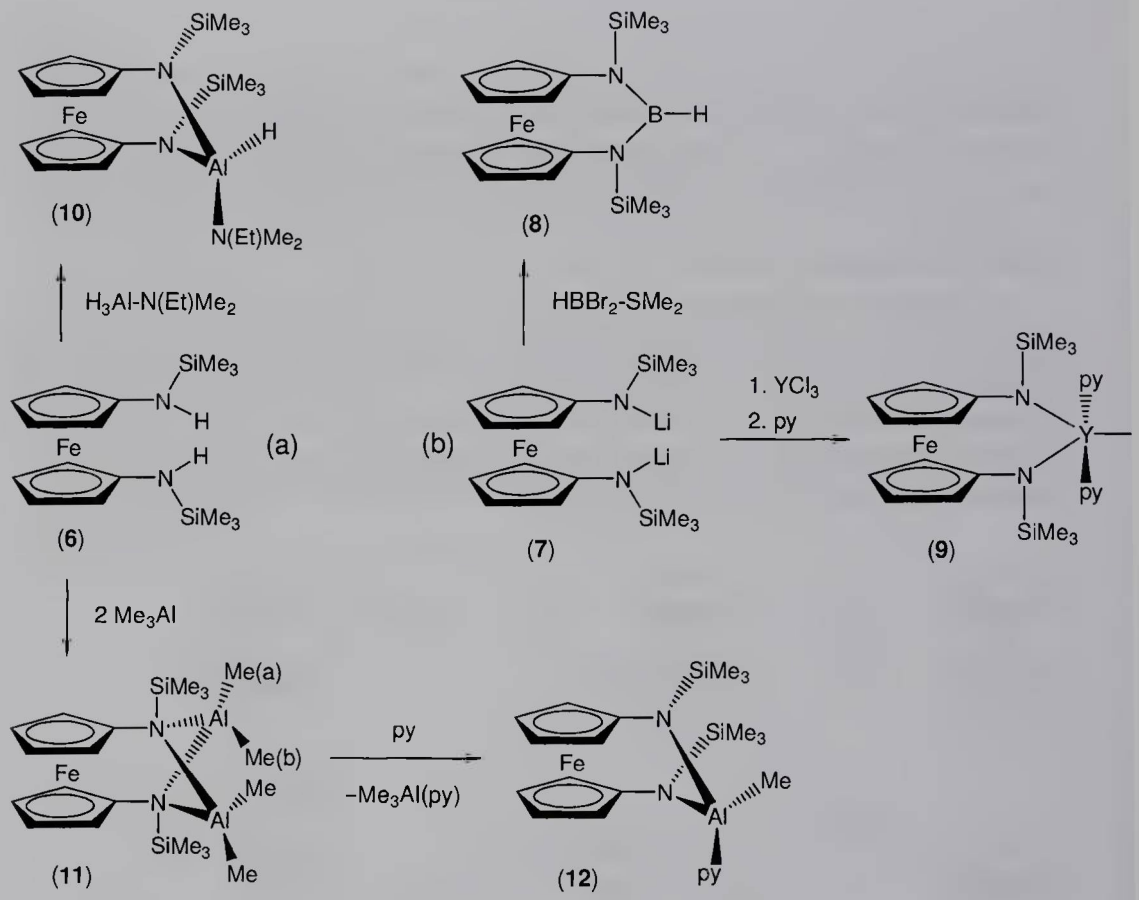
Representative examples of the application of (**6**) (Scheme 4.15.2 a) or (**7**) (Scheme 4.15-2 b) are shown here for an aminoborane (**8**) [8], three different types of aluminium–nitrogen compounds (**10–12**) [9] and an yttrium complex (**9**) [10], all of which are reactive species and also can be used for various synthetic purposes. Other applications have been reported in the synthesis of 1,1′-diaza-[*n*]ferrocenophanes with $n = 3$ [11], with $n > 38$ [12] or with $n = 3$ and other metals, such as Mg [6], Sn [13], Ti, Zr [6, 14], V [15] and U [16]. In addition, transition metal complexes were prepared in which the $SiMe_3$ are replaced by $Si(t\text{Bu})Me_2$ groups [17]. 1,3-Diaza-2-metalla-[3]ferrocenophanes bearing substituents other than silyl groups at the nitrogen atoms have also been synthesized [18].



Scheme 4.15-2

The 1,1′-diaminoferrocene (**5**) [4] and most of its derivatives are structurally characterised in the solid state by X-ray crystallography [4, 6, 18]. Solution-state multinuclear NMR spectroscopy (Table 4.15-1) reveals both molecular structures (Figs. 4.15-1 to 4.15-3) and molecular dynamics (Figs. 4.15-2 and 4.15-3) of these compounds. The latter is shown in Figure 4.15-2 for $^1H\{^1H\}$ one-dimensional NOE difference spectra [19], showing the spatial proximity of respective groups, and in Fig. 4.15-3 by two-dimensional (2D) ^{13}C 2D EXSY [20] spectroscopy, indicating the ring inversion

Table 4.15-1 ^{1}H, ^{13}C and ^{29}Si NMR spectroscopic data [a), b)].

	^{1}H NMR				^{13}C NMR					^{29}Si NMR	Solvent	Ref.
	H(2,5)	H(3,4)	Element-R	$SiMe_3$	C(1)	C(2,5)	C(3,4)	Element-R	SiMe	SiMe		
(1)	4.18				67.9						$CDCl_3$	
(3)	4.16, 4.42		–	–	78.2	69.9, 72.6		–	–		$CDCl_3$	
(4)	4.16, 4.34		–	–	100.3	61.4, 66.4		–	–		$CDCl_3$	
(5)	3.89, 3.77 3.73, 3.65		2.56 (NH_2) 1.87 (NH_2)	– –	103.7 104.7	60.5, 64.2 60.2, 64.2		–			$CDCl_3$ C_6D_6	
(6)	3.71, 3.69 3.81, 3.78		2.29 (NH) 2.01 (NH)	0.18 0.15	106.6 105.9	59.7, 64.3 60.3, 64.6		–	0.2 0.3	2.8 2.3	CD_2Cl_2 C_6D_6	[6]
(8)	3.86	3.99	4.31 (BH)	0.13	101.7	69.3	67.8	–	1.2	11.1	CD_2Cl_2	[8]
(9)	2.92	4.13	7.44 (py) 7.83 (py) 8.87 (py)	–0.04	101.8	67.0	66.9	124.7 (py) (br) 138.3 (py) (br) 150.2 (py) (br)	1.2	–6.0 (d)[c)]	CD_2Cl_2	[10]
(10)	3.44 [H(2)] 4.00 (H(5))	3.86	0.63 (t, CCH_3) 2.08 (s, NCH_3) 2.70 (q, NCH_2)	0.26	106.4	66.8 (C(2)) 69.8 (C(5))	64.5 65.0	52.5, 6.0 (NCH_2CH_3) 43.5 (NMe)	3.0	2.7	Toluene-[d_8]	[9a]
(11)	4.11	3.90	–0.21 (Me_b) –0.12 (Me_a)	0.15	94.1	72.9	68.0	4.3 [br], (Me_a) 1.6 [br], (Me_b)	1.6	14.9	Toluene-[d_8]	[9b]
(12)	3.52	3.69	–0.60 (AlMe) 7.69 (py) 8.09 (py) 8.96 (py)	–0.06	107.1	67.9 (br)	64.2	–5.6 [br] (AlMe) 125.9 (py) (C_β) 141.2 (py) (C_γ) 148.6 (py) (C_α)	2.5	3.4	CD_2Cl_2	[9b]

a) The assignment of the NMR signals is based on $^{1}H\{^{1}H\}$ NOESY and 2D $^{13}C/^{1}H$ HSQC experiments.

b) [br] denotes broad ^{13}C resonances of aluminium-bonded atoms; (br) denotes broad ^{13}C resonances due to dynamic effects.

c) $^{2}J(^{89}Y,^{29}Si) = 1.6$ Hz.

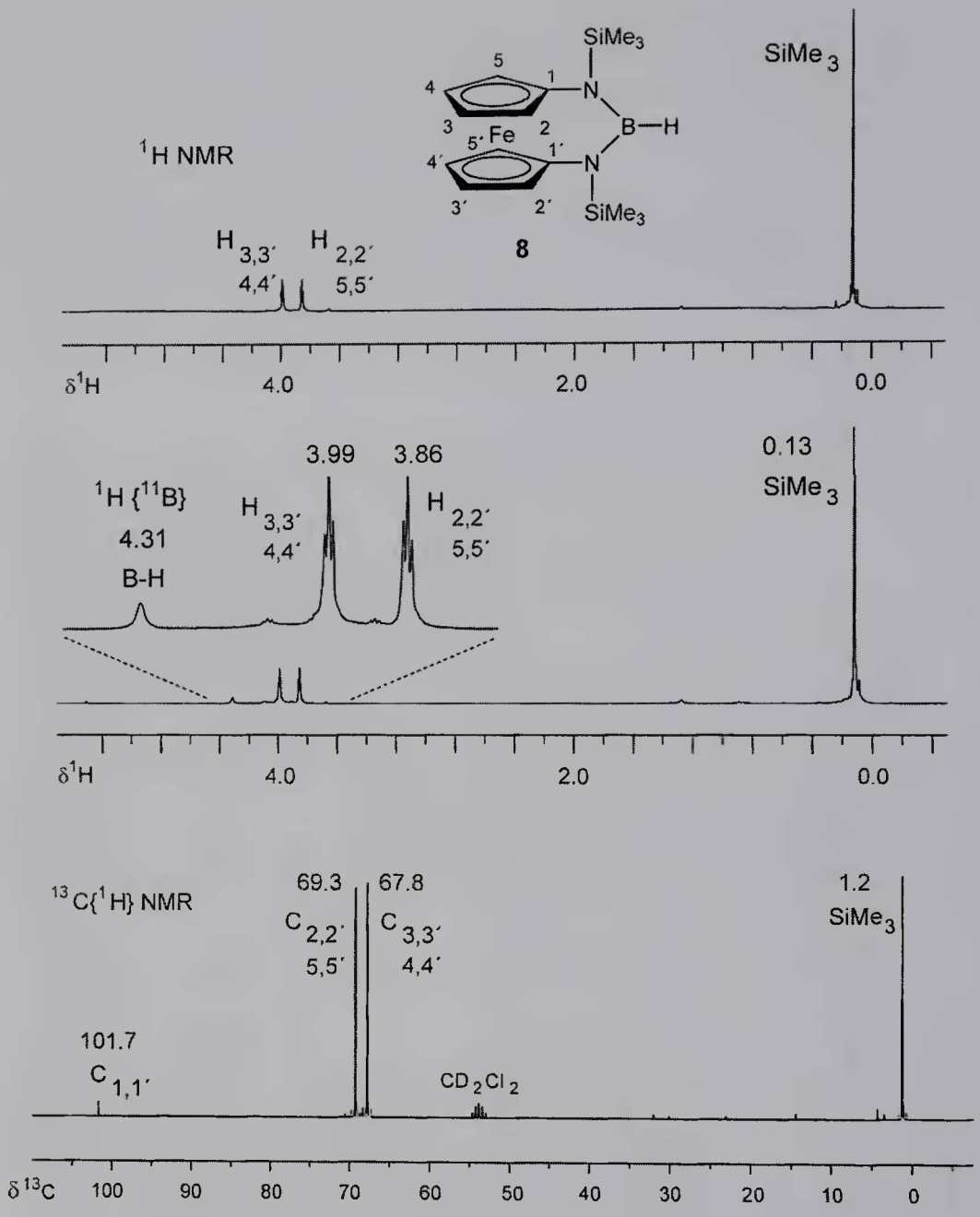


Fig. 4.15-1 250.1 MHz ^{1}H NMR and 62.9 MHz ^{13}C{^{1}H} NMR spectra of (8) in CD_2Cl_2.

which is slow on the time-scale of conventional NMR experiments. Frequently, the understanding of structural features and NMR parameters is aided by quantum chemical calculations [21].

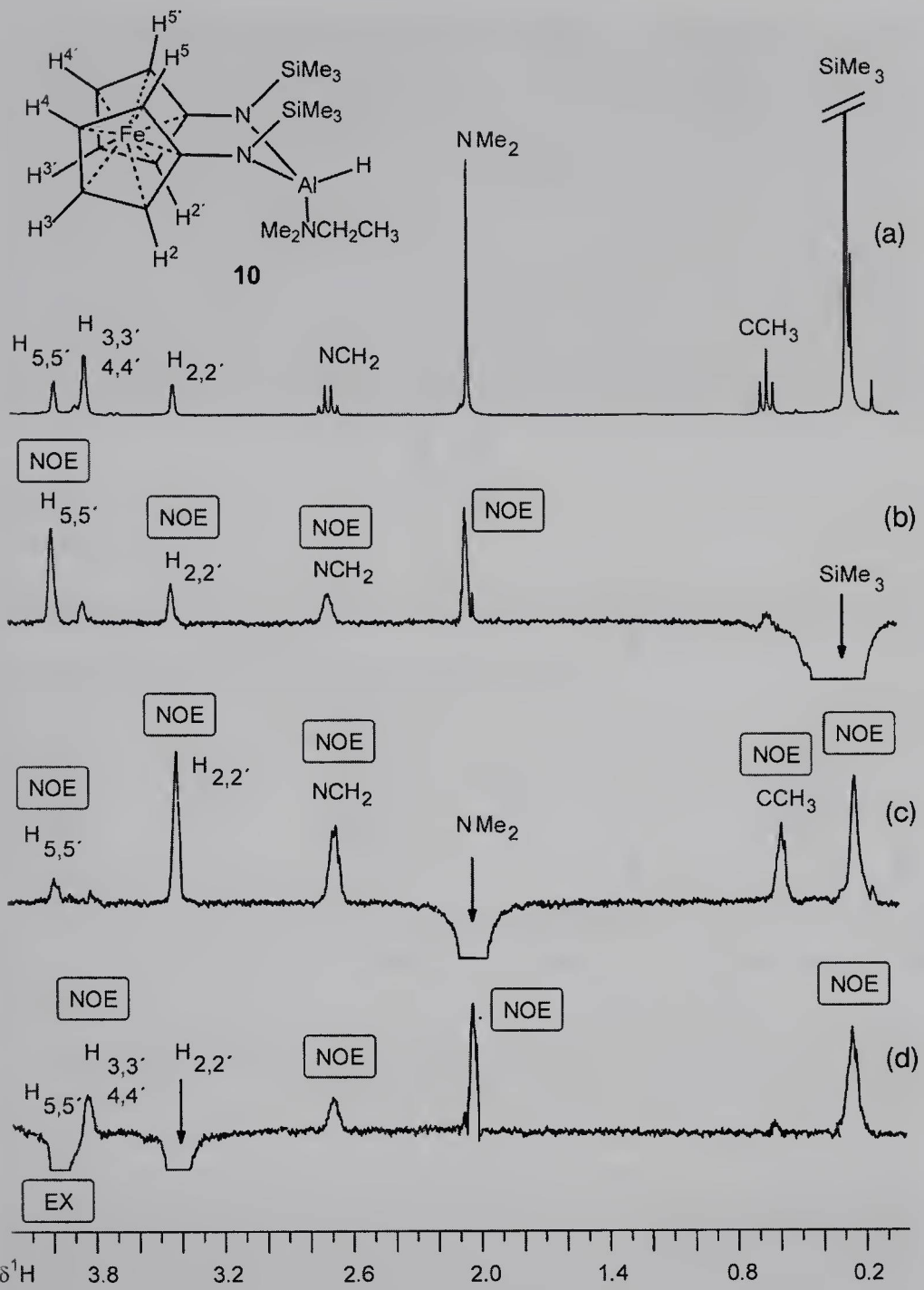


Fig. 4.15-2 400 MHz $^1H\{^1H\}$ NOE difference spectra (gradient enhanced [19a]) of **10** (10% in toluene-d_8 at 23 °C; relaxation delay 1.5 seconds; mixing time 0.6 seconds; 30 minutes of spectrometer time). The irradiated resonance signals are marked by arrows; the intensities as response arising from NOE or exchange (magnetisation transfer) are marked. (a) Normal ^1H NMR spectrum. (b) The $NSiMe_3$ resonance was irradiated. (c) The NMe_2 resonance was irradiated. (d) The $H^{2,2'}$ resonance of the cyclopentadienyl groups was irradiated.

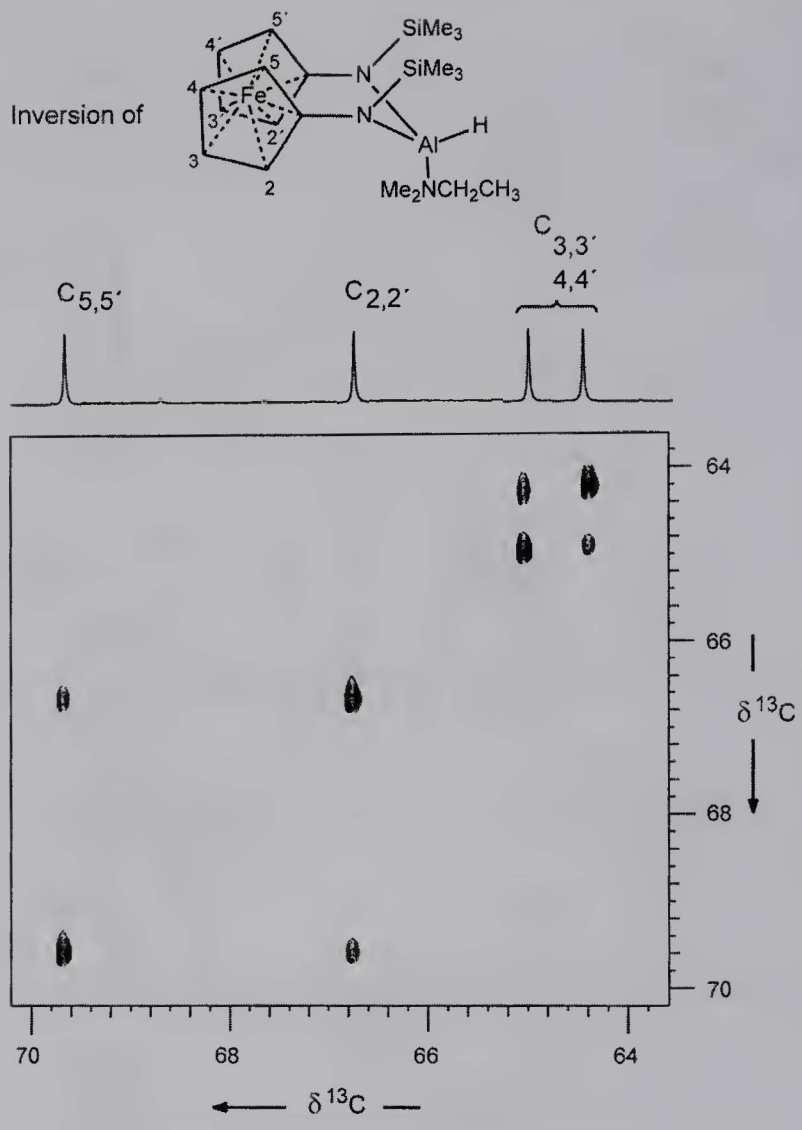


Fig. 4.15-3 ^{13}C 2D EXSY NMR spectrum[20] of compound (**10**) (100.5 MHz, 10% in toluene-d_8, at 23 °C); relaxation delay 2.0 seconds; mixing time 1.0 seconds.

Special Safety Precautions

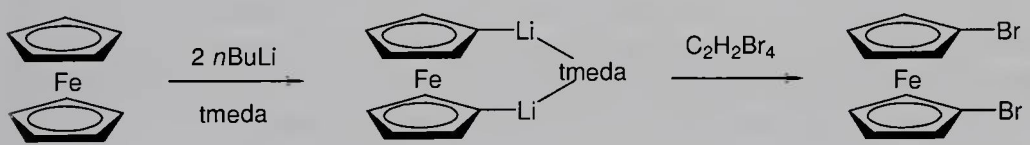
1. All preparative work and handling of the samples is carried out observing precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware are used throughout.
2. Instead of argon, dry and oxygen-free dinitrogen can be used as inert gas.
3. Handling of the commercially available solutions of *n*-butyl lithium (*n*BuLi) in hexane, AlH_3-N(Et)Me_2 in hexane, $AlMe_3$ in hexane and $HBBr_2$-SMe_2 in CH_2Cl_2 requires inert gas (argon or dinitrogen).

4. Solid 1,1′-dilithioferrocene (2) and $fc(NSiMe_3)_2Li_2$ (6) are extremely sensitive to air and pyrophoric.
5. Solids separated by filtration can be pyrophoric and should be allowed to hydrolyse and oxidise slowly in air.
6. 1,1′-Diaminoferrocene and many 1,*n*-diaza-[*n*]ferrocenophanes are light and temperature sensitive.
7. Extreme care should be exercised when handling solid 1,1′-diazidoferrocene, as it is prone to explosion if heated rapidly[4] above 56 °C (melting point).
8. All contact of the products with the skin should be avoided.

4.15.1 Experimental

a) Synthesis of 1,1′-Bis(trimethylsilylamino)ferrocene, $fc(N(H)SiMe_3)_2$ (6) (Scheme 1)

1,1′-Dilithioferrocene (2) and 1,1′-Dibromoferrocene (3)



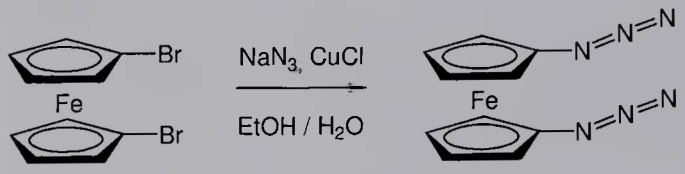
(1) (2) (3)

In a 1 l three-necked flask, containing a magnetic stirring bar, flushed with argon, ferrocene (1) (20.9 g; 112.3 mmol) is dissolved in hexane (400 cm^3). Freshly distilled tetramethylethylenediamine (tmeda) (37.7 ml; 249.8 mmol), is added and then *n*BuLi (147 cm^3; 1.6 M solution in hexane, 235.2 mmol) is injected slowly through a syringe within 20 minutes. The reaction mixture is stirred for 1 hour and kept at complete rest for further 18 hours. The formation of red–orange needles is observed. The suspension is cooled to 0 °C in an ice bath and the supernatant liquid phase carefully decanted via a cannula. The remaining precipitate is washed with hexane (150 cm^3) and finally dried under high vacuum to give of $fc(Li)_2$(tmeda) (2) as an orange solid.

In the same 1 l three-necked flask, equipped with a mechanical stirrer and a dropping funnel, a suspension of $fc(Li)_2$(tmeda) (2) in hexane (300 cm^3) is prepared under argon and cooled to –70 °C. Then 1,1,2,2-tetrabromoethane ($C_2H_2Br_4$) (26.2 cm^3, 224.6 mmol) is slowly added to the suspension with vigorous stirring over a period of 1.5 hours. The reaction mixture is allowed to reach ambient temperature (about 1.5 hours) and kept stirring for further 12 hours. The resulting red–brown solution is hydrolysed with 40 ml of H_2O. From this point, the workup is done in air. The mixture is stirred for additional 10 minutes, during which a layer of black oil forms at the bottom. The top red layer is decanted and the remaining oil is washed with hexane (2 × 150 cm^3). The decanted solution and the hexane fractions are combined and the sol-

vent is removed *in vacuo* to give a red solid. The solid is extracted with Et_2O and filtered off, resulting in a red–brown solution. The ether is evaporated *in vacuo* and the residue is redissolved in hot MeOH (30 ml) and crystallized at –20 °C to give 1,1′-dibromoferrocene (**3**) as orange–red crystals, yield 25.3 g [66% calculated on ferrocene (**1**)].

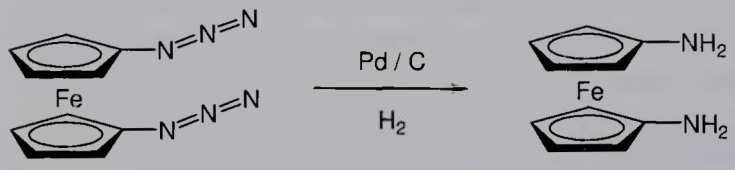
1,1′-Diazidoferrocene (4)



(**3**) (**4**)

The following procedure is carried out in air. A mixture of 1,1′-dibromoferrocene (**3**) (13.71 g, 39.9 mmol), CuCl (8.50 g, 85.9 mmol) and 300 ml of 95% EtOH is prepared in a 500 cm^3 two-necked flask, equipped with a magnetic stirring bar. A solution of NaN_3 (10.36 g, 159.4 mmol) in 32 cm^3 of H_2O is added, resulting in the formation of a dark-brown suspension. The reaction flask is wrapped in foil and the suspension stirred for 48 hours. The mixture is then poured into H_2O (450 cm^3) and stirred for an additional 10 minutes. The top layer is decanted and extracted with Et_2O (2 × 100 cm^3) in a separating funnel. The solid is extracted with Et_2O (5 × 100 cm^3) and filtered off, resulting in a red solution. The combined ether extracts are dried over anhydrous Na_2SO_4, concentrated to 150 cm^3 and cooled to –30 °C to give 1,1′-diazidoferrocene (**4**) as yellow crystals, yield 4.5 g (44%).

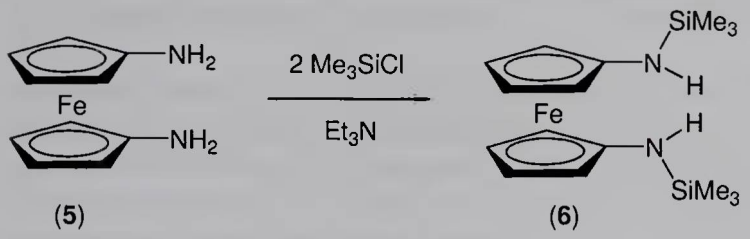
1,1′-Diaminoferrocene (5)



(**4**) (**5**)

In a 500 cm^3 three-necked flask with an inlet and an outlet for argon, containing a magnetic stirring bar, a solution of 1,1′-diazidoferrocene (**4**) (8.2 g, 30.6 mmol) in 310 cm^3 of anhydrous MeOH is prepared and degassed for 5 min by bubbling argon through it using a stainless-steel cannula. To this solution is added 0.1 g of Pd/C (10% Pd) powder under argon and H_2 gas is bubbled through the solution at a moderate rate for 7.5 hours. The outlet for H_2 leads to the bottom of an open beaker filled with water (height 20 cm) in order to have a count of the bubbles of unconsumed H_2 and, at the same time, to increase slightly the H_2 pressure in the flask. Otherwise the yield drops significantly. The reaction mixture is filtered, concentrated to 200 cm^3 and cooled to –20 °C to give 1,1′-diaminoferrocene (**5**) as yellow crystals. Further concentration and cooling of the filtrate afford a larger amount of (**5**). Total yield: 5.1 g (77%).

1,1′-Bis(trimethylsilylamino)ferrocene (6)



(5) (6)

A suspension of 1,1′-diaminoferrocene (5) (1.3 g; 6.0 mmol) in hexane (150 cm^3) is prepared under argon in a 250 cm^3 Schlenk tube containing a magnetic stirring bar and freshly distilled Et_3N (1.82 cm^3; 13.1 mmol) is added. Then the orange suspension is cooled to 0 °C in an ice bath and Me_3SiCl (1.62 cm^3; 12.8 mmol) is slowly added through a syringe. The green–yellow suspension is stirred at room temperature for 12 hours. All insoluble material is then filtered off (under argon) and the solvent hexane is removed from the filtrate *in vacuo*. The remaining solid is dissolved in hexane (50 cm^3) and the hexane solution is filtered. The solvent is removed *in vacuo* to give 1.63 g (75%) of 1,1′-bis(trimethylsilylamino)ferrocene (6) as a yellow–orange solid.

b) Synthesis of *N,N′*-Dilithio-1,1′-bis(trimethylsilylamino)ferrocene ($fc(NSiMe_3)_2Li_2$) (7)

All precautions to exclude oxygen and moisture must be strictly followed. In a 100 cm^3 Schlenk tube containing a magnetic stirring bar, flushed with argon, a solution of $fc(NHSiMe_3)_2$ (6) (350 mg; 0.97 mmol) in hexane (25 cm^3) is prepared and cooled to –78 °C. *n*BuLi (1.21 cm^3; 1.6 M solution in hexane, 1.94 mmol) is slowly added through a syringe. The reaction mixture is stirred at –78 °C for 1 hour, then allowed to reach ambient temperature and kept stirring for a further 30 minutes. The formation of a red–orange precipitate is observed. The suspension is centrifuged (without removing the magnetic stirring bar) and the supernatant liquid phase is carefully decanted. The solid is dried under high vacuum to give 340 mg (94%) of $Fc(NSiMe_3)_2Li_2$ (7) as an orange powder.

c) Synthesis of 1,3-Bis(trimethylsilyl)-2-hydro-1,3,2-diazabora-[3]ferrocenophane (8)

Freshly prepared $fc(NSiMe_3)_2Li_2$ (7) (357 mg, 0.96 mmol) (in a 100 cm^3 Schlenk tube, equipped with a magnetic stirring bar) is taken up in hexane (20 cm^3) under argon; the suspension is cooled to –70 °C and $HBBr_2$-SMe_2 (0.96 cm^3; 1.0 M solution in CH_2Cl_2, 0.96 mmol) is injected slowly through a syringe. After stirring the reaction mixture for 2 hours at –70 °C and then for 2 hours at ambient temperature, insoluble materials are separated by centrifugation and the clear liquid is carefully collected. Volatile materials are removed *in vacuo* and the resulting oil is dissolved in hexane (18 cm^3). After centrifugation, the solvent is removed *in vacuo* to give 170 mg (48%) of (8) as a yellow solid.

d) Synthesis of 1,3-Bis(trimethylsilyl)-2-chloro-2,2-dipyridine-1,3-diaza-2-yttria-[3]ferrocenophane (9)

A solution of freshly prepared $Fc(NSiMe_3)_2Li_2$ (7) (288 mg, 0.77 mmol) in toluene (20 cm^3) is cooled to –78 °C and added to pure (degassed, flushed with argon) anhydrous yttrium trichloride, YCl_3 (151 mg; 0.77 mmol) in a 100 cm^3 Schlenk tube containing a magnetic stirring bar at –30 °C via a cannula. The reaction mixture is stirred at –78 °C for 40 minutes, then anhydrous pyridine (0.249 cm^3, 3.10 mmol) is injected slowly through a syringe. After stirring the reaction mixture for 1 hour at –70 °C and then for 18 hours at ambient temperature, insoluble materials are separated by centrifugation and the clear liquid is carefully collected. Volatile materials are evaporated, the remaining oil is washed with hexane (10 cm^3) and the resulting mixture is centrifuged. The liquid phase is carefully decanted and the solid is dried *in vacuo* to give the yttrium complex (9) as a brown–green powder (231 mg; 47%).

e) Synthesis of 1,3-Bis(trimethylsilyl)-2-dimethyl(ethyl)amine-2-hydro-1,3,2-diazaalumina-[3]ferrocenophane (10)

A solution of 1,1′-bis(trimethylsilylamino)ferrocene (6) (176 mg, 0.49 mmol) in toluene (10 cm^3) is prepared under argon atmosphere in a 100 cm^3 Schlenk tube containing a magnetic stirring bar and cooled to 0 °C in an ice bath. A solution of AlH_3-N(Et)Me_2 (0.98 cm^3; 0.5 M solution in toluene, 0.49 mmol) is added dropwise through a syringe. While stirring, gas evolution is observed. The reaction mixture is stirred at 0 °C for 1 hour, then allowed to reach ambient temperature and kept stirring for 20 hours. Volatile materials are removed *in vacuo*, the remaining yellow–green oil is dissolved in hexane (20 cm^3) and the solution is centrifuged. The clear liquid is carefully collected, the solvent is removed *in vacuo* to give 190 mg (85%) of (10) as a yellow–orange oil.

f) Synthesis of μ-[Ferrocene-1,1′-diylbis(trimethylsilylamido)]tetramethyldialane (11)

A solution of 1,1′-bis(trimethylsilylamino)ferrocene (6) (230 mg, 0.64 mmol) in hexane (30 cm^3) is prepared under argon in a 100 cm^3 Schlenk tube containing a magnetic stirring bar and cooled to –78 °C. A solution of $AlMe_3$ (0.64 cm^3; 2.0 M solution in hexane, 1.28 mmol) is added dropwise through a syringe. The reaction mixture is stirred at –78 °C for 1 hour, then allowed to reach ambient temperature and kept stirring for 48 hours. Volatile materials are removed *in vacuo*, the remaining yellow oil is dissolved in hexane (20 ml) and the resulting mixture is centrifuged. The clear liquid is carefully collected, the solvent is removed *in vacuo* to give 290 mg (96%) of (11) as a yellow–orange oil.

g) Synthesis of 1,3-bis(trimethylsilyl)-2-methyl-2-pyridine-1,3,2-diazaalumina-[3]ferrocenophane (12)

A solution of (11) (90 mg; 0.19 mmol) in toluene-d_8 (1 cm^3) is prepared under argon, cooled to 0 °C and anhydrous pyridine (0.030 cm^3, 0.38 mmol) is added. The mixture is stirred for 2 hours and analysed to contain about 70% of the adduct (12), together with (6) and $Me_3Al(py)$. Crystallisation from toluene-d_8 gives, after 5 days at –20 °C, orange crystals of (12); m.p. 140–150 °C.

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4.16
Organometallic Molybdenum Compounds

Manfred Bochmann and Petr Klian

Transition metals in low oxidation states are able to form complexes with many unsaturated organic ligands, e.g. CO, olefins and acetylenes. This ability to coordinate such molecules and to activate them for subsequent reactions has led to an extremely rich chemistry and constitutes the basis of many important industrial catalytic processes. When CO or alkenes coordinate to a metal centre, mutually reinforcing interaction between σ donation from ligand to metal and π back-donation from metal to ligand takes place. This is known as the 'Dewar–Chatt–Duncanson model' of ligand bonding. CO is particularly powerful in withdrawing electron density from the metal in this way, i.e. it is a strong 'π-acid'. Since the C–O stretching mode is easily observed in the IR spectrum, the position of this band is a sensitive probe for the electron density of the metal centre, its oxidation state and the overall charge.

The following experiments illustrate several aspects of the chemistry of metal carbonyl complexes:

a) Some, but rarely all, CO ligands in the metal carbonyl complex can be displaced by other ligands such as alkenes. In our experiment, a cyclic olefin, cycloheptatriene, is used as the displacing ligand.
b) The cycloheptatriene ligand has a polar C–H bond. Hydride abstraction generates an η^7-C_7H_7 (tropylium) complex, a representative of the large family of 6 arene complexes. *Cationic and neutral Mo(0) and Mo(II) complexes are generated in experiments a) and b) whose IR spectra show typical shifts in the CO band patterns.*
c) Cationic complexes are susceptible to nucleophilic attack, either on one of the ligands or on the metal centre.

Some of the following preparations work best if carried out under a protective atmosphere of nitrogen; use a nitrogen manifold in a fume cupboard. A rotary vacuum pump is recommended for the thorough drying of some of the products. Ask a demonstrator to instruct you in the use of these pieces of equipment.

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Special Safety Precautions

$Mo(CO)_6$ and cycloheptatriene are toxic. Perform the reaction in a fume cupboard.

4.16.1 Experimental

a) Cycloheptatriene Molybdenum Tricarbonyl

The experimental set-up is shown in Figure 3.19-3. The compound is prepared by refluxing a mixture of $Mo(CO)_6$ and cycloheptatriene in a high-boiling solvent under nitrogen. Use thoroughly dry glassware. To 5 mmol $Mo(CO)_6$ in 15 cm^3 of sodium-dried *n*-octane in a 100 cm^3 flask add 8 mmol cycloheptatriene. Purge the flask with a stream of N_2 to expel the air and stopper it quickly. Assemble the straight condenser with a T-piece, connect the N_2 supply to the T-piece and purge the condenser with N_2. Maintain the N_2 stream while you quickly exchange the stopper on your flask for the condenser assembly. In this way, you should have avoided the entry of air as far as possible. Reflux the mixture for 5–6 hours or until no more $Mo(CO)_6$ is seen to sublime. The oil bath temperature should be 160 °C. Make sure the solvent level inside the flask is slightly higher than the oil bath level to avoid the decomposition of the product on overheated glass walls. During the refluxing, unreacted molybdenum hexacarbonyl sublimes out of the reaction mixture and is washed back into the flask by the refluxing octane. If a significant accumulation occurs, taking great care not to splash hot oil and heating only as high as necessary, use a hot air blower to warm the 'air condenser' part of the assembly occasionally to help dissolve the $Mo(CO)_6$. Avoid driving the sublimate up inside the water jacket. There is little chance of blockage occurring but the bath temperature must be checked frequently and the assembly must not be left unattended for long periods.

The resulting deep-red solution is evaporated on a rotary evaporator (water bath temperature 70 °C), leaving a deep-red solid. This is extracted with 15 cm^3 of diethyl ether. The solution is filtered quickly through a glass sinter. Since any unreacted $Mo(CO)_6$ is less soluble in diethyl ether than the product, most of it is left on the filter. The filtrate is immediately taken to dryness on a rotary evaporator (water bath at room temperature). The bright-red product may still contain small amounts of $Mo(CO)_6$ but should be pure enough for the subsequent reaction.

You will need about 2 mmol of crude product for the subsequent synthesis. Obtain a pure sample for analysis by dissolving the remainder in heptane at room temperature, filtering if required, then leaving stoppered in a refrigerator. If no crystals grow, leave the solution unstoppered in your cupboard overnight. The crystalline material is relatively stable but it decomposes rapidly in solution or when finely powdered. For IR spectroscopy, prepare a KBr disc quickly, then use it without delay. For NMR spectroscopy, measure the freshly made solution without delay.

b) Cycloheptatrienyl Molybdenum Tricarbonyl Tetrafluoroborate

To a solution of $(C_7H_8)Mo(CO)_3$ (2 mmol) in dichloromethane (15 cm^3) add rapidly with swirling a solution of trityl tetrafluoroborate (2 mmol) in dichloromethane (15 cm^3). Some oily residue from the Ph_3CBF_4 may remain undissolved – take care not to transfer it to the carbonyl solution. Stir for a few minutes, then filter off the product, an orange precipitate, on a glass sinter, wash it with a few small portions of diethyl ether, suck dry very briefly, then dry *in vacuo*. The product is obtained as an orange powder in almost quantitative yield. As above, prepare a KBr disc quickly, then use it without delay. For NMR spectroscopy, measure the freshly made solution without delay.

Note: $[C_6H_5)_3C]BF_4$ is the salt of a stable carbocation. Although it can be handled briefly in air, it is very susceptible to nucleophilic attack, e.g. by atmospheric moisture. It must be weighed out quickly and protected from moisture by dissolving it immediately in dry CH_2Cl_2. The container of $[(C_6H_5)_3C]BF_4$ must always be stored in a desiccator over a powerful drying agent (P_2O_5 with moisture indicator). Good quality material is orange to yellow–brown; brown or colourless material (hydrolysis!) gives poor results.

c) Cycloheptatrienyl Molybdenum Dicarbonyl Bromide

This experiment is best carried out in a fume cupboard. $[(C_7H_7)Mo(CO)_3]BF_4$ (1.5 mmol) is added in small portions to a stirred solution of 1.7 mmol of anhydrous LiBr in 25 cm^3 of dry, degassed acetone under a moderate counter-current of nitrogen. (Acetone is dried over molecular sieves. Oxygen is removed by bubbling nitrogen through it for 2–3 minutes).

Stop stirring briefly and add a little $[(C_7H_7)Mo(CO)_3]BF_4$. What do you observe? Continue stirring for 20 minutes, remove the acetone *in vacuo*, extract the residue with 20 cm^3 of dichloromethane and filter in air through a glass sinter (S3). $LiBF_4$ and unreacted $[(C_7H_7)Mo(CO)_3]BF_4$ are left behind. Wash with another 15 cm^3 CH_2Cl_2, concentrate the combined filtrate to 3 cm^3 (rotary vacuum pump), stopper the flask and leave on an ice bath to complete the crystallisation. If crystals fail to form, add a few cm^3 of diethyl ether with a Pasteur pipette. The green–black crystalline product is collected on a sintered glass filter. Yields of 60–70% can be expected.

d) Characterisation

Record the IR spectra of $Mo(CO)_6$ and of your products as KBr discs. Adjust the thickness of the mull so that the CO stretching bands are well resolved. Interpret your IR spectra, and also the Raman spectra shown in Figure 4.16-1, paying particular attention to the CO stretching region.

Record the ^1H NMR spectra of cycloheptatriene (in CCl_4 or $CDCl_3$) and of each of your products $[(C_7H_8)Mo(CO)_3$ in $CDCl_3$, the others in acetone-d_6]. Use only freshly prepared solutions. ^1H, $^{13}C\{^1H\}$, H–H COSY and H–C HSQC spectra of

$(C_7H_8)Mo(CO)_3$ are shown in Figure 4.16-2; assign the 1D spectra as much as possible (with the help of 2D spectra) and show how the reaction sequence can be deduced from these data. ^1H and $^{13}C\{H\}$ NMR spectra of $[(C_7H_7)Mo(CO)_3]BF_4$ are shown in Figures 4.16-3 and 4.16-4. Figures 4.16-5 and 4.16-6 show the mass spectra of $(C_7H_8)Mo(CO)_3$ and $[(C_7H_7)Mo(CO)_3]BF_4$; interpret the spectra as far as possible. Calculate isotopic patterns of expected ions/fragments and compare them with the observed spectra. Calculations can be performed online using Chemputer at http://winter.group.shef.ac.uk/chemputer/isotopes.html.

4.16.2 Exercises

1. How is spectroscopic (and other) evidence used to arrive at chemical conclusions?
2. Write down the chemical equations, including possible reaction mechanisms and suggest the structures of your products.

Further Reading

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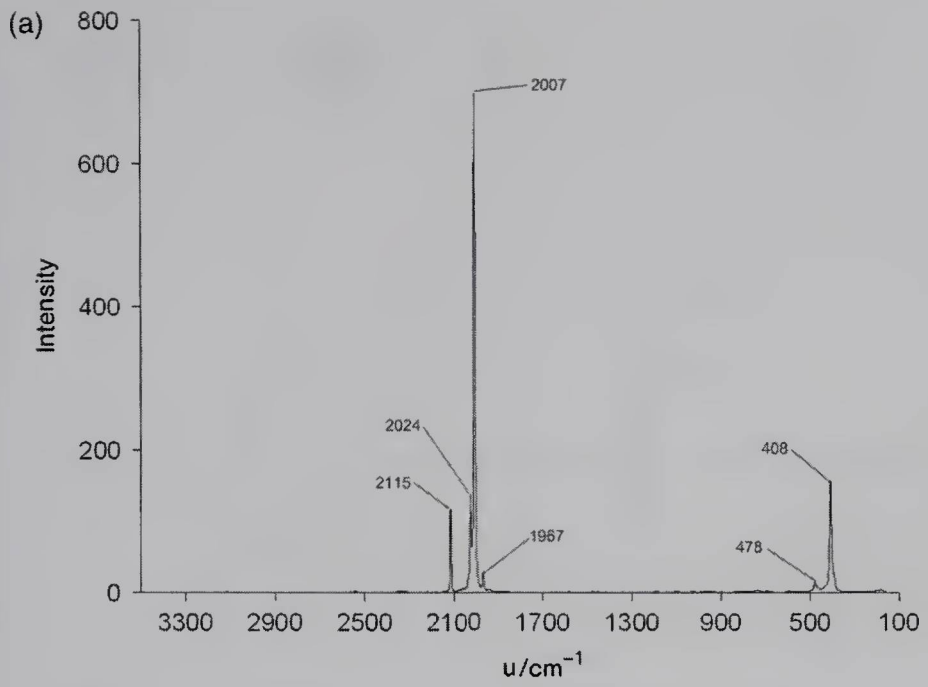


Fig. 4.16-1 (a) Raman spectrum of $Mo(CO)_6$.

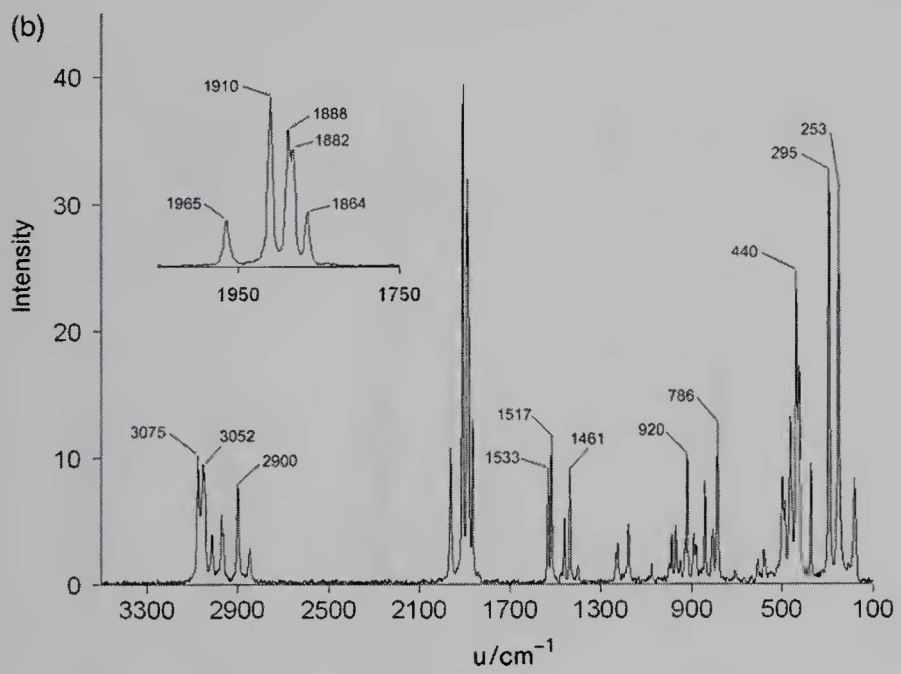


Fig. 4.16-1 (b) Raman spectrum of cycloheptatriene molybdenum tricarbonyl.

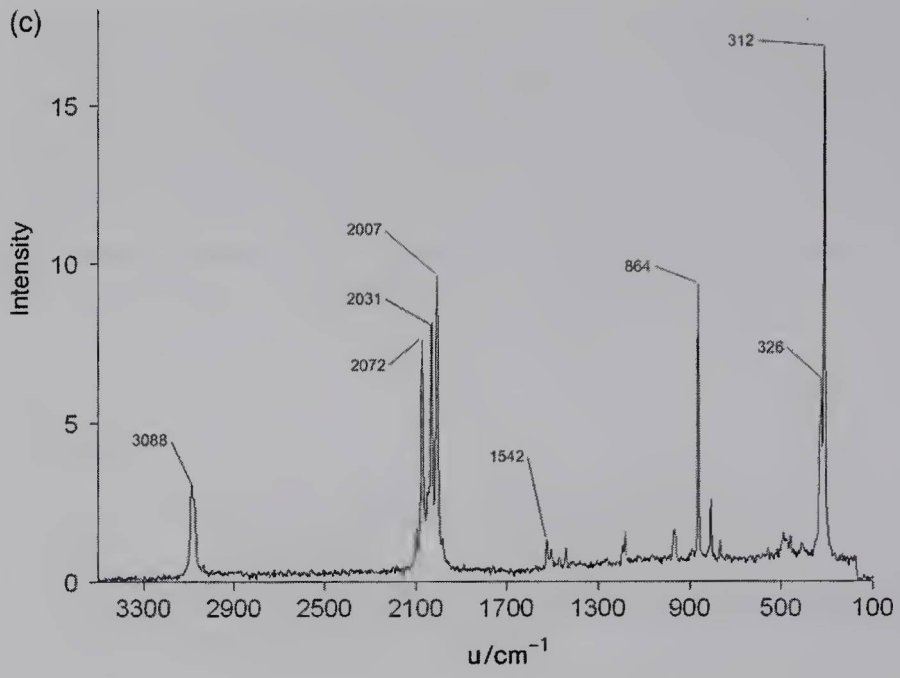


Fig. 4.16-1 (c) Raman spectrum of cycloheptatrienyl molybdenum tricarbonyl tetrafluoroborate.

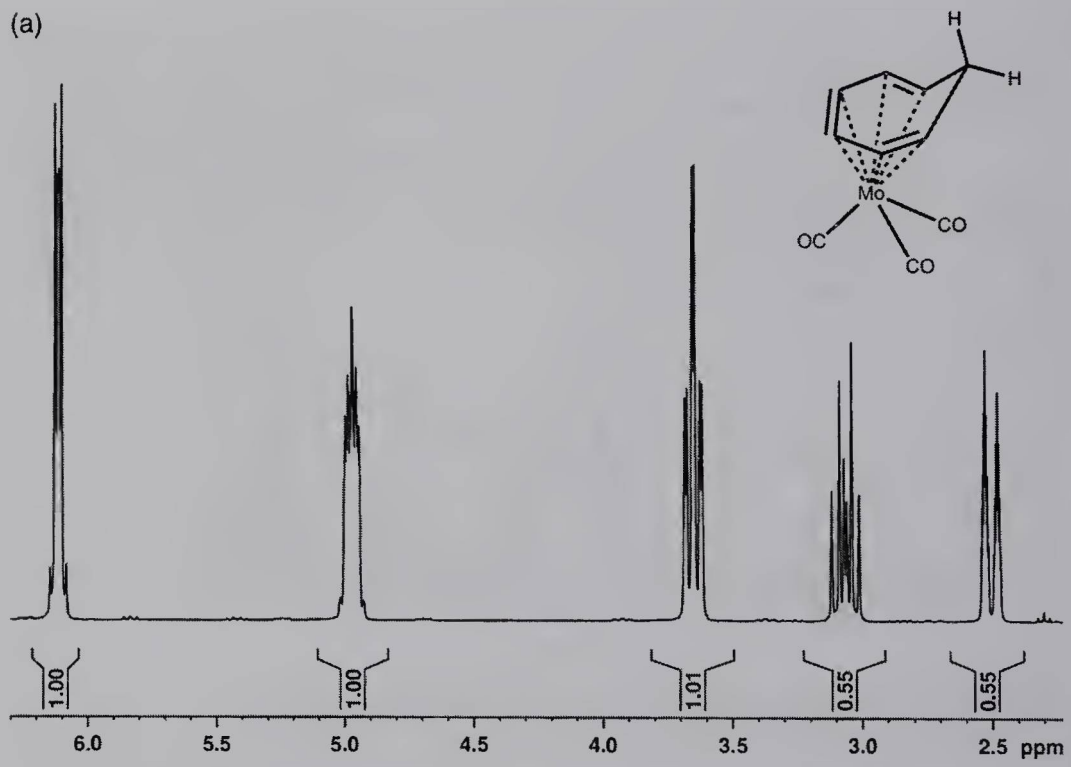


Fig. 4.16-2 (a) ^{1}H NMR spectrum of cycloheptatriene molybdenum tricarbonyl in $CDCl_3$.

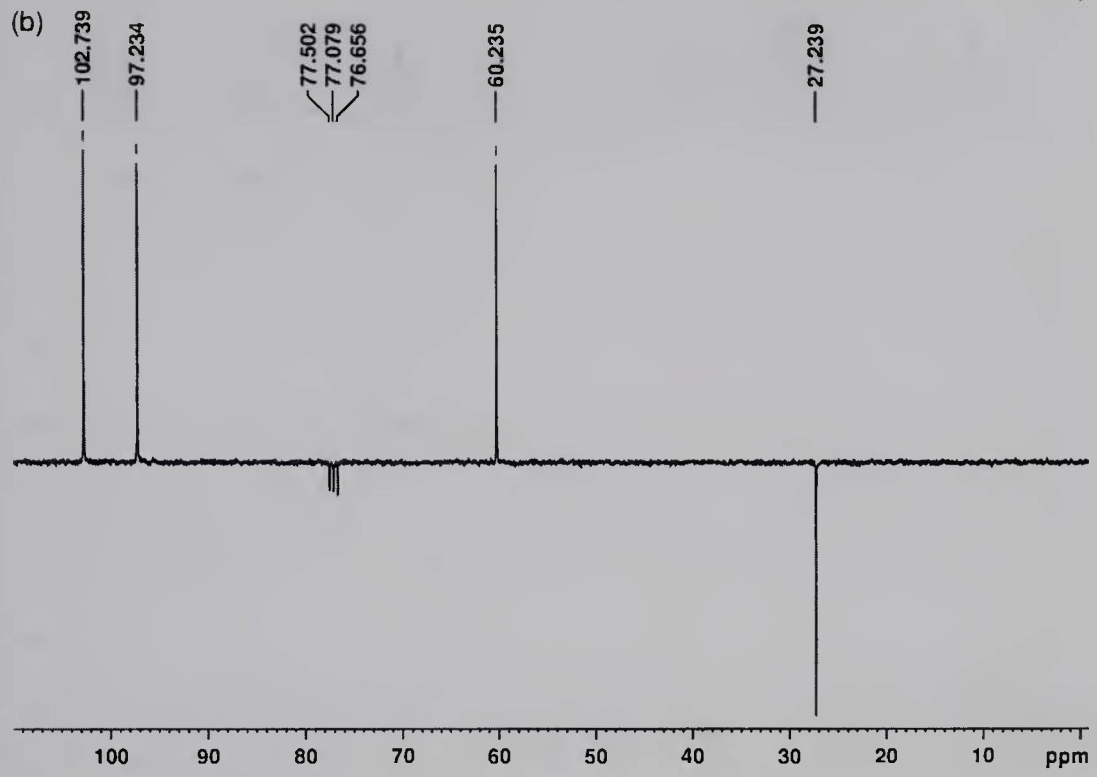


Fig. 4.16-2 (b) 13C{^{1}H} NMR spectrum of cycloheptatriene molybdenum tricarbonyl in $CDCl_3$.

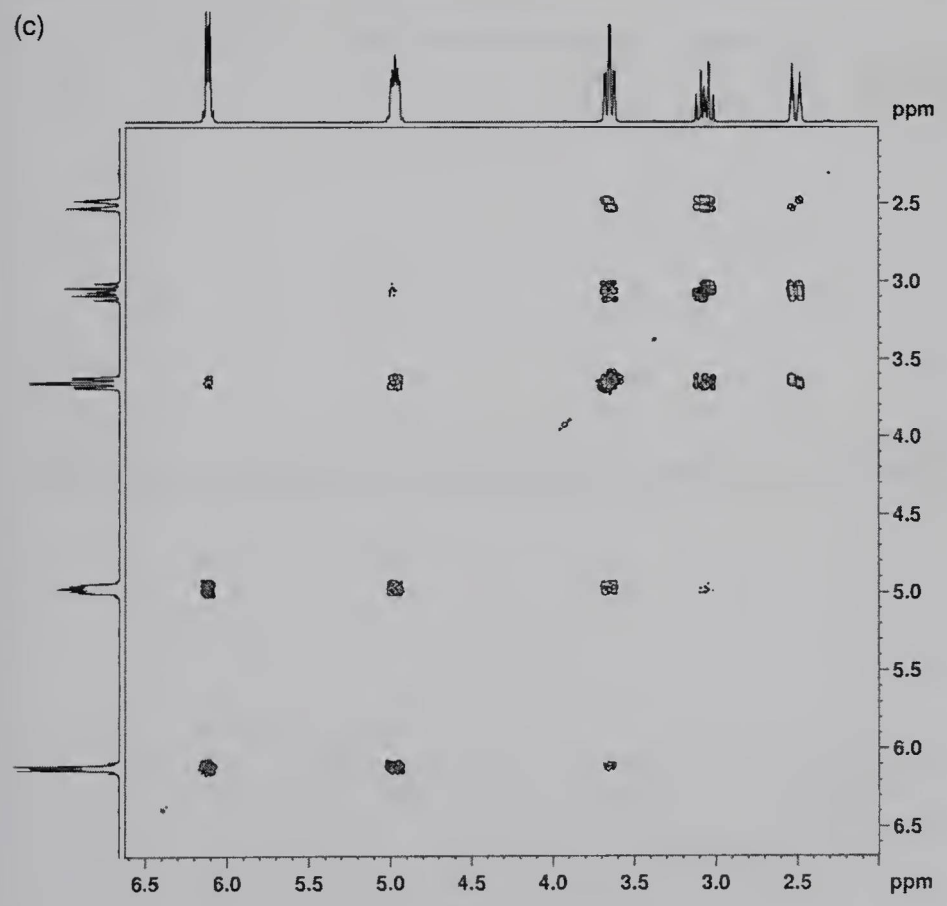


Fig. 4.16-2 (c) H–H COSY spectrum of cycloheptatriene molybdenum tricarbonyl in $CDCl_3$.

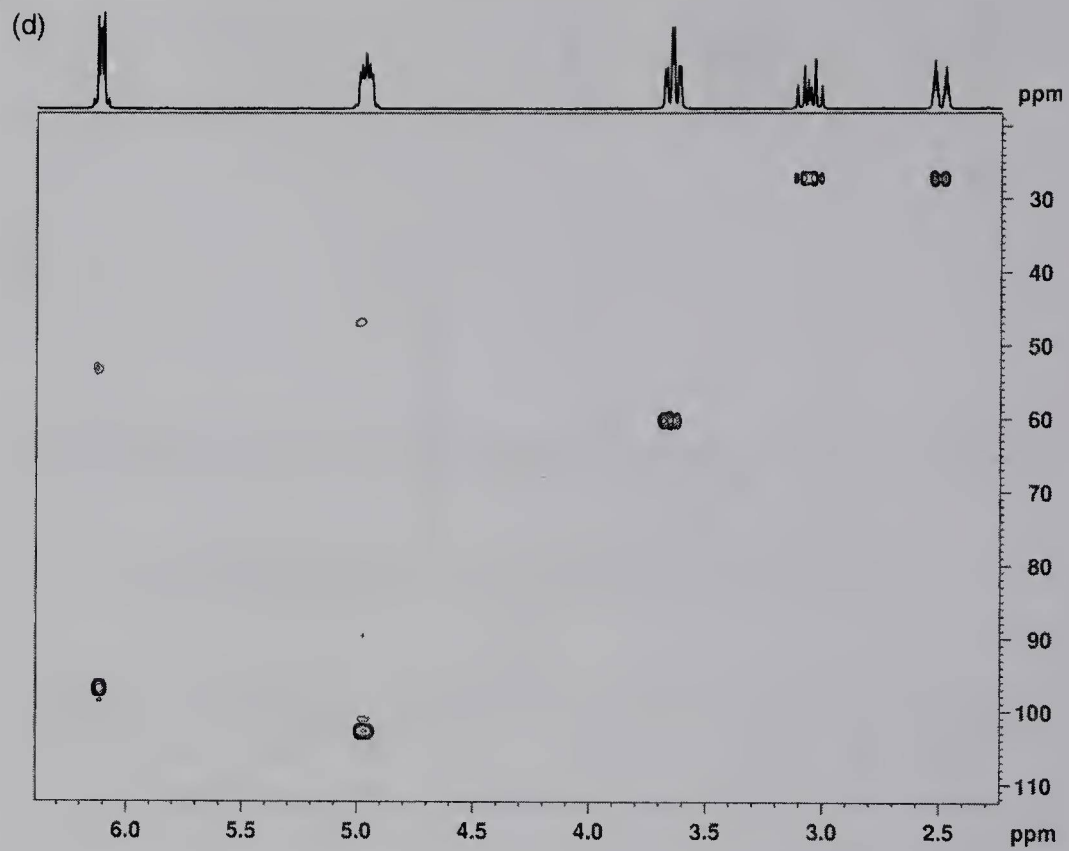


Fig. 4.16-2 (d) H–C HSQC spectrum of cycloheptatriene molybdenum tricarbonyl in $CDCl_3$.

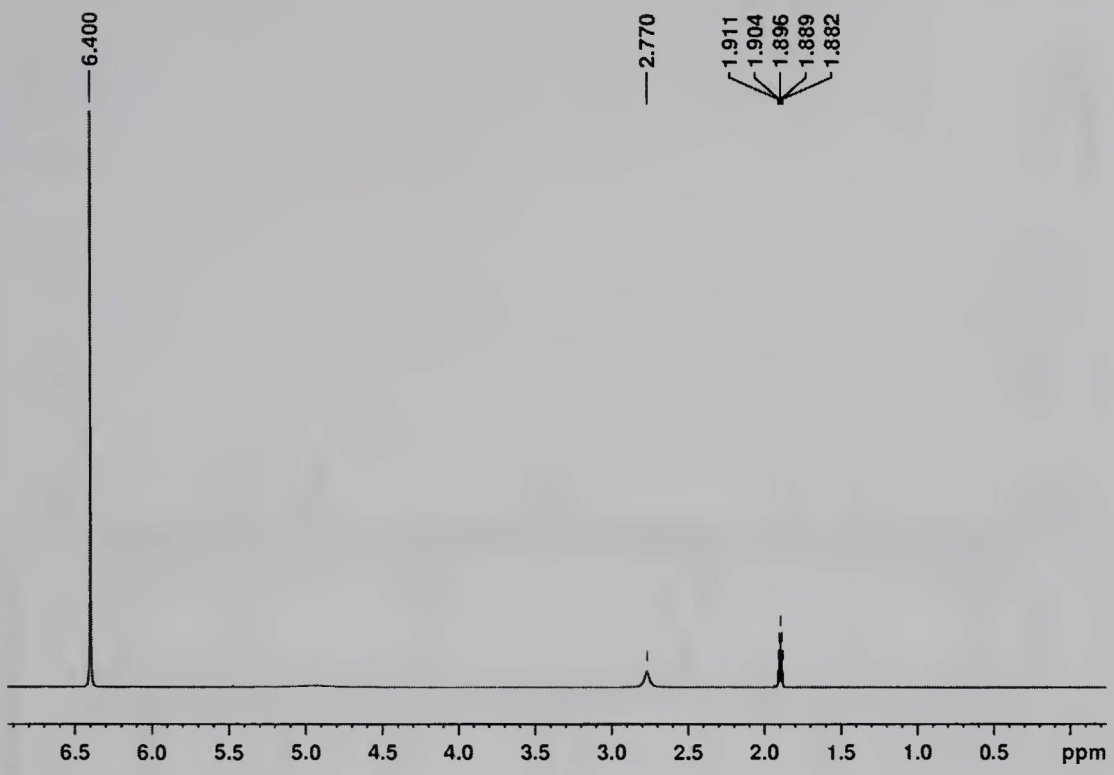


Fig. 4.16-3 ^{1}H NMR spectrum of cycloheptatrienyl molybdenum tricarbonyl tetrafluoroborate in acetone-d_6.

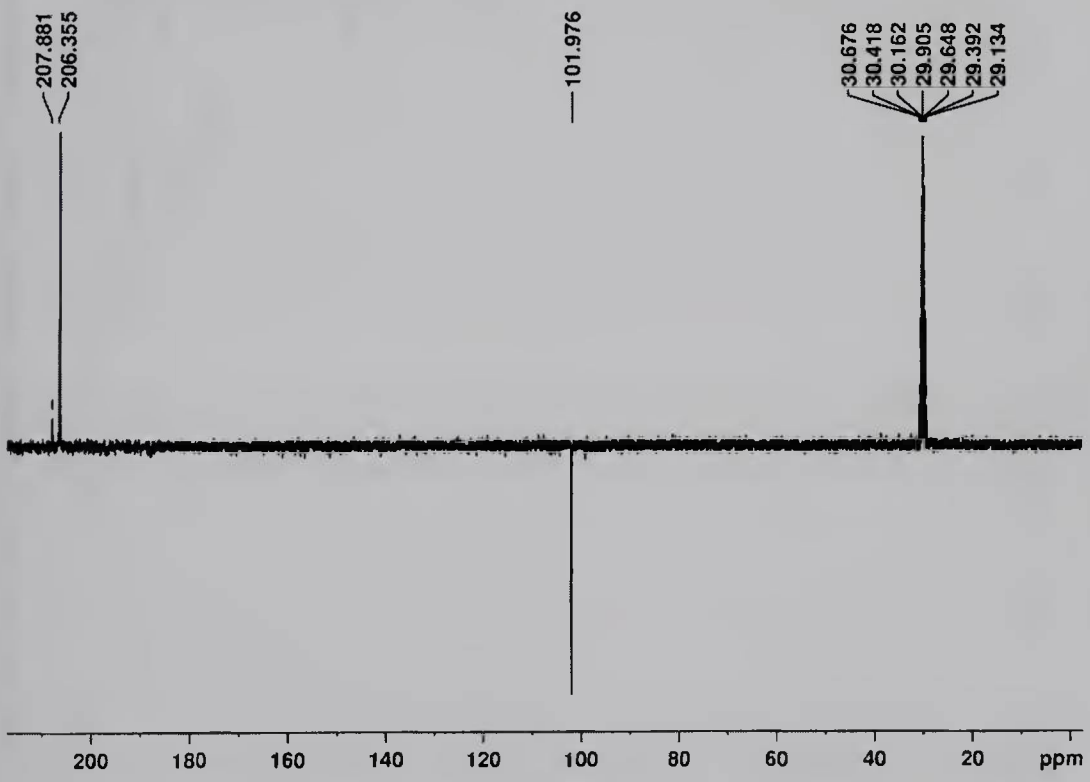


Fig. 4.16-4 $^{13}C\{^{1}H\}$ NMR spectrum of cycloheptatrienyl molybdenum tricarbonyl tetrafluoroborate in acetone-d_6.

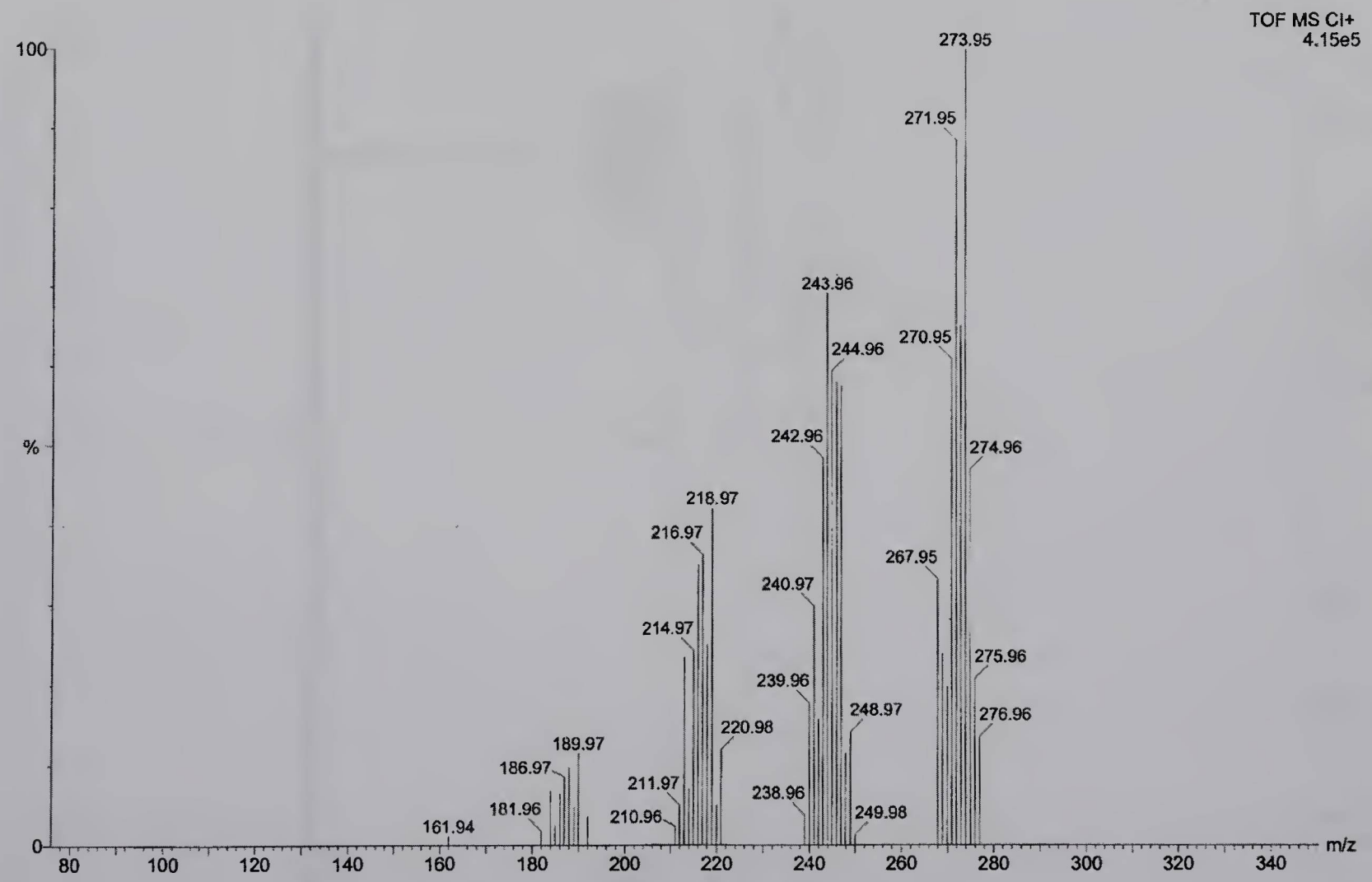


Fig. 4.16-5 Mass spectrum (chemical ionization, positive) of cycloheptatriene molybdenum tricarbonyl.

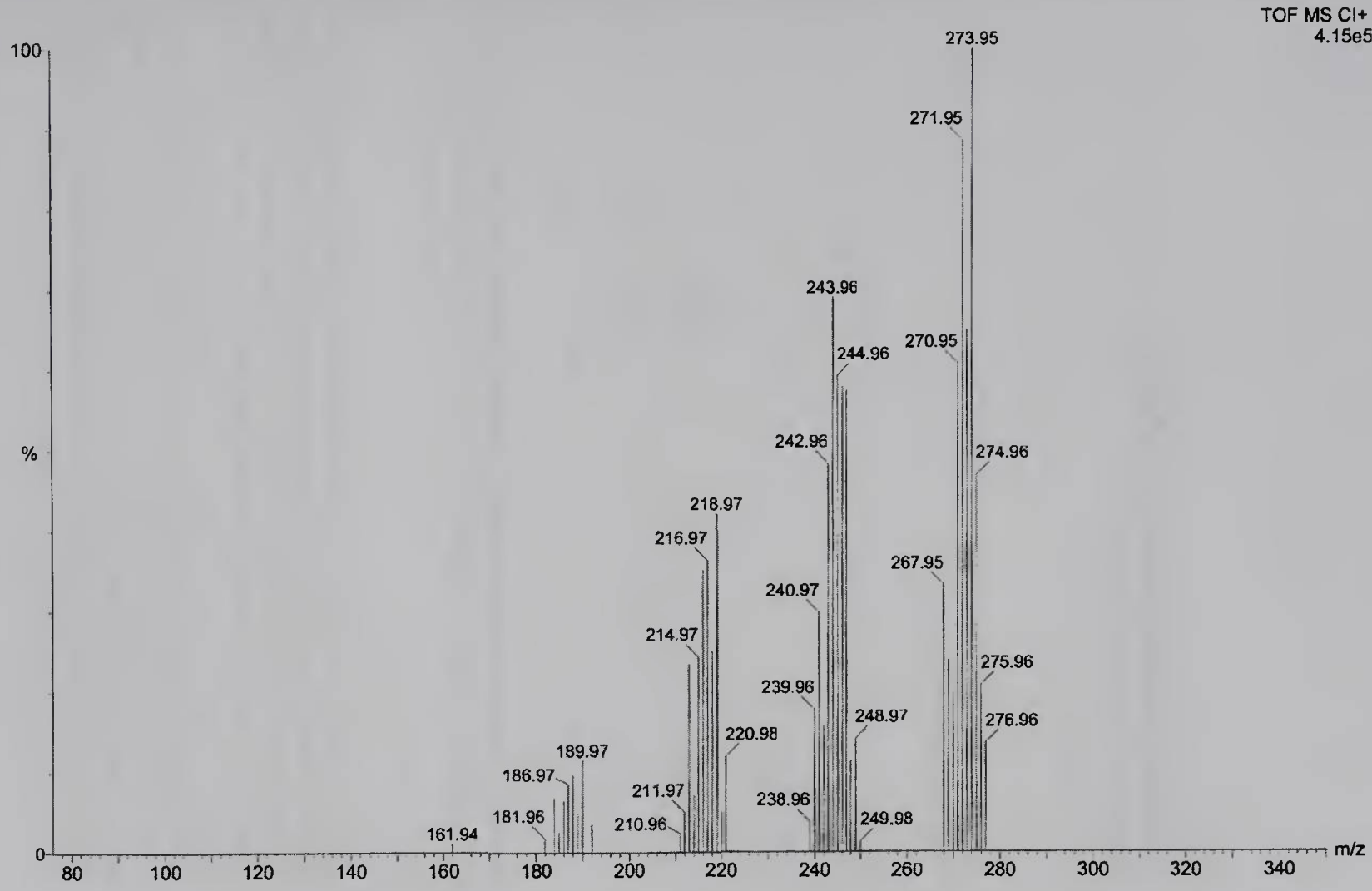
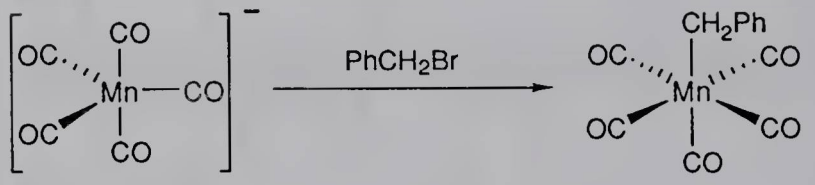


Fig. 4.16-6 Mass spectrum (electrospray, positive) of cycloheptatrienyl molybdenum tricarbonyl tetrafluoroborate, overview and detail.

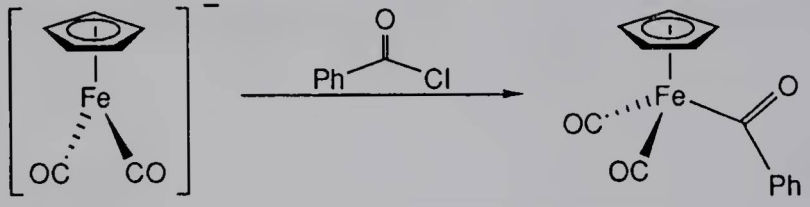
4.17
Migratory Insertion Reactions in Organo Transition-Metal Chemistry

Mark J. Winter

Many transition metal anions are *nucleophilic*. They can therefore replace the halides of alkyl halides (Eqs. 1 and 2).



(1)



(2)

Migratory insertion reactions (or simply "insertion reactions") are those in which an atom, or group of atoms, is inserted between two mutually bonded atoms (Eq. 3).

$$M\text{–}L \xrightarrow{XY} M\text{–}XY\text{–}L \qquad (3)$$

The term "insertion reaction" is a little unfortunate since many intramolecular rearrangements and intermolecular additions are classified under the same heading. Migratory insertion reactions are very important in industrial homogeneous catalysis as well as synthetic organotransition metal chemistry in university research laboratories.

Of particular interest is the transformation of alkyl carbonyl complexes into acyl species. The incoming ligand L′ may be an entity such as phosphine, amine, halide ion or carbon monoxide itself. Examples of such transformations are known for most transition metals. One reaction that has been studied particularly extensively is that of alkyl complexes $MnR(CO)_5$ with ligands such as PPh_3 or CO (Eq. 4).

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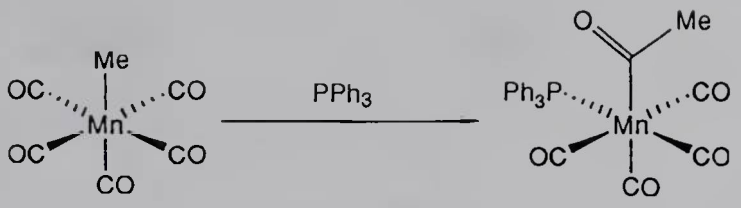
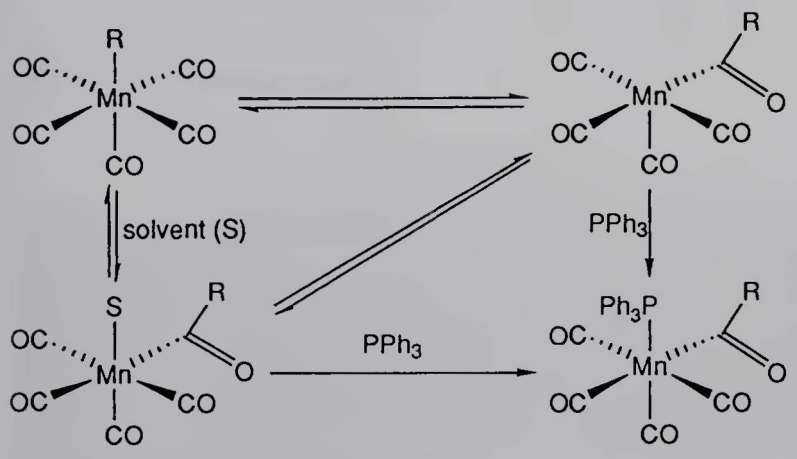


(4)

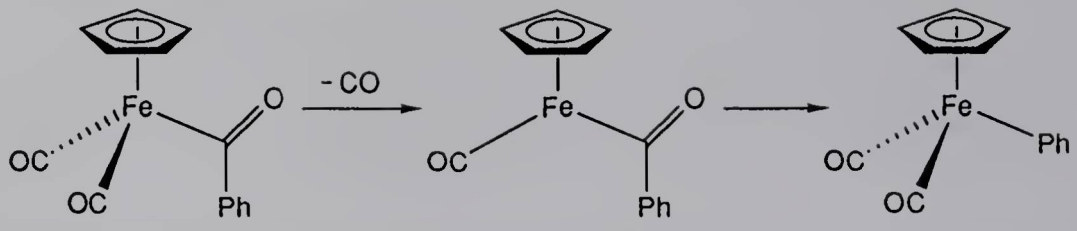
These studies, and those on some other systems, produced a set of observations consistent with a general reaction sequence for the alkyl to carbonyl insertion reaction. It is generally assumed that all alkyl to carbonyl reactions proceed in a similar fashion. You must understand that this is a tacit assumption and it does not necessary follow that all alkyl to carbonyl insertions proceed by the same mechanism (there are a few examples of those that do not).

The following five points refer to Scheme 4.17-1.

1. The R group migrates to an *adjacent* (that is, *cis*) carbonyl group.
2. In a second step, the coordinatively unsaturated (16 e^-) intermediate is attacked by the incoming (nucleophilic) ligand.
3. The 16 e^- intermediate may be "transiently stabilised" by a solvent molecule. This is particularly likely when the solvent has coordinating ability of its own, good examples are ethers and acetonitrile. Donation of a lone pair from an ether or acetonitrile transforms the 16 e^- intermediate into an 18 e^- intermediate, but one with a very loose ligand (the solvent). Although this intermediate has a stable 18 e^- configuration, it behaves essentially as an entity with a vacant coordiantion site.
4. If the alkyl group possesses chirality, retention of configuration is observed.
5. First row transition metal complexes react more quickly than either second or third row compounds. the M-alkyl bond is stronger for second and third row transition metals and therefore more difficult to break (a necessary step to achieve the migratory insertion step).



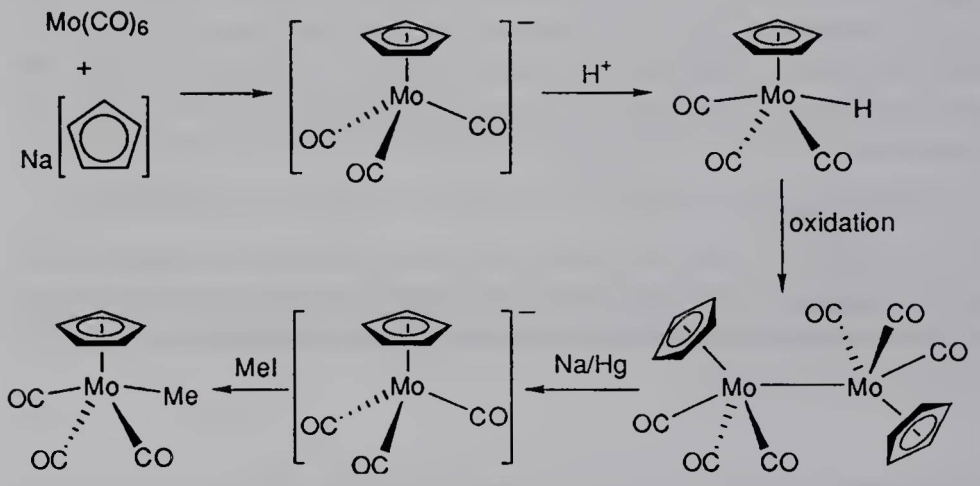
Scheme 4.17-1



The *reverse* of the alkyl to carbonyl insertion process is also known, in which case it is sometimes referred to as an *extrusion*. This process is frequently achieved by thermal or photochemical activation. An elegant series of labelling studies have demonstrated that the mechanism is the microscopic reverse of the migratory insertion process.

In the extrusion reaction a carbonyl ligand is lost and this is followed by phenyl migration to the resulting vacant coordination site.

It would be possible in a practical assignment of this type to study the manganese systems above (Scheme 4.17-1), but we choose not to do so as the compounds are rather volatile and (perhaps more to the point!) very pricey. Instead, we shall examine a series of related reactions based upon the molybdenum complex $MoMe(CO)_3(\eta^5\text{-}C_5H_5)$ shown in Scheme 4.17-2.



Scheme 4.17-2

Special Safety Precautions

The reactions described should all be carried out in a fume cupboard. Mercury gives off a dangerous vapour; sodium chips react violently with water to give flammable gas; tetrahydrofuran is extremely flammable, may form peroxides and is irritating to the eyes and the respiratory system. MeI is toxic in contact with the skin and gives off a poisonous vapour.

4.17.1 Experimental

a) [MoMe(CO)$_3$(η^5-C$_5$H$_5$)]

It is most important to exclude air from the apparatus until the reaction with MeI is complete, the anion [Mo(CO)$_3$(η^5-C$_5$H$_5$)]$^-$ is particularly air sensitive. Discuss how to do this with a demonstrator. Set up the apparatus *in a fume cupboard* as shown in Figure 4.17-1.

Flush out the apparatus with N_2, add mercury (5 cm^3) and a magnetic stir bar. Add sodium chips (0.3 g, weighed under light petroleum, cut into 5–6 pieces) one at a time and stir rapidly until the sodium reacts with the mercury (*exothermic, vigorous reaction, fumes*). Amalgam formation is best achieved with fresh sodium surfaces. If there is a problem, try holding the sodium chip under the mercury surface with a spatula and press it firmly against the glass wall of the Schlenk tube to create a new surface.

After the amalgam has formed, add tetrahydrofuran (THF) (50 cm^3, freshly distilled) followed by [Mo(CO)$_3$(η^5-C$_5$H$_5$)]$_2$ (1.0 g). Stir under N_2 until the maroon colour of the dimer is discharged (about 20 minutes to 2 hours). The idea is to stir the mixture as fast as possible in order to facilitate the reduction. The resulting murky yellow-green solutions contains [Mo(CO)$_3$(η^5-C$_5$H$_5$)]$^-$ and is very air sensitive. *The introduction of any air once the anion is generated will cause a pink colouration as the dimer is reformed.* If this happens, continue stirring over the amalgam until the pink colour is discharged.

Separate the anion solution from excess amalgam with a syringe. Stop stirring the reaction and rotate the Schlenk tube until it is nearly horizontal and allow any solids to settle. This may take a couple of minutes. Set up a *second* Schlenk tube and flush it out with N_2. Transfer the anion solution to the second tube *via* syringe. Use Suba-Seals to prevent air getting into either Schlenk tube.

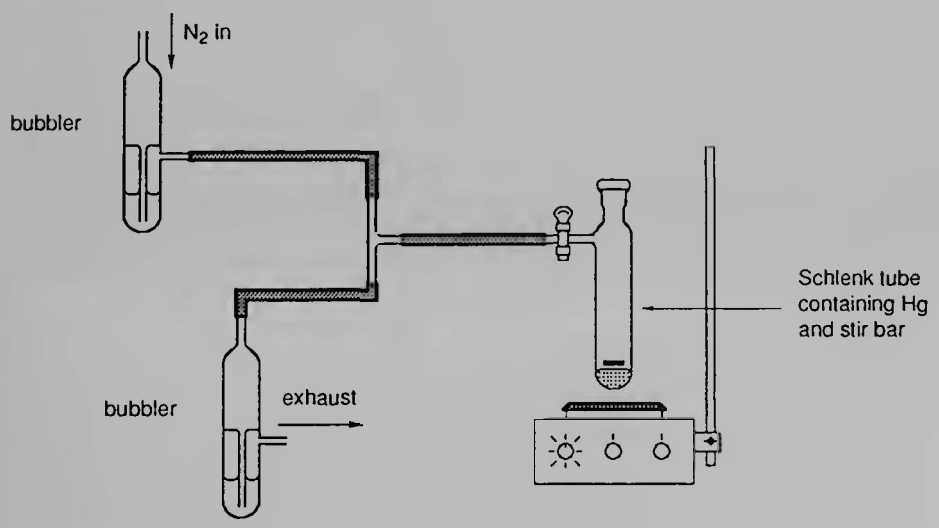


Fig. 4.5-1 Apparatus for synthesis under N_2.

Add more THF (10 cm^3, freshly distilled) to the first tube and stir for a minute or so. If there is a pink colouration (a little oxidation of the anion), continue stirring until the colour is discharged. Allow the solution to settle and transfer the second batch of anion solution to the second Schlenk tube in the same way as before.

Add MeI (1.0 g) (weigh out and handle in fume cupboard) to the anion solution, replace the Suba-Seal with a glass stopper, close the sidearm tap and leave to stir overnight.

Remove the solvent under reduced pressure, *at ambient temperature.* Extract the solid into light petroleum (*extremely flammable*) (4 × 20 cm^3 portions or until colourless), and filter the resulting solution through a short Al_2O_3 plug (about 2.5 cm in a filter stick). Allow the product to pass through the alumina under gravity. Wash through with extra light petroleum until the eluate is colourless.

Remove the solvent. Scrape all the solid into a sublimation unit and sublime out the product under vacuum ($<10^{-1}$ Torr, about 40–60 °C, use a water bath for heating). It is most important to maintain a good vacuum while this is going on.

Record the IR spectrum of your product as a *solution* in light petroleum (CaF_2 cells) in the range 2200–1500 cm^{-1}, determine the yield.

b) $[Mo(CO)_2(COMe)(\eta^5\text{-}C_5H_5)(PPh_3)]$

Stir an acetonitrile (10 cm^3) solution containing $MoMe(Co)_3(\eta^5\text{-}C_5H_5)$ (0.13 g, 0.5 mmol) and PPh_3 (0.2 g, 0.76 mmol) under nitrogen overnight.

This should give a bright yellow precipitate. Collect the yellow solid $[CpMo(COMe)(CO)_2(PPh_3)]$ on a sinter and wash with a little light petroleum. Dry under vacuum. If the product looks a little grubby, recrystallise from CH_2Cl_2 and light petroleum.

Record the *solution* IR spectrum of the product in CH_2Cl_2(CaF_2 cells) in the range 2200–1500 cm^{-1}. Determine the yield.

4.18
A Transition-Metal Alkylidyne Complex

Stephen Anderson, Darren Cook, and Anthony F. Hill

Although alkylidyne complexes *i.e.* compounds with metal-carbon triple bonds, were once considered exotic laboratory curiosities, they have now found wide application in organic synthesis and as catalysts for alkyne polymerisation and metathesis. This experiment involves the synthesis of a thermally stable alkylidyne complex of tungsten, $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_2(tmen)]$, via the abstraction of oxide from an anionic tungsten acylate, following a method originally described by Mayr. The bromide ligand results from CF_3CO_2/Br metathesis by excess bromide present in the lithium reagent with an initially formed trifluoroacetato complex $[W(\equiv CC_6H_4Me\text{-}4)(O_2CCF_3)(CO)_2(tmen)]$.

Special Safety Precautions

1. Tungsten hexacarbonyl and trifluoroacetic anhydride are extremely toxic. Deuterochloroform is highly toxic, mutagenic and an irritant. Accordingly, all manipulations should be carried out in an efficient fume cupboard. *N,N,N′,N′*-tetramethylethylenediamine (tmen) and diethyl ether are flammable liquids.
2. Lithium metal and organolithium reagents react violently with water so every effort must be made to exclude moisture. Unrequired excess lithium reagents may be destroyed by slow addition to propan-2-ol followed by ethanol and finally water.
3. Carbon monoxide is liberated in the decarbonylation step and so caution must be exercised.

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4.18.1 Experimental

Equation (1) shows the reaction sequence to be performed.

$$[W(CO)_6] \xrightarrow[\text{(ii) } (CF_3CO)_2O,\ -78\,^\circ C\ \text{(iii) tmen}]{\text{(i) } LiC_6H_4Me/LiBr} [W(\equiv CC_6H_4Me)Br(CO)_2(tmen)] \quad (1)$$

All manipulations must be carried out under anaearobic conditions in a fume cupboard. It is essential that sodium-dried diethyl ether is used due to the moisture sensitive nature of the intermediates. All glassware should be oven dried and assembled whilst hot, flushing with nitrogen. High-sodium grade lithium (1% Na) gives the best results for the synthesis of the 4-lithiotoluene.

a) An Ether Solution of LiC_6H_4Me-4

A three-necked 250 cm^3 round-bottomed flask equipped with a reflux condenser, a paraffin bubbler, a pressure-equalised dropping funnel and magnetic stir bar is flushed with nitrogen for 3–5 minutes. Lithium metal (1.2 g), cut into small pieces, is then added under a counterflow of nitrogen followed by petroleum ether (30 ml). The petroleum ether is then removed by syringe and discarded (to remove the protective coating of paraffin from the lithium). Diethyl ether (DRY, 50 ml) is then added and the flask immersed in an ice bath. A solution of 4-bromotoluene (10.0 g) in dry diethyl ether (25 ml) is then added via a dropping funnel over a period of 1 hour. The mixture is left to warm slowly to room temperature overnight by which time the bulk of the lithium metal should have dissolved.

b) [W-(CC_6H_4Me-4)$Br(CO)_2$(tmen)]

A three-necked 250 cm^3 round-bottomed flask equipped with a paraffin bubbler, a pressure-equalised dropping funnel and magnetic stir bar is flushed with nitrogen for 3–5 minutes. Tungsten hexacarbonyl (finely ground, **CAUTION**, 5.0 g) is then added against a counterflow of nitrogen followed by dry diethyl ether (100 ml). The solution of 4-lithiotoluene (50 ml) prepared in a) above is then transferred via syringe (or cannula) to the dropping funnel. The solution is then added dropwise to the tungsten hexacarbonyl solution with rapid stirring. After approximately 25 ml has been added, a solution infra-red spectrum should be measured to estimate the extent of reaction ($\nu(CO)_{max}$ $W(CO)_6$ = ca. 1970 cm^{-1}). Further aliquots of the 4-lithiotoluene solution are added whilst monitoring the effect by IR spectroscopy until only a trace of $[W(CO)_6]$ remains (<2%). The dropping funnel is then removed and the remaining lithium reagent destroyed by adding slowly to propan-2-ol (50 ml). The flask is then immersed in a dry-ice/acetone bath and stirred for 5–10 minutes to ensure that the reaction mixture has cooled adequately. Trifluoroacetic anhydride (1.50 ml) is then added dropwise whereupon a red colour appears and then dissi-

pates. The mixture is stirred for a further 10 minutes and then removed from the dry-ice bath. After stirring for a further 10 minutes, *N,N,N′,N′*-tetramethylethylenediamine (tmen) (3 ml) is then added and the mixture stirred for 10 minutes. Stirring is then stopped and the mixture allowed to warm up slowly overnight (**CAUTION:** CO evolves). The brown supernatant is then removed by decantation whilst a flow of nitrogen is maintained over the surface of the mixture. Dry diethyl ether (50 ml) is added and the mixture stirred and then left to settle. The ether is removed by decantation and the flask transferred to a rotary evaporator to remove the last traces of ether. The yellow solid should be transferred to a vial which has been flushed with nitrogen and stored in the dark.

Measure the yield, melting point, infra-red spectra (Nujol and dichloromethane) and ^{1}H NMR spectrum ($CDCl_3$, 60 MHz). NB: The ^{1}H NMR spectrum should be measured as soon as possible after preparing the solution in $CDCl_3$. Prolonged storage of such aerated solutions will lead to decomposition. After obtaining these data, you will be provided with a $^{13}C\text{-}\{^{1}H\}$ NMR spectrum, a full analysis of which should include identification of J ($^{183}W^{13}C$) for the carbonyl and alkylidyne carbon nuclei. Use the spectroscopic data obtained to determine the stereochemistry at the tungsten centre and explain why this is the most stable ligand arrangement. Briefly discuss the steps involved in the formation of the alkylidyne complex and suggest why $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_2(tmen)]$ is a more stable compound than $[W(\equiv CC_6H_4Me\text{-}4)Br(CO)_4]$.

4.18.2 Technical Notes

1. Diethyl ether should be dried over sodium wire.
2. Lithium wire containing 1% sodium (e.g. Aldrich: 27,832–7) should be used to ensure that there are no problems with the initiation of the lithiation step.
3. Because of the extreme moisture sensitivity of trifluoroacetic anhydride, for large classes this should be stored in a Schlenk or Youngs tube and dispensed by syringe. Ill treated and aged samples of the anhydride will contain considerable amounts of the acid which seriously diminishes the overall yield.
4. All other reagents may be used as received from commercial sources.
5. The procedure also works well for a wide range of aryl bromides and also for $[Mo(CO)_6]$, however, that illustrated here is chosen for the simplicity of the NMR interpretation.

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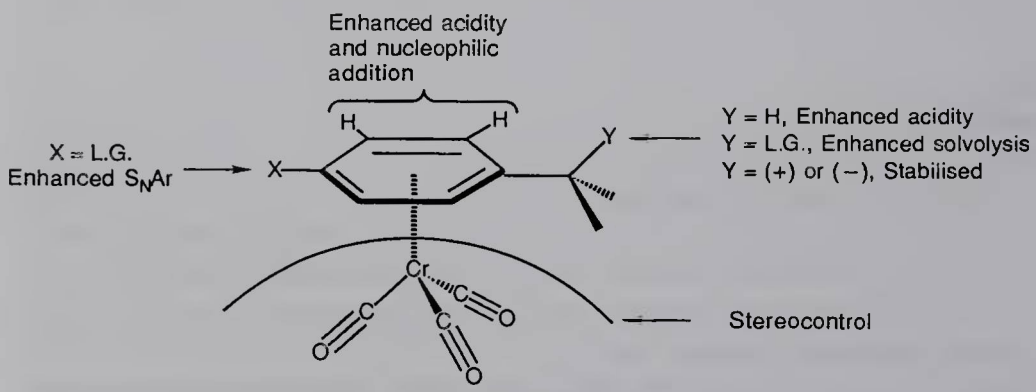
4.19
The Synthesis of η^6-Arenetricarbonyl Chromium(0) Complexes

David A. Widdowson

The exploitation of the modification of reactivity of an organic molecule by complexation to a metal is one of the major areas of development in organic synthesis in recent times. One particular area is the study of the enhanced reactivity of arenes upon complexation by Group VI metal and manganese carbonyls. By far the most studied among these are the arenechromiumtricarbonyl complexes. The effect of the metal moiety on the arene ring is an apparent electron withdrawal from the π-system and this manifests itself in a variety of ways as shown below.



It is important for the ease of use of such complexes that they should be readily prepared and efficiently decomplexed. This experiment demonstrates the most convenient method of preparation *via* the use of the Strohmeier apparatus and a simple vacuum line/nitrogen manifold (Schlenk line). The complexes are synthesised by the direct reaction between the arene and chromium hexacarbonyl in an ether solvent mixture (Bu_2O : THF 10 : 1).[1)]

1) This solvent mixture has been determined empirically to give the optimum reaction temperature and a good backwash of the volatilised chromium hexacarbonyl (see C. A. L. Mahaffy, P. L. Pauson, *Inorg. Synth.* **1979**, *19*, 154).

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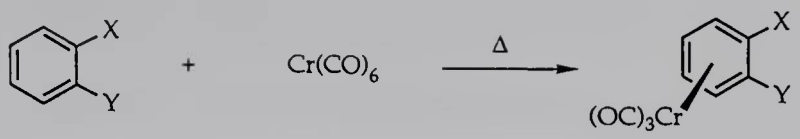

The need for the Schlenk line arises from the fact that the intermediates generated during the synthesis, the coordinatively unsaturated chromium carbonyl species, are very oxygen sensitive and so rigorously anaerobic conditions are essential. Once formed, the arene complexes are air stable in the solid state and can be handled without difficulty by conventional techniques.

The Strohmeier apparatus is, in effect, an inverted condenser. This is a convenient way of dealing with the problem of the volatility of the metal carbonyl which tends to condense above the level of the solvent in a normal condenser and block it. In the Strohmeier apparatus, any hexacarbonyl condensing ahead of the solvent is washed back into the reaction vessel *via* the syphon.

Special Safety Precautions

Chromium hexacarbonyl is a colourless crystalline solid with a high vapour pressure. Highly toxic by ingestion or inhalation. All manipulations should be carried out in a fume cupboard.

4.19.1 Experimental

A mixture of di-*n*-butyl ether (purified by distillation from sodium-benzophenone[2] (60 cm^3), THF (purified by distillation from sodium-benzophenone (6 cm^3), the arene (*e.g.* fluorobenzene, chlorobenzene, anisole, 1-(tri-*iso*propylsilyl)indole, 2-methylthiophene; quantity: 1 equivalent – for valuable substrates – or 10 cm^3 – for readily available substrates) and chromium hexacarbonyl (1.0 g) are placed, together with a magnetic stirrer bar, in a 100 cm^3 round-bottomed flask and attached to the Strohmeier apparatus. The assembly is connected to the Schlenk line using semi-pressure tubing.

Check that all joints are sealed, then evacuate the apparatus by carefully turning the 3-way tap on the line. As soon as the solvent begins to boil, let in the dry, oxygen-free nitrogen *via* the 3-way tap. Repeat this cycle nine more times to ensure that the system is completely anaerobic. With the system maintained under a slight positive pressure of nitrogen, commence stirring and heating the contents of the flask. Maintain the solution at a steady reflux for $\approx$24 hours.

At the end of the reaction, the flask is cooled then detached from the Strohmeier apparatus. The solution is chromatographed over a short ($\sim$5 cm) column of silica

2) A special communal still for the purification of this solvent should be set up in a fume cupboard. It is essential that you consult a demonstrator or a technician before you use it.

gel 60 using ether to effect the elution of the yellow-orange complex. Evaporation of the solvents yields the product.

Record the m.p. and record and interpret the IR and NMR spectra. Comment on the synthetic uses of these complexes.

Further Reading

For broad surveys of organometallic chemistry in organic syntheses see: (a) *Comprehensive Organometallic Chemistry,* Vols. 7 and 8 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, **1982**; (b) S. G. Davies, *Organotransitionmetal Chemistry: Applications to Organic Synthesis,* Pergamon Press, Oxford, **1982**; (c) E.-I. Negishi, *Organometallics in Organic Synthesis,* Wiley-Interscience, New York, **1980**.

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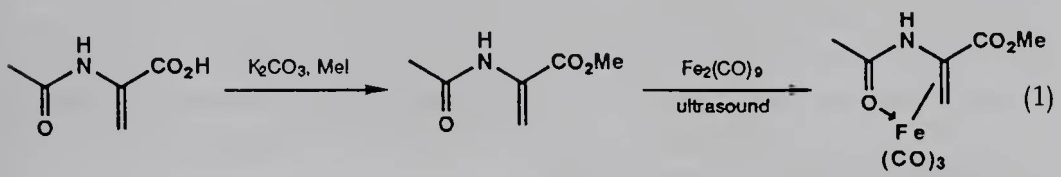
4.20
Preparation of the Iron Tricarbonyl Complex of Methyl-2-Acetamidoacrylate

M. Elena Lasterra-Sanchez and Susan E. Gibson

Many organic compounds form stable iron carbonyl complexes. By forming these complexes, organic molecules which are too reactive to be isolated can be stabilised and studied, olefinic groups can be protected during the course of a multi-step organic synthesis, the chemical reactivity of organic compounds can be modified and the stereochemical course of organic reactions can be altered. In this experiment, you will form the iron tricarbonyl complex of the amino acid dehydroalanine using ultrasound (Eq. 1). Formation of its iron carbonyl complex modifies the chemical reactivity of the dehydroalanine and this has been exploited in a synthetic route to unusual highly branched amino acids.



(1)

Special Safety Precautions

1. Methyl 2-acetamidoacrylate can act as a skin and nasal irritant. Wash off with alcohol followed by copious quantities of water.
2. Diethyl ether is highly flammable and should be handled in a fume cupboard.
3. Iodomethane is highly toxic and volatile. It must be handled with disposable gloves in a fume cupboard.
4. Di-iron nonacarbonyl is harmful and should also be handled in a fume cupboard.

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4.20.1 Experimental

a) Methyl-2-acetamidoacrylate

2-Acetamidoacrylic acid (2.33 g, 18 mmol) is dissolved in dry acetone (300 cm^3) in a two-neck round-bottomed flask fitted with a condenser (carrying a $CaCl_2$ drying tube) and a stopper. To this solution is added K_2CO_3 (5.45 g, 39.5 mmol) and iodomethane (2.24 cm^3, 36 mmol). The mixture is then heated under reflux for 3 hours, after which time additional iodomethane (1.12 cm^3, 18 mmol) is carefully added and the heating maintained for a further 3 hours. The solution is then allowed to cool and the solid material removed by filtration and washed with dry acetone. The acetone solution and the acetone washings are evaporated to dryness (using a rotary evaporator) and the residue is redissolved in hot chloroform (700–800 cm^3) and filtered. Removal of the chloroform *in vacuo* affords the product either as white crystals or as an oil, which forms white crystals on standing overnight. Record the melting point, the IR spectrum (KBr) and the ^1H NMR spectrum ($CDCl_3$) of your white crystals.

b) (Methyl-2-acetamidoacrylate)tricarbonyliron(0)

The ester prepared above (1.5 g, 10.5 mmol) is dissolved in sodium-dried diethyl ether (75 cm^3) in a three-neck round-bottomed flask fitted with a condenser and a gas inlet. Nitrogen gas is bubbled through the stirred solution for 5 minutes to saturate the solution with nitrogen and then $Fe_2(CO)_9$ (7.65 g, 21 mmol) is added carefully. Taking care to maintain the nitrogen atmosphere, the apparatus is placed in an ultrasonic bath and sonicated at 35 °C for approximately 30 minutes. The product mixture is then filtered through deactivated alumina or celite using diethyl ether as eluent and the solvent is removed *in vacuo*.

If the product contains $Fe_3(CO)_{12}$ impurities (green in colour), it may be purified by column chromatography (SiO_2; 2:3 ethyl acetate: –40–60 °C petroleum ether) to give the iron complex as an air stable yellow-orange crystalline material. Record the melting point, the IR spectra (KBr and hexane solution) and the ^3H NMR spectrum ($CDCl_3$) of your product.

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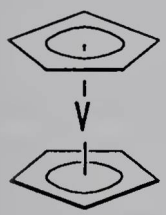
4.21
Halfsandwich Carbonyl Vanadium Complexes

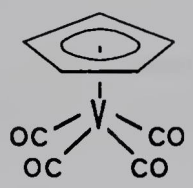
Max Herberhold and Matthias Schrepfermann

Following the synthesis of the first sandwich complex, di(cyclopentadienyl)iron ("ferrocene", $Fe(\eta^5\text{-}C_5H_5)_2$) in 1951/52, a series of sandwich and halfsandwich compounds of other transition metals has been described. In the case of vanadium, the halfsandwich complex η^5-cyclopentadienyl tetracarbonylvanadium, $(\eta^5\text{-}C_5H_5)V(CO)_4$ (**2**), can be prepared starting from either vanadocene, $V(\eta^5\text{-}C_5H_5)_2$ (**1**), or hexacarbonylvanadium, $V(CO)_6$ (**3**).



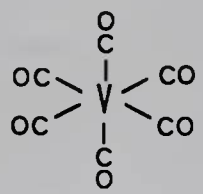
$V(\eta^5\text{-}C_5H_5)_2$

1



$(\eta^5\text{-}C_5H_5)V(CO)_4$

2



$V(CO)_6$

3

In contrast to the paramagnetic compounds **1** and **3**, the diamagnetic halfsandwich complex $(\eta^5\text{-}C_5H_5)V(CO)_4$ (**2**) conforms to the 18-electron rule (5 (V) + 5 (C_5H_5) + (4 × 2 (CO)) = 18 electrons). Halfsandwich carbonyl-metal complexes such as **2** are good precursors for oligonuclear $(\eta^5\text{-}C_5H_5)V$ compounds; they may also serve as models for either ring substitution or photo-induced displacement of CO ligands in organometallic complexes. The ring ligand $(\eta^5\text{-}C_5H_5)$ is able to screen one hemisphere of the coordination shell of the metal; the permethylated cyclopentadienyl ring ligand $(\eta^5\text{-}C_5Me_5)$ is an even better protecting group.

Although **2** is conveniently obtained by high pressure carbonylation of $V(\eta^5\text{-}C_5H_5)_2$ (**1**), the synthesis of halfsandwich carbonylvanadium complexes is generally carried out via hexacarbonylvanadium, $V(CO)_6$ (**3**), a blue-black 17-electron compound. The first two parts of this experiment describe the preparation of the homoleptic carbonyl-metal complex, $V(CO)_6$ (**3**), by reductive high pressure carbonylation of VCl_3 to give a [sodium(diglyme)$_2$]$^+$ salt of the hexacarbonylvanadate anion, $[V(CO)_6]^-$ (Eq. 1). (A synthesis of the $[V(CO)_6]^-$ anion by reductive carbonylation of VCl_3 under atmospheric pressure in the presence of cyclooctatetraene (C_8H_8)

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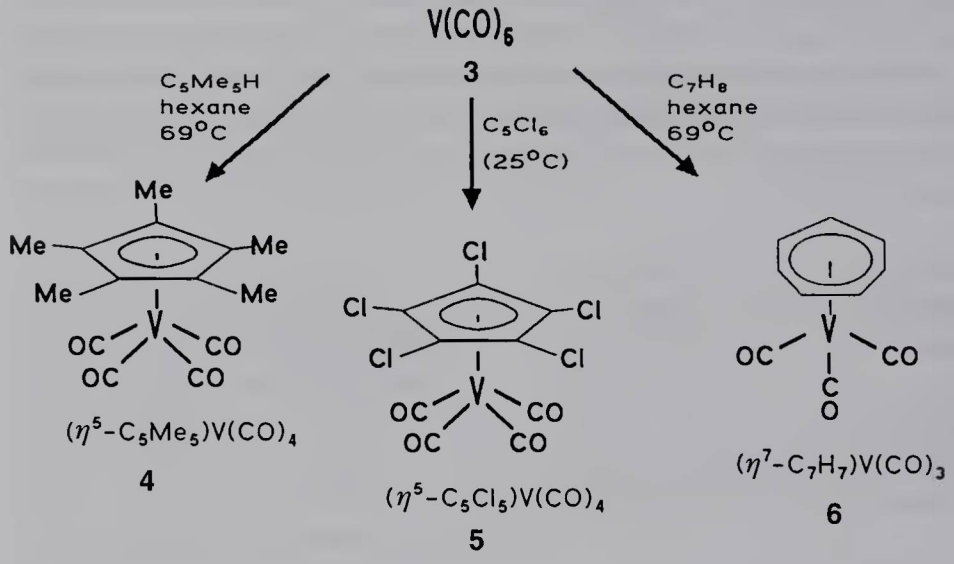
in tetrahydrofuran (THF) solution has also been described, however, the salt $[Na(THF)_x][V(CO)_6]$ cannot be oxidised subsequently to $V(CO)_6$, which loses CO easily in the presence of THF).

$$VCl_3 \xrightarrow[\substack{\text{diglyme}\\ 200\text{ bar CO}}]{4\text{ Na (sand)}} [Na(C_6H_{14}O_3)_2^+][V(CO)_6]^- \xrightarrow[-1/2\ H_2]{H_3PO_4} \underset{\mathbf{3}}{V(CO)_6} \qquad (1)$$

Protonation of the $[V(CO)_6]^-$ anion by anhydrous phosphoric acid and thermal decomposition of the intermediate $iHV(CO)_6o$ leads to $V(CO)_6$ (**3**) in ca. 90% yield.

Three examples of the conversion of **3** into halfsandwich carbonylvanadium complexes such as **4–6** are presented, using the reactions with pentamethylcyclopentadiene, hexachlorocyclopentadiene and 1,3,5-cycloheptatriene.



Special Safety Precautions

1. Carbon monoxide, CO, is very toxic (MAK value 33 mg m^{-3}, 30 ppm). During the manipulations with the autoclave, a CO warning sensor (threshold value 30 ppm!!) should be worn.
2. Sodium sand is pyrophoric and must be handled under inert gas (N_2 or Ar). Excess sodium sand from the filtration of the autoclave reaction mixture should be destroyed by treating the residue with *i*PrOH, EtOH and water subsequently.
3. $V(CO)_6$ and $(\eta^7\text{-}C_7H_7)V(CO)_3$ are pyrophoric; $V(CO)_6$ loses CO slowly.
4. The residues of all filtration steps are pyrophoric and are allowed to decompose slowly in the fume cupboard after being poured into a large glass dish.

4.21.1 Experimental

a) Di[bis(2-methoxyethyl)ether]sodium-hexacarbonylvanadate(−1), $[Na(diglyme)_2][V(CO)_6]$

$$VCl_3 + 4Na + 2C_6H_{14}O_3 \xrightarrow[(Fe(CO)_5)]{\substack{160\,^\circ C \\ 200\ bar\ CO}} [Na(C_6H_{14}O_3)_2][V(CO)_6] + 3NaCl \qquad (2)$$

A 0.5 l autoclave (pressure capacity 300 bar) is charged with 15 g sodium sand (650 mmol), 17.2 g VCl_3 (109 mmol), 200 cm^3 "diglyme" (bis(2-methoxyethyl) ether) and 1 cm^3 $Fe(CO)_5$ under an inert gas. The autoclave is first flushed with nitrogen (50 bar, to check leaks) and then CO (50 bar). After expanding, 200 bar CO is pressed on the system which is then slowly heated to 160 °C under stirring.

After 48 h, the autoclave is allowed to cool down to room temperature and the reaction mixture is filtered over Na_2SO_4 (10 × 3 cm). The residue is washed with Et_2O until the filtrate has become colourless. The yellow solution is then extracted with 1 l hexane in a separatory funnel. The brown layer separating at the bottom of the funnel is allowed to drop slowly into cold (−78 °C) hexane (ca. 100 cm^3). This leads to precipitation of the hexacarbonylvanadate salt, $[Na(diglyme)_2][V(CO)_6]$.

The crude orange-red product is sticky and therefore reprecipitated several times by redissolving it in a small amount of Et_2O (30–40 cm^3), adding 100 ml hexane via syringe and decanting the pink supernatant solution as soon as possible. This procedure is repeated until the product is obtained as a yellow powder, which is then dried at the oil pump.

Yield: 27.8–33.4 g (50–60 %).

The product should be stored in a refrigerator (−20 °C) in the dark.

b) Hexacarbonylvanadium, $V(CO)_6$ (3)

$$[Na(C_6H_{14}O_3)_2][V(CO)_6] + H_3PO_4 \xrightarrow{via\ [HV(CO)_6]} V(CO)_6 + 1/2\ H_2 + NaH_2PO_4 + 2C_6H_{14}O_3 \qquad (3)$$

3

All manipulations must be carried out under inert gas (N_2 or Ar).

In a special sublimation vessel (Fig. 4.21-1), about 15 g P_4O_{10} are dissolved in ca. 65 ml commercial orthophosphoric acid (85 % H_3PO_4) at 0 °C (charge the vessel without inert gas stream!). A 10 g portion of dry $[Na(diglyme)_2][V(CO)_6]$ (19.6 mmol) is added through a long funnel to the surface of the anhydrous acid. The lower end of the sublimation tube is loosely fitted with a lump of glass wool to protect the $V(CO)_6$ (3) product at the sublimation finger against the squirting acid during the sublimation process. Then the cooling finger is attached above the glass wool (2–3 cm) and fixed by a small clamp.

The cooling finger is cooled to −30 °C using a cryostat (isopropanol), and high vacuum (ca. 10^{-2} mbar) is applied. Whereas the water bath is heated to 40 °C, the blue-

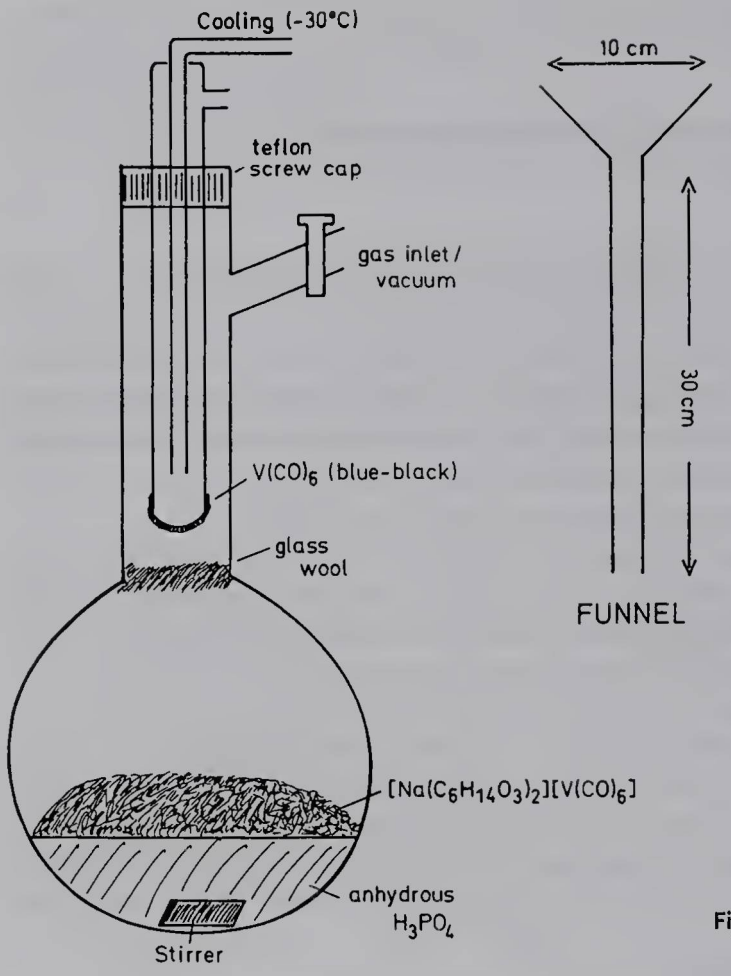


Fig. 4.21-1 Sublimation vessel.

black $V(CO)_6$ (3) is subliming to the finger (the vacuum should be re-applied periodically). As soon as the phosphoric acid becomes slightly green, the sublimation is discontinued and the detached sublimation finger is placed on a frit. The product $V(CO)_6$ (3) is removed from the finger, washed with degassed air-free water (degassed for ca. 15 minutes at the aspirator vacuum) and finally dried at the aspirator vacuum until the product can be poured into an appropriate Schlenk tube. The blue-black crystals should be so dry that formation of ice is not observed when the tube is stored at –20 °C).

Yield: 3.8 g (90 %), m.p. 70 °C (dec.).

c) (η^5-Pentamethylcyclopentadienyl)tetracarbonylvanadium, (η^5-C_5Me_5)$V(CO)_4$ (4)

$$\underset{\mathbf{3}}{V(CO)_6} + C_5Me_5H \rightarrow \underset{\mathbf{4}}{(\eta^5\text{-}C_5Me_5)V(CO)_4} + 2CO + 1/2\ H_2 \qquad (4)$$

All manipulations are carried out under inert gas (N_2 or Ar), and the direct influence of sun or UV light should be avoided.

In a Schlenk tube, 1.3 g $V(CO)_6$ (3) (5.94 mmol) are dissolved in 75 cm^3 hexane (not completely soluble!) and treated with 1.15 cm^3 (7.12 mmol) distilled penta-

methylcyclopentadiene, C_5Me_5H. The reaction mixture is heated to boiling (paraffin valve at the reflux condenser) in a preaheated oil bath (ca. 100 °C) until all the $V(CO)_6$ (**3**) is consumed (ca. 1–2 hours; monitor by IR spectroscopy!).

The cold mixture is chromatographed over silica[1] (5 × 3 cm) using hexane/toluene (5:1) as the eluant. The solvent is removed from the orange solution at the oil pump vacuum, the crude product is redissolved in 5 ml pentane and stored on dry ice overnight.

The supernatant liquid is discarded and the orange residue is dried at the aspirator vacuum. The crude $(\eta^5\text{-}C_5Me_5)V(CO)_4$ (**4**) product is then sublimed in a high vacuum using a water bath (90–100 °C). The sublimate can be scratched off the finger in the presence of air, but the pure product should be stored under inert gas. It can be kept at room temperature in the dark for unlimited periods.

Yield: 1.15 g (65%), orange needles, m.p. 144 °C.

d) $(\eta^5$-Pentachlorocyclopentadienyl)tetracarbonylvanadium, $(\eta^5\text{-}C_5Cl_5)V(CO)_4$ (5)

$$\underset{\mathbf{3}}{4V(CO)_6} + 3C_5Cl_6 \rightarrow \underset{\mathbf{5}}{3(\eta^5\text{-}C_5Cl_5)V(CO)_4} + VCl_3 + 12CO \qquad (5)$$

All manipulations are carried out under inert gas and the direct influence of sun or UV light should be avoided.

In a Schlenk tube, 0.25 g $V(CO)_6$ (**3**) (1.14 mmol) are dissolved in 30 cm^3 hexane (not completely soluble!) and treated with 0.18 ml (1.14 mmol) distilled hexachlorocyclopentadiene, C_5Cl_6. After a few minutes, complex **5** is formed in the solution, while VCl_3 precipitates. The mixture is chromatographed over silica[1] (5 × 3 cm) using hexane as the eluant. The solvent is removed from the orange solution under reduced pressure and the product **5** is dried at the oil pump.

Yield: 0.2 g (45%), orange needles, m.p. 71 °C.

$(\eta^5\text{-}C_5Cl_5)V(CO)_4$ (**5**) should be stored under argon at –20 °C in the dark and prepared freshly for reactions.

e) $(\eta^7$-Cycloheptatrienyl)tricarbonylvanadium, $(\eta^7\text{-}C_7H_7)V(CO)_3$ (6)

$$\underset{\mathbf{3}}{V(CO)_6} + C_7H_8 \longrightarrow \underset{\mathbf{6}}{(\eta^7\text{-}C_7H_7)V(CO)_3} + 3CO + 1/2\,H_2$$

$$\xrightarrow{\text{by-product}} 1/2\,[(\eta^7\text{-}C_7H_7)V(\eta^6\text{-}C_7H_8)][V(CO)_6] + 3CO + 1/4\,H_2 \qquad (6)$$

All manipulations are carried out under inert gas.

In an appropriate Schlenk tube, 6.11 g $V(CO)_6$ (**3**) (27.9 mmol) are dissolved in 220 cm^3 hexane (not completely soluble!) and treated with 6.7 ml (65.0 mmol) dis-

1) The silica used for column chromatography should be periodically degassed under high vacuum and subsequently loaded with inert gas (N_2 or Ar) before use.

tilled 1,3,5-cycloheptatriene, C_7H_8. The mixture is refluxed in a preheated oil bath (ca. 100 °C) for 90 minutes (paraffin valve at the reflux condenser).

The cold reaction mixture is filtered over a fine glass frit to remove the brown by-products (such as $[(\eta^7\text{-}C_7H_7)V(\eta^6\text{-}C_7H_8)][V(CO)_6]$). The residue is repeatedly washed with 30 cm^3 portions of hexane until the filtrate becomes colourless. The volume of the solution is reduced to ca. 60 cm^3. In case there should be unreacted $V(CO)_6$ in the cooling trap, the solution is brought to dryness and the residue is redissolved in 60 ml hexane. The hexane solution is kept on dry ice overnight. The halfsandwich complex **6** forms dark green needles. If the product is amorphous, it can be recrystallised easily from hexane.

The supernatant solution is decanted, and the product **6** is dried in a high vacuum. It should be stored under argon.

Yield: 2.14 g (34%), dark green crystals, m.p. 134–137 °C (dec.).

All complexes described can be characterised easily by ^{51}V NMR spectroscopy (with the exception of paramagnetic $V(CO)_6$ (**3**)) and IR spectroscopy. The spectroscopic data are summarised in Table 4.8-1.

Table 4.21-1 Characteristic spectroscopic data.

Complex	$\delta(^{51}V)$[a]	IR(ν(CO), [cm^{-1}])[b]
$[Na(diglyme)_2][V(CO)_6]$	−1945	1861[c]
$V(CO)_6$ (**3**)	paramagn.	1974
$(\eta^5\text{-}C_5Me_5)V(CO)_4$ (**4**)	−1466	2015 s, 1915 vs
$(\eta^5\text{-}C_5Cl_5)V(CO)_4$ (**5**)	−1008	2046 s, 1963 vs
$(\eta^7\text{-}C_7H_7)V(CO)_3$ (**6**)	−1518	1997 vs, 1901 vs

a) In C_6D_6 solution rel. neat $VOCl_3$ ($\delta(^{51}V) = 0$); b) in hexane solution; c) in Et_2O solution.

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4.22
Covalent and Ionic Metallocene Hexafluoroarsenate Complexes

Inis C. Tornieporth-Oetting and Thomas M. Klapötke

The complex $Cp_2Ti(AsF_6)_2$ ($Cp = \eta^5$-C_5H_5), prepared either from Cp_2TiF_2 and AsF_5 or from Cp_2TiCl_2 and $AgAsF_6$, was the first metallocene hexafluoroarsenate complex containing a direct M···F···E interaction (E = P, As, Sb or Bi). It fertilised both the high oxidation-state organometallic chemistry of the early transition elements and the chemistry of cationic metallocene species.

The cationic metallocene dichloride salts $[Cp_2MCl_2]^{n+}[AsF_6]^-_n$ ($n = 1$: M = V, Nb, Ta; $n = 2$: M = Mo, W; $n = 3$: M = Re) were synthesised quantitatively by oxidation of the lower valent metallocene dichlorides with AsF_5. All group 5 ionic metallocene complexes possess pronounced antitumor properties against experimental as well as human tumours heterotransplanted to athymic mice tumours.

Special Safety Precautions

1. Arsenic pentafluoride, AsF_5, and many non-metal fluorides are oxidisers, fluorinators and are toxic. Extensive care must be taken to avoid contact between the fluorides and oxidisable materials. The whole AsF_5 cylinder should be securely clamped inside a fume cupboard.
2. Hydrolysis of AsF_5 (and AsF_5/AsF_6^- containing compounds) can produce HF. Hydrogen fluoride (HF) can cause severe burns.
3. Protective clothing and face masks should be worn all times.
4. Sulfur dioxide is toxic and corrosive (bp: –10 °C, P(20 °C) : 3.30 bar).
5. The residues from both preparations (also cold trap, etc.) can be decomposed by slow addition of aqueous sodium bicarbonate.
6. If in any doubt whatsoever about safe operation, consult a demonstrator.

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4.22.1 Experimental

a) $Cp_2Ti(AsF_6)_2$

$$Cp_2TiCl_2 + 2\,AgAsF_6 \rightarrow Cp_2Ti(AgF_6)_2 + 2\,AgCl \quad (1)$$

In a dry box or glove bag, silver hexafluoroarsenate (1.00 g, 3.37 mmol) is placed in one 25 cm^3 bulb of a two-bulb Pyrex glass vessel (equipped with a J. Young Teflon-stemmed glass valve and a medium sintered glass frit; Fig. 4.22-1). Titanocene dichloride (0.42 g, 1.69 mmol) is placed in the other 25 cm^3 bulb. The vessel is evacuated and at –78 °C (acetone/dry-ice) sulfur dioxide (dried over CaH_2) is now condensed onto both compounds (10 cm^3 each). The solution of $AgAsF_6$ is poured at room temperature onto the solution of Cp_2TiCl_2. The mixture is stirred for 2 hours. The solution is filtered and the precipitate (AgCl) washed twice with recondensed solvent (10 cm^3). The solvent is removed under a dynamic vacuum leaving a dark red solid – $Cp_2Ti(AsF_6)_2$ – and AgCl. In the dry box or glove bag, the product is placed in a clean and dry two-bulb vessel (see above) and recrystallised from 10 cm^3 sulfur dioxide.

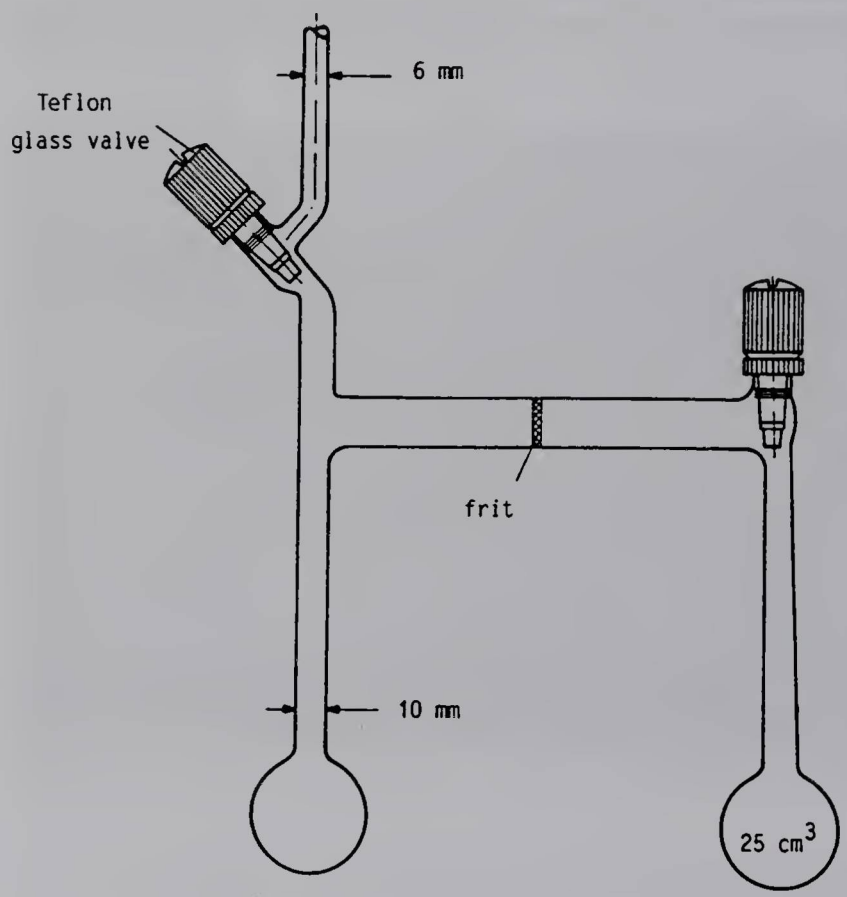

Fig. 4.22-1 Two-bulb glass vessel.

Calculate the yield of your product and measure its IR (glove bag, Nujol mull, KBr plates) and ^1H NMR ($CDCl_3$) spectra. Seal the product in a glass ampoule.

b) $[Cp_2MoCl_2]^{2+}[AsF_6]_2^-$

$$Cp_2MoCl_2 + 3AsF_5 \rightarrow [Cp_2MoCl_2]^{2+}[AsF_6]_2^- + AsF_3 \quad (2)$$

Molybdenocene dichloride (1.01 g, 3.40 mmol) is placed in one 25 cm^3 bulb of a dry two-bulb Pyrex glass vessel (equipped with a Young Teflon-stemmed glass valve and a medium sintered glass frit, Fig. 4.22-1). The vessel is evacuated and 15 cm^3 sulfur dioxide (dried over CaH_2) are condensed onto the Cp_2MoCl_2 at –78 °C (acetone/dry-ice). The SO_2 solution is frozen in liquid nitrogen and arsenic pentafluoride (1.73 g, 10.20 mmol) is condensed onto the frozen solution. The mixture is warmed to room temperature and stirred for 30 minutes. The solution is filtered (although there is nearly no precipitate) and the volatile materials (SO_2, AsF_3) are removed under a dynamic vacuum leaving a black solid. In a dry box or glove bag, the product is placed in a clean and dry two-bulb vessel (see above) and recrystallised from 15 cm^3 sulfur dioxide.

Calculate the yield of your product and measure its IR (glove bag, Nujol mull, KBr plates) and ^1H NMR spectra (sealed NMR tube, SO_2 solution). Seal up the product in a glass ampoule.

Instead of Cp_2MoCl_2 you can use Cp_2WCl_2 (1.20 g) and AsF_5 (1.58 g).

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4.23
The Preparation of *rac*-Ethylene-1,2-bis(1-indenyl)zirconium Dichloride and Dibenzyl Complexes

Manfred Bochmann and Simon J. Lancaster

Bis(cyclopentadienyl) metal dichloride complexes of titanium, zirconium and hafnium in the presence of aluminum alkyls as activators are well known catalyst precursors for the polymerisation of olefins. If the cyclopentadienyl ligands carry suitable substituents and are connected to each other by a bridge, stereorigid complexes result which are able to control the stereochemistry of the growing polymer chain during the polymerisation of 1-alkenes, notably propene. The best known example for complexes of this type is *rac*-ethylene-1,2-bis(1-indenyl)zirconium dichloride ($C_2H_4Ind_2ZrCl_2$), which possesses C_2 symmetry and leads to the formation of highly *isotactic* polypropene. The second possible isomer of the complex, with *meso* configuration, has C_s symmetry and is a minor by-product which is removed during the purification process; it is undesirable since it exhibits no stereocontrol.

Special Safety Precautions

1. All experimental procedures should be carried out on a vacuum/inert-gas manifold in a fume cupboard.
2. Petroleum ether, diethyl ether and indene are flammable. THF is both flammable and an irritant, toluene is flammable and toxic.
3. Zirconium(iv) chloride is corrosive and liberates HCl on hydrolysis; its inhalation must be avoided.
4. Dibromoethane is toxic and a suspect cancer agent. It should be handled in a fume cupboard.
5. Benzyl chloride is a lachrymator. It should be handled using rubber gloves in a fume cupboard.
6. Butyllithium is pyrophoric and reacts violently with water. It should be manipulated under inert gas using stainless-steel cannulae and gas-tight syringes. Rubber gloves should be worn!

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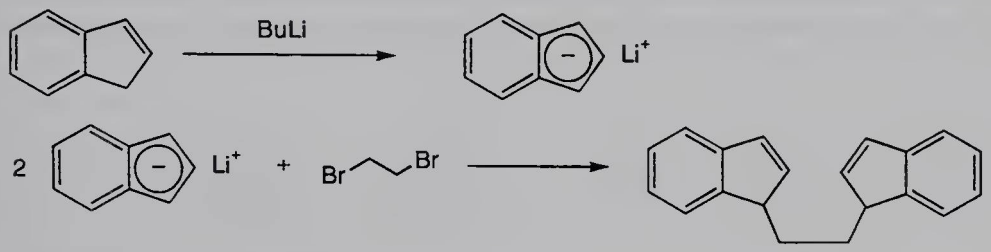
4.23.1 Experimental

a) The Ligand

Required are a 1 l flask with central B24 neck and two outer B19 necks equipped with magnetic stir bar, a dropping funnel with 200 cm^3 capacity, a B19 stopcock adaptor, two B19 stoppers, a B19 Suba-Seal, a large insulated dry-ice/acetone bath, two 100 cm^3 glass syringes, a 2 l separatory funnel, a large sintered glass frit and a 2 l Büchner flask.



Assemble the three-necked flask with dropping funnel and evacuate on a vacuum line, flame dry the flask and allow to cool before filling it with dry argon or nitrogen. Weigh 56.7 g (0.49 mol) indene (*Note:* to ensure purity, indene should be distilled on a long vigreux column and stored in a freezer) in the 100 cm^3 syringe and transfer to the flask through the Suba-Seal. Add 300 ml dry, degassed THF through the Suba-Seal. Cool the solution to –78 °C on the dry-ice/acetone bath. Taking a clean 100 cm^3 syringe, and with great care, charge the dropping funnel with 195 cm^3 of a 2.5 M solution of *n*-BuLi. Add the *n*-BuLi dropwise over a period of one hour. The solution will turn red in colour. After complete addition, warm the solution to room temperature and stir for a further hour to ensure complete deprotonation.

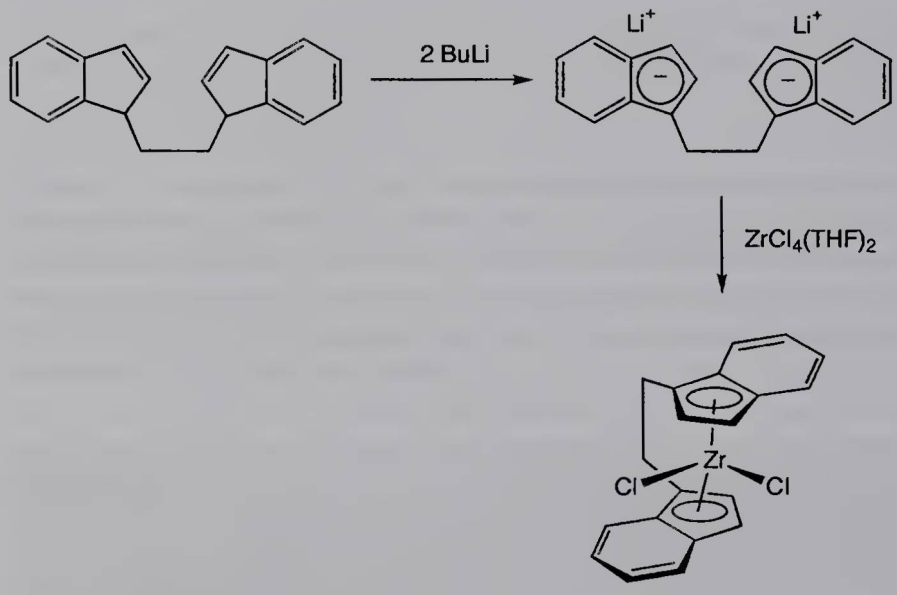
Cool the solution again to –78 °C on a dry-ice/acetone bath and via the dropping funnel add 45 g 1,2-dibromoethane dissolved in a further 50 cm^3 dry degassed THF dropwise with stirring over one hour. Then allow the reaction mixture to warm very slowly to room temperature over a period of two hours before stirring for a further two hours. Cool the reaction mixture to 0 °C in an ice bath, quench with 100 cm^3 of a saturated solution of ammonium chloride and add a further 200 cm^3 of distilled water to dissolve the LiCl. The procedure can pause overnight at this point.

Transfer the contents of the flask to a large separatory funnel and add a further 200 ml petroleum ether to dilute the organic phase. Discard the aqueous phase and wash the organic phase with a further two 200 cm^3 portions of distilled water. Clean the original flask, remove the dropping funnel and transfer the organic phase to the flask. Add approximately 30 g anhydrous magnesium sulfate and stir for one hour to dry. Separate the magnesium sulfate by filtration through a G3 sintered glass frit. Reduce the solvent volume to about 100 cm^3 or until crystals persist at 50 °C on a rotary evaporator. Allow the solution to cool slowly; the product will crystallise as off-white crystals which are filtered off and dried *in vacuo* for several hours. Yield: 40 g, 64.5%. The ligand is of sufficient purity for the preparation of the zirconocene

dichloride. An analytically pure sample is obtained by recrystallisation from ethanol/acetone. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.95 (br s, 4H), 3.35 (br s, 4H), 6.29 (br s, 2H), 7.21 (d, 2H, $J = 6.9$ Hz), 7.31 (t, 2H, $J = 7.3$ Hz), 7.40 (d, 2H, $J = 7.3$ Hz), 7.48 (d, 2H, $J = 6.9$ Hz).

b) $C_2H_4Ind_2ZrCl_2$

The zirconocene dichloride complex was first prepared by Brintzinger *et al.* The following procedure is a modification of the original procedure and has proved more reliable, with less formation of the undesirable *meso* isomer, than variations published subsequently. The yield is not adversely affected by an increase in scale and gives typically and reliably 40–50% yields of the *rac* product. (*Note:* The synthesis of $ZrCl_4(THF)_2$ is described in the reference by Manzer.)



Required are two 250 cm^3 flasks with central B24 and two outer B19 necks each equipped with magnetic stirrer-hotplates and bars, 100 cm^3 dropping funnels, stopcock adaptors, two B19 stoppers, two bent fingers for solid handling, 20 cm^3 glass syringe, transfer tubing, filtration cannula, two B19 Suba-Seals, one water bath and one dry-ice/acetone bath.

The first three-necked flask should be equipped with a dropping funnel and stopcock adaptor and evacuated before flame drying, then filled with inert gas. Using the bent-finger for weighing and transfer, place 6 g of the prepared ligand (23 mmol) in the flask and dissolve in 70 ml of dried, degassed THF. Cool to –78 °C using a dry-ice/acetone bath. Using the syringe, add 18.4 cm^3 of a 2.5 M solution of *n*-BuLi (46 mmol) to the dropping funnel and add dropwise to the THF solution with stirring. The solution will become dark red in colour. In some cases, the dianion may be observed to precipitate as a cream coloured solid, causing difficulties with stirring. If this occurs, and after addition of all the *n*BuLi, the flask should be removed from the bath and allowed to warm to room temperature, at which point all the dianion will

dissolve. To ensure complete deprotonation, the reaction should be stirred for a further 1 hour at room temperature.

The second flask should be prepared in the same manner as the first. Using a bent-finger for weighing and transfer, add 8.75 g $ZrCl_4(THF)_2$ (23 mmol) to the flask. Add 70 cm^3 dried and degassed THF and place the flask in a water bath at 60 °C and stir to give a suspension.

The dianion solution should be transferred to the dropping funnel of the second flask using stainless-steel transfer tubing. Allow the dianion to add to the suspension of $ZrCl_4(THF)_2$ dropwise with vigorous stirring over a period of two hours, maintaining the temperature at 60 °C. The reaction mixture will become yellow and gradually darken while the suspended $ZrCl_4(THF)_2$ dissolves. Towards the end of the addition, some precipitation of a fine yellow solid may be observed. After complete addition of the dianion, stir for a further hour at 60 °C before stirring overnight at room temperature. A microcrystalline yellow solid separates from solution. This fraction should be filtered off using a filter cannula and washed with anhydrous, degassed diethyl ether. Further fractions can be obtained by concentration of the THF solution and/or addition of diethyl ether and cooling overnight at –16 °C. A yield of 4.2 g (44%) is typical. Over-concentration and addition of too much diethyl ether may lead to product contamination with the more soluble minor *meso* isomer, unreacted $ZrCl_4(THF)_2$ and other impurities. Although the material obtained is frequently very pure (by ^1H NMR), purification can be achieved by recrystallisation from hot anhydrous, degassed toluene. Elemental analysis: calcd. for $C_{20}H_{16}ZrCl_2$: C, 57.40; H, 3.86; Cl 16.94. found: C, 57.04; H, 3.78; Cl, 16.02. ^1H NMR (400 MHz, $C_2D_2Cl_4$, 25 °C): δ 3.66–3.82 (m, 4H, CH_2CH_2), 6.25 (d, 2H, C_5 of Ind, $J = 2.7$ Hz), 6.61 (d, 2H, C_5 of Ind, $J = 2.7$ Hz), 7.26 (m, 2H, Ar), 7.38 (m, 2H, Ar), 7.52 (m, 2H, Ar), 7.72 (m, 2H, Ar).

c) The Dibenzyl Complex, $C_2H_4Ind_2Zr(CH_2Ph)_2$

Required are two 250 cm^3 flasks each with central B24 neck and two outer B19 necks, both equipped with magnetic stir bar, B19 stopcock adaptors, one with a 100 cm^3 dropping funnel; a filter cannula, two B19 Suba-Seals and a dry-ice/acetone bath.

Equip one 250 cm^3 flask with the dropping funnel, flame dry and fill with inert gas. Add 1.1 g (3 mmol) of the dichloride complex to the flask using a bent-finger. Add 20 cm^3 dry and degassed diethyl ether and cool to –78 °C. Fill the dropping funnel with 60 cm^3 of a 0.1 M solution of $PhCH_2MgCl$ in diethyl ether (6 mmol). Add the Grignard solution dropwise to the suspension of the dichloride complex over a period of 20 minutes and then warm slowly to room temperature. The solution will take on a yellow colour which will increase in intensity to orange. To ensure complete reaction, stir for 4 hours at room temperature and then remove the diethyl ether under vacuum. Extract the residue with 50 cm^3 of a 9:1 mixture of anhydrous degassed toluene/petroleum ether and filter by cannula into the second flame dried flask. Place this flask in the freezer overnight. Small orange cubic crystals of the product are formed. The product may take some time to crystallise and further concen-

tration of the filtrate may be required. Yield: 0.6 g, 38%. If, for whatever reason, the product is impure, it should be recrystallised from toluene. Elemental analysis: calcd. for $C_{34}H_{30}Zr$: C, 77.07; H, 5.72. Found: C, 75.90; H, 5.68. ^{1}H NMR (90 MHz, C_6D_6); δ −0.34 (d, 2H, J = 11.3 Hz, CH_2Ph), 0.70 (d, 2H, J = 11.3 Hz, CH_2Ph), 2.57 (m, 4H, CH_2CH_2), 5.34 (d, 2H, Cp, J = 3.4 Hz), 5.69 (d, 2H, Cp, J = 3.4 Hz), 6.53–7.13 (m, 18H, Ar).

$C_2H_4Ind_2ZrCl_2$, activated by a large excess of methylaluminoxane, $[(-AlMe-O-)_n]$, is a highly active catalyst for the stereoselective synthesis of isotactic polypropene. The catalytically active species are cationic complexes of the type $[Cp_2ZrR]^+$. The reaction of $C_2H_4Ind_2Zr(CH_2Ph)_2$ with $[CPh_3)^+[B(C_6F_5)_4]^-$ gives such a cationic complex which has been shown to possess high activity for the isotactic polymerisation of propene in the absence of aluminum alkyl activators.

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4.24
One-Pot Preparation of $Ru_3(CO)_{12}$ from $RuCl_3 \cdot 3\ H_2O$

Guy Lavigne, Catherine Saccavini, and Remi Chauvin

There are numerous published procedures for the preparation of $Ru_3(CO)_{12}$ [1]. High pressure methods are generally well adapted to large scale preparation, but require specific high pressure equipment that is often unavailable in the laboratory.

The new low pressure method reported here is ideally suited for the rapid (3–4 hours) conversion of moderate quantities of commercially available $RuCl_3 \cdot 3\,H_2O$ into pure $Ru_3(CO)_{12}$ under 1 atm CO, in yields exceeding 90%.

The present synthetic strategy rests on the fundamental principle of Hieber's "base reaction" [2], which has only recently been applied to carbonylhaloruthenium(II) complexes [3]. The method combines the advantages of simplicity, rapidity, high efficiency and insensitivity to moisture, thereby allowing direct use of all commercial reagents as received.

The reaction sequence to be performed is as follows:

$$RuCl_3.\,3\,H_2O \xrightarrow[\text{CO stream, 1 atm}]{\text{2-methoxyethanol}} \underset{\text{i) 80°C, 1h;}\ \text{ii) 124°C, 45 min}}{[Ru(CO)_2Cl_2]_n \rightleftharpoons [Ru(CO)_3Cl_2]_2} \quad \textit{yellow solution}$$

$$\left\{ \begin{array}{c} [Ru(CO)_2Cl_2]_n \\ \Updownarrow \\ [Ru(CO)_3Cl_2]_2 \end{array} \right\} \xrightarrow[\text{CO stream, 1 atm}]{\text{+ KOH (2 equiv.)}} \underset{\textit{90\% yield}}{Ru_3(CO)_{12} + KCl + H_2O} \quad \text{75°C, 20 min}$$

The first step is a CO-induced reductive carbonylation of $RuCl_3 \cdot 3H_2O$ producing *in situ* an equilibrium mixture of two $16e^-$ carbonylchlororuthenium(II) complexes, $[Ru(CO)_2Cl_2]_n$ and $[Ru(CO)_3Cl_2]_2$. The second step involves further reduction to $Ru^{(0)}$ upon treatment of the latter mixture by KOH under CO at 75 °C. The incipient anionic hydroxycarbonyl adduct "$[Ru(CO)_2\{C(O)OH\}Cl_2]^-$" thus generated [3] decarboxylates to give an "acidic" hydrido $Ru^{(II)}$ intermediate ultimately producing $Ru^{(0)}$ via formal reductive elimination of HCl (subsequently neutralized by the excess of base). A detailed analysis of the second reduction step has revealed the intermediacy of a

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transient dimeric $Ru^{(I)}$ species, which undergoes a *CO-induced disproportionation* [4, 5] to give $Ru^{(0)}$ (recovered as $Ru_3(CO)_{12}$) and $Ru^{(II)}$ (recovered as $K[Ru(CO)_3Cl_3]$). The latter $Ru^{(II)}$ species reacts further with KOH (present in excess) to enter a new reduction cycle beginning with the same hydroxy-carbonyl adduct $[Ru(CO)_2\{C(O)OH\}Cl_2]$ until total consumption of $Ru^{(II)}$ has been achieved.

Special Safety Precautions

CO gas and phosgene (which may be formed as a volatile by-product) are highly toxic! Caution must be exercised and all manipulations must be carried out in a highly efficient fume cupboard.

4.24.1 Experimental

4.24.1.1 General

a) Chemicals

2 g of $RuCl_3 \cdot 3H_2O$ (Johnson Matthey) – 100 cm^3 of 2-methoxyethanol (Fluka, ref. 64720) taken directly from the bottle – KOH pellets (Riedel, or any other label) – CO gas cylinder (Air Liquide, N20 grade).

b) Apparatus

Heating magnetic stirrer and oil bath – large (olive shaped) magnetic stirbar – three-necked round-bottomed 250 cm^3 (or 500 cm^3) flask equipped with a reflux condenser the upper part of which is connected to a gas bubbler and a hose sending toxic vapors to the top of the hood. One lateral neck of the flask is equipped with a CO gas inlet consisting of a glass bubbler (steel needles are *not* convenient) of sufficiently large diameter (2–3 mm) to avoid clogging by accumulation of solid $Ru_3(CO)_{12}$. The second lateral neck is used to introduce KOH pellets in the second reaction step (vide infra).

Step I: Reduction of $Ru^{(III)}$ to $Ru^{(II)}$ (Reaction Time: 1 hour 45 minutes)

2 g of $RuCl_3$, $3H_2O$, and 100 ml of 2-methoxyethanol are introduced into the flask. The solution is simply deaerated under reduced nitrogen atmosphere for a few minutes. The flask is then connected to the reflux condenser, whereupon the CO gas inlet is introduced. A fast CO stream (ca. 2 bubbles per second) and vigorous agitation are needed in this first reduction step. The temperature is first raised to 80 °C for 1 hour, during which the colour progressively turns blood red. It is then increased up

to 125 °C (reflux) for 30/45 minutes, namely, until a perfectly limpid *golden yellow solution* is obtained.

IR spectrum of the yellow solution: ν (CO) = 2135.5 m, 2063.6 s, 1992.9 m, cm^{-1}.

Step II: Reduction of $Ru^{(II)}$ to $Ru^{(0)}$
(Time: 20–30 minutes + 30 minutes for Slow Crystallization)

Once the characteristic yellow colour is obtained, the temperature of the bath is allowed to cool to 75 °C and regulated. The rate of CO bubbling may then be reduced to ca. 1 bubble per second. KOH pellets (850 mg) are then added directly into the solution by using the lateral neck of the flask (cautiously opened for just a few seconds). A progressive darkening of the solution is then observed over the next 15 minutes after which the orange crystalline $Ru_3(CO)_{12}$ begins to appear on the walls of the glassware. (*Note:* Spectacular fumes (looking like an English fog (!)) may spontaneously evolve from the solution after about 20 minutes). After a total time of 20–30 minutes, the heater is stopped, but CO bubbling and moderate agitation are maintained. The flask is kept in the oil bath in order to allow a very slow cooling down to room temperature during the crystallization of $Ru_3(CO)_{12}$, which occurs particularly efficiently between 70 and 50 °C. A limpid and *almost colourless* solution is obtained at the end.

Since $Ru_3(CO)_{12}$ is totally insoluble in 2-methoxyethanol, its characteristic IR absorption bands (ν (CO) = 2060 vs, 2030 s, 2011 m cm^{-1}) never appear in the final solution spectrum, which generally shows only traces of two remaining species, *i.e.* the anionic Ru(II) complex $[Ru(CO)_3Cl_3]$ (ν (CO) = 2126 m; 2048 s cm^{-1}) and small amounts of a soluble minor species, previously identified as the known di-anionic Ru(I) oxo derivative $[Ru_4(\mu_4\text{-}O)(\mu\text{-}Cl)_4(CO)_{10}]^{2-}$ (ν (CO) = 2014 s, 1939 m, 1733 w cm^{-1}) reflecting the presence of traces of water [4].

If necessary, further transformation of the residual $[Ru(CO)_3Cl_3]^-$ into $Ru_3(CO)_{12}$ can be achieved upon addition of 10 to 20% more KOH at 25 °C followed by treatment with CO at 75 °C for another 20 minutes period. (*Note:* When carrying out such a complementary experiment, there is no need to separate crystals of $Ru_3(CO)_{12}$ which are already present at the bottom of the flask. Indeed, they will be unaffected by the added KOH, the latter reacting preferably with the soluble salt $[Ru(CO)_3Cl_3]^-$, provided the temperature does *not* exceed 80 °C).

Crystals of $Ru_3(CO)_{12}$ are perfectly air stable. They can be easily recovered by filtration on a frit after venting the solution under nitrogen for a few minutes to evacuate CO. They generally need to be washed with alcohol and/or water to remove traces of KCl. The crystals are subsequently dried under vacuum and weighted (ca. 1.55 g). Currently, our yields, based on 10 experiments, are consistently around 90%.

4.24.1.2
Scaling-up

The reaction can be readily scaled up to transform 5 g of $RuCl_3 \cdot 3\ H_2O$ in one batch. This is done by simply multiplying the amounts of KOH and solvent by 2.5 (in a

500 ml flask). In that case, the time required to obtain the yellow solution in the first step will be longer (ca. 3 hours), whereas the time required in the second step will be the same, ca. 30 minutes.

4.24.2
Frequently Asked Questions About this System

4.24.2.1
What is the Exact Nature of the "Yellow Solution"?

The yellow solution is a mixture of two $Ru^{(II)}$ species, namely, the polymeric $[Ru(CO)_2Cl_2]_n$ (IR ν(CO) = 2063 s, 1993 s cm^{-1}) and the dimeric $[Ru(CO)_3Cl_2]_2$ (IR ν(CO) = 2135 s, 2065 s cm^{-1}) [6]. The mixture thus gives a characteristic 3 band pattern, with a very strong central peak (common to the two species). The polymeric complex $[Ru(CO)_2Cl_2]_n$ (characteristic gold yellow colour) can be totally converted into the dimeric species $[Ru(CO)_3Cl_2]_2$ (characteristic lemon yellow colour) upon prolonged treatment with CO (3–5 hours) at room temperature. However, such a transformation is not required in the present preparation since any of the two above complexes is prone to act as a convenient precursor in the present preparation of $Ru_3(CO)_{12}$

4.24.2.2
Is Water a Problem?

There is no need to use distilled solvents since the ruthenium salt *is already hydrated.* The existence of a green chloro-carbonyl aqua Ru complex (stable up to 200 °C!) was mentioned a long time ago by Halpern *et al.* [7]. However, this undesirable very characteristic green complex is susceptible to be formed only at the reflux temperature of 2-methoxyethanol (124 °C). In the present procedure, the initial temperature of 80 °C in the first step is sufficient to allow efficient reductive carbonylation of $Ru^{(III)}$ to $Ru^{(II)}$ while still permitting complete removal of water along with the fast CO stream before the reflux temperature is reached (this is facilitated by turning the cooler circulation off in the reflux condenser during the first hour). This simple strategy allows a significant reduction of the time required to obtain the yellow solution.

4.24.2.3
How to Avoid the Formation of $K[HRu_3(CO)_{11}]$?

The weight of KOH we are now using effectively corresponds to *two equivalents* per Ru, namely, twice the amount used in the original procedure [3]. Such a modification was justified by the observation that in practice, the released HCl gas is not quantitatively evacuated and tends to neutralize part of the base needed for the reduction.

A critical point is that $Ru_3(CO)_{12}$ is *also susceptible to reaction with excess KOH, albeit only above 85 °C* to produce the soluble complex $K[HRu_3(CO)_{11}]$. This is avoided

by careful temperature control in the second step, allowing $Ru_3(CO)_{12}$ to precipitate as soon as it is generated, within the temperature range 70–75 °C.

If the temperature incidentally exceeds 85 °C in the second step, the soluble salt $K[HRu_3(CO)_{11}]$ will be *rapidly and quantitatively* produced, giving a characteristic violet colour and a characteristic IR pattern (ν(CO) = 2016 vs, 1989 s, 1953 mw, 1732 w cm^{-1}): Yet, even in such cases, recovery of $Ru_3(CO)_{12}$ is still possible (albeit in lower yield) by slow dropwise addition of fluoroboric acid diethyl ether complex (1 M solution) under CO according to the following reaction sequence [8]:

$$[HRu_3(CO)_{11}]^- + H^+ \rightarrow H_2Ru_3(CO)_{11}$$

$$H_2Ru_3(CO)_{11} + CO \rightarrow Ru_3(CO)_{12} + H_2$$

Titration by the acid requires IR monitoring, following the disappearance of the characteristic bands of $[HRu_3(CO)_{11}]^-$. It should also be borne in mind that $[HRu_3(CO)_{11}]^-$ is a hydride transfer agent [9]: Thus, its reaction with small amounts of water under CO atmosphere will slowly produce $Ru_3(CO)_{12}$ according to the basic principle of the water gas shift reaction [9]:

$$[HRu_3(CO)_{11}]^- + H_2O + CO \rightarrow Ru_3(CO)_{12} + H_2 + OH^-$$

Effectively, dark solutions resulting from incidental thermal treatment above 85 °C (and hence containing $[HRu_3(CO)_{11}]^-$) are seen to become clearer upon prolonged treatment with CO at 25 °C, with concomitant production of $Ru_3(CO)_{12}$. Such a reaction also suggests that traces of water may also play a role in the regeneration of hydroxide ions.

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4.25
Synthesis of Well-defined Organometallic Hydroxides: $[LCaOH]_2$, LAl(Me)OH and LGeOH

Herbert W. Roesky

The design and synthesis of well-defined organometallic hydroxides has developed rapidly in the last few years. The organometallic hydroxides are important precursors for the preparation of heterobimetallic compounds, which turned out, for example in the case of LAl(Me)OZrRCp$_2$, to be very effective living polymerization catalysts for olefins with high turnover frequencies.

Here the preparation of $[LCaOH]_2$, LAl(Me)OH and LGeOH is described, where L is a β-diketiminate ligand of composition HC[(CMe)(2,6-iPr$_2$C$_6$H$_3$N)]$_2$. The protonated LH ligand is prepared in the first step from 2,4-pentanedione and 2,6-diisopropylaniline.

Special Safety Precautions

1. All compounds except LH are air and moisture sensitive. Therefore, experimental manipulations should only be performed under an atmosphere of dry nitrogen gas in Schlenk flasks or in a dry-box.
2. All solvents must be carefully dried and distilled before use.
3. All chemicals used for the preparation should be handled in a well-ventilated hood or on a vacuum line.
4. Aluminium alkyls and lithium alkyls react explosively with water. Therefore, gloves and a protective shield should be used when reactions with these chemicals are carried out.
5. Safety glasses and protective gloves must be used at all times.
6. The toxicity of the resulting products is not known. Therefore, contact with eyes and skin should be avoided.

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4.25.1 Experimental

a) Synthesis of $CH[(CMe)_2(2,6\text{-}iPr_2C_6H_3NH)(2,6\text{-}iPr_2C_6H_3N)]$ (LH)

Concentrated HCl (0.40 cm^3; 4.8 mmol) is added to a solution of 2,4-pentanedione (0.50 cm^3, 4.0 mmol) and 2,6-diisopropylaniline (1.96 g, 11.0 mmol) in ethanol (20 cm^3). The reaction mixture is heated at reflux for 3 days and then concentrated to a brown residue. The crude product (LH·HCl) is extracted with 10 cm^3 of methylene chloride. After stirring with 20 ml of saturated sodium carbonate, LH is extracted into methylene chloride. Evaporation of the solvent and recrystallisation from methanol affords LH as a white crystalline solid (1.50 g, 73% yield) with a melting point of 140–141 °C.

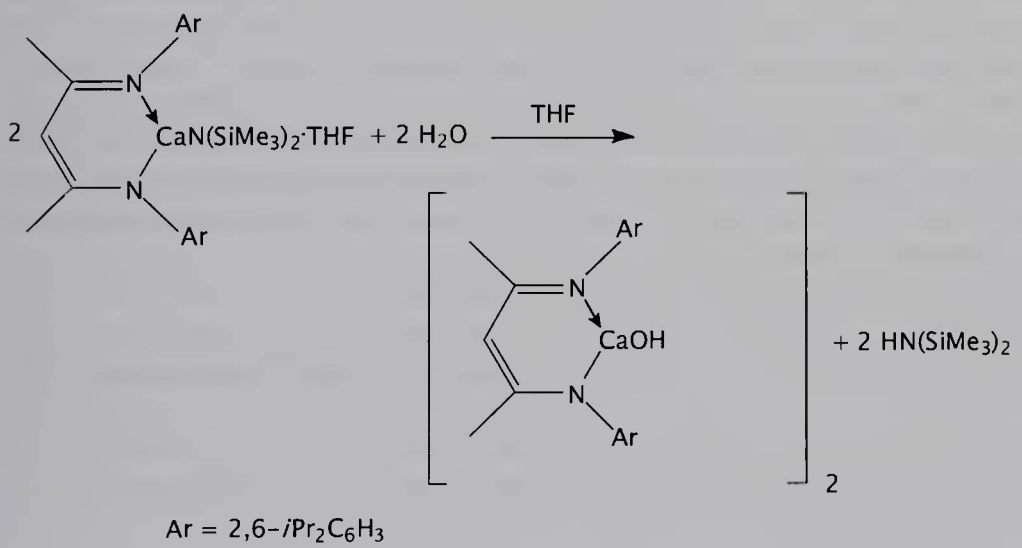
Measure the ^1H and ^{13}C NMR spectra and the mass spectrum.

^1H NMR ($CDCl_3$, 25 °C): δ 12.12 (br, 1H, NH), 7.12 (m, 6H, H_{aryl}), 4.84 (s, 1H, H_β), 3.10 (mult, 4H, C*H*Me_2), 1.72 (s, 6H, α-Me), 1.22 (d, 12H, CH*Me*Me′), 1.12 (d, 12H, CHMe*Me*′). ^{13}C NMR ($CDCl_3$, 25 °C): δ 161.4 ($C_{\acute{a}}$), 142.6 (C_{ipso}), 140.9 (C_o), 125.3 (C_p), 123.2 (C_m), 93.4 (C_β), 28.4 (*C*HMe_2), 24.5 (CH*Me*Me′), 23.4 (CHMe*Me*′), 21.0 (α-Me). MS: *m/z* 418.333 (calculated 418.335).

b) Synthesis of $LCaN(SiMe_3)_2 \cdot THF$ (L = $HC[(CMe)(2,6\text{-}iPr_2C_6H_3N]_2$)

The reaction of 2 equiv. of $KN(SiMe_3)_2$ with 1 equiv. of LH followed by the addition of this mixture to 1 equiv. of CaI_2 resulted in the formation of $LCaN(SiMe_3)_2 \cdot THF$ in THF solution with yields up to 80%. The compound is very moisture sensitive.

c) Synthesis of $[LCa(OH)]_2$ (L = $HC[(CMe)(2,6\text{-}iPr_2C_6H_3N)]_2$



Ar = 2,6-$iPr_2C_6H_3$

Scheme 4.25-1

Degassed water (40 µl, 2.22 mmol) is added to a solution of $LCaN(SiMe_3)_2 \cdot THF$ (1.50 g, 2.18 mmol) in THF at –40 °C and then allowed to warm to room temperature. After stirring at room temperature for 30 minutes, the slurry is dried *in vacuo*. The resulting solid $[LCaOH]_2$ is washed with hexane (8 cm^3) and finally dried *in vacuo*. Yield: 1.06 g, 1.94 mmol, 89%. The product can be recrystallised by cooling a saturated hot toluene solution to 0 °C. M.p. 277–280 °C. Elemental analysis (%): calculated for $C_{66}H_{100}Ca_2N_4O_4$ (M = 1093.68) C, 72.48; H 9.22; N, 5.12; found C, 72.82; H, 8.87; N, 4.90.

Measure the mass spectrum, the ^1H and ^{13}C NMR spectra and the IR spectrum in the range 4000–600 cm^{-1}.

MS (70 eV) m/z (%): 202 (100) $[Pr_2NCCCH_3]^+$. ^1H NMR (300 MHz, C_6D_6): δ –0.78 (s, 2H, Ca–OH), 1.05 [d, J = 6.9 Hz, 24H, $CH(CH_3)_2$], 1.22 [d, J = 6.8 Hz, 24H, $CH(CH_3)_2$], 1.41 (m, 8H, THF), 1.69 (s, 12H, CH_3), 3.15 [sept, J = 6.9 Hz, 8H, $CH(CH_3)_2$], 3.48 (m, 8H, THF), 4.74 (s, 2H, CH–backbone), 7.06 (s, 12H, Ar–H). ^1H NMR (300 MHz, THF-d_8): δ –1.09 (s, 2H, Ca–OH), 0.87 [d, J = 6.9 Hz, 24H, $CH(CH_3)_2$], 1.01 [d, J = 6.8 Hz, 24H, $CH(CH_3)_2$], 1.44 (s, 12H, CH_3), 1.73 (m, 8H, THF), 2.96 [sept, J = 6.9 Hz, 8H, $CH(CH_3)_2$], 3.58 (m, 8H, THF), 4.44 (s, 2H, CH–backbone), 6.87 (s, 12H, Ar–H). ^{13}C NMR (75 MHz, C_6D_6): δ 24.2, 24.3, 25.0, 25.3, 27.8, 68.4, 93.0, 123.2, 123.4, 141.3, 147.6, 164.4. IR (Nujol): $\tilde{\nu}$ = 3679, 3646, 1623, 1548, 1511, 1461, 1406, 1378, 1313, 1225, 1168, 1098, 1037, 1018, 924, 881, 784, 757 cm^{-1}.

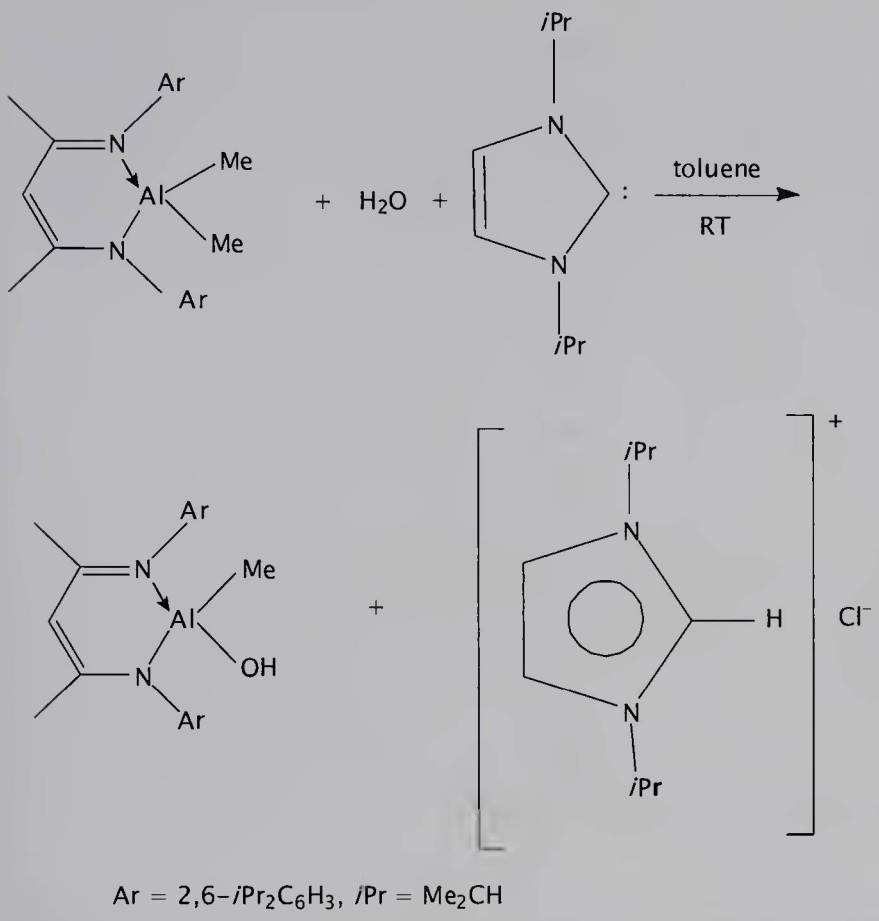
d) Synthesis of LAl(Me)OH (L = HC[(CMe)(2,6-*i*$Pr_2C_6H_3N$)]$_2$

For the preparation of LAl(Me)OH, the starting material LAl(Me)Cl is prepared from LLi and stoichiometric amounts (1:1) of $MeAlCl_2$ in toluene at room temperature. The yield of LAl(Me)Cl is more than 80%.

Amounts of 6 mmol of LAl(Me)Cl and 6 mmol of (iPrNCH)$_2$C (1,3-diisopropylimidazol-2-ylidene) are dissolved in 120 cm^3 of toluene. To this mixture is added with a microsyringe H_2O (6 mmol). A white precipitate of the HCl · *N*-heterocyclic carbene adduct is formed, which is removed by filtration after about 1–2 hours, when the reaction is complete. The filtrate is concentrated to about 15 cm^3. White crystals of LAl(Me)OH are formed, which are recovered by filtration. Subsequent partial removal of the solvent from the mother liquor resulted in an additional crop of LAl(Me)OH. The total yield is about 80%.

Measure the melting point, IR and ^1H NMR spectra.

M.p. 192 °C. IR (Nujol): $\tilde{\nu}$ = 3728, 1552, 1530, 1373, 1316, 1256, 1189, 1178, 1106, 1056, 1023, 940, 878, 805, 768, 757, 689, 614 cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 7.16–7.07 (m, *Ar*), 4.93 (s, 1H, γ-*CH*), 3.69 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, *CH*Me_2), 3.25 (sept, $^3J_{HH}$ = 6.8 Hz, 2H,*CH*Me_2), 1.57 (s, 6H, C*Me*), 1.32 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH*Me*$_2$) 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CH*Me*$_2$), 0.53 (s, 1H, O*H*), –0.88 (s, 3H, Al*Me*).



Ar = 2,6-iPr$_2$C$_6$H$_3$, iPr = Me$_2$CH

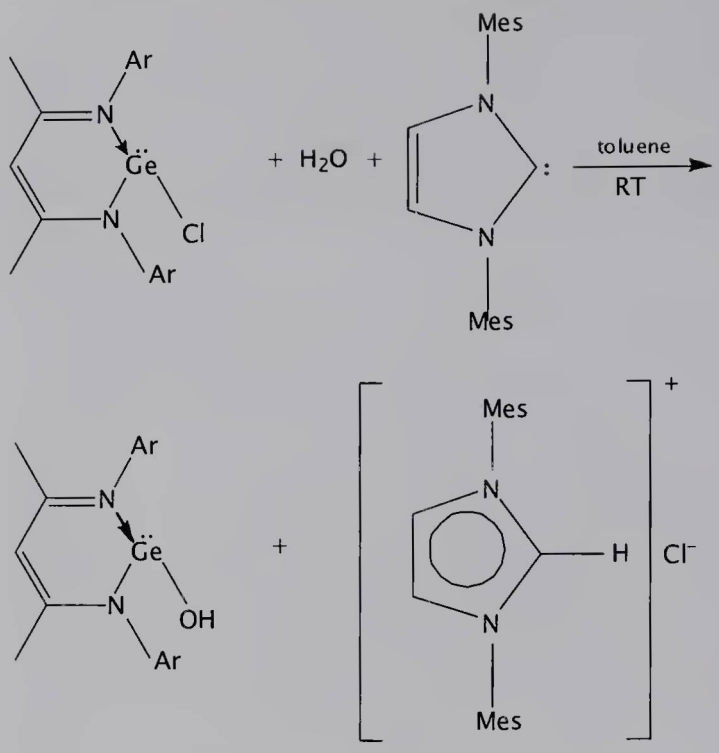
Scheme 4.25-2

e) Synthesis of LGeOH

LGeCl (1.28 g, 2.43 mmol) prepared from LLi and $GeCl_2$·dioxane and 1,3-dimesitylimidazol-2-ylidene (*N*-heterocyclic carbene, 0.74 g, 2.43 mmol) are dissolved in 20 ml toluene. Then water (87.5 µl, slight stoichiometric excess) is slowly added with stirring. A white precipitate of the adduct HCl·*N*-heterocyclic carbene is immediately formed. The reaction mixture is stirred for about 15 minutes and then the white precipitate is separated by filtration *in vacuo*. The remaining colourless solution is evaporated and the resulting yellow solid LGeOH is rinsed with hexane ($2 \times 10\ cm^3$) and dried *in vacuo*. Yield: 1.04 g (84%).

Measure the IR, ^1H and ^{13}C NMR spectra and the EI mass spectrum and the melting point.

M.p. 140 °C. IR (KBr): $\tilde{\nu}$ = 3571, 2964, 2867, 1623, 1554, 1383, 1320, 1174, 1100, 1018, 918, 853, 795, 758, 588, 521, 366 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ = 7.15 (m, 6H, 2,6-iPr$_2$C$_6$H$_3$), 4.91 (s, 1 H, γ-CH), 3.60–3.80 [sept, 2H, $(CH_3)_2$], 3.20–3.40 [sept. 2H, $(CH_3)_2$], 1.60 (s. 6H, CH_3), 1.54 (s, 1H, OH), 1.33 [d, 6H, $CH(CH_3)_2$], 1.29



Ar = 2,6-iPr$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$

Scheme 4.25-3

[d, 6H, $CH(CH_3)_2$], 1.21 [d, 6H, $CH(CH_3)_2$], 1.12 ppm [d, 6H, $CH(CH_3)_2$]. ^{13}C NMR (50.327 MHz, THF): δ = 163.31 (NC), 146.37 (NC), 143.62 (ArC), 141.00 (ArC), 124.87 (ArC), 124.06 (ArC), 96.98 (γ-C), 29.16 [$CH(CH_3)_2$], 28.02 [$CH(CH_3)_2$], 26.69 [$CH(CH_3)_2$], 24.73 [$CH(CH_3)_2$], 24.57 [$CH(CH_3)_2$], 24.08 [$CH(CH_3)_2$], 23.25 ppm [$NC(CH_3)$]. MS (EI): m/z (%) 508 (25) $[M]^+$, 403 (100) $[M - Me - Ge - OH]^+$. Elemental analysis (%): calculated for $C_{29}H_{42}GeN_2O$ (507.24) C 68.67, H 8.35, N 5.52; found C 69.20, H 8.48, N 5.52.

LGeOH is a remarkably stable germylene compound which shows no rearrangement to the corresponding aldehyde. A stable carbon congener is not known.

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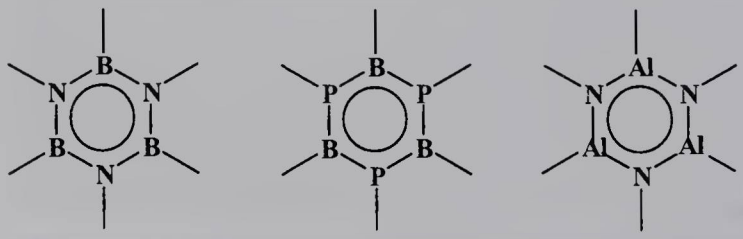
4.26
Alumazene – Inorganic Benzene Analogue

Jiri Pinkas

Inorganic main-group rings analogous to benzene are traditionally represented by large families of cyclophosphazene and borazine derivatives, first reported in 1834 and 1926, respectively. Other systems are much rare and also they were prepared relatively recently. Examples of the group 13/15 compounds include B–P, Al–N, Al–P, Al–As, and Ga–P six-membered cycles. Among these heavier borazine congeners, boraphosphabenzenes and alumazene are unique in possessing planar central cores with non-alternating and short intraring bond distances. Spectroscopic data and theoretical calculations show delocalization in boraphosphabenzenes similar to borazine while alumazene exhibits only a minor degree of π stabilization. Chemical reactivity of alumazene was only recently explored in reactions with silanetriols, triaminosilanes, and organometallic trifluorides. The resulting products exhibit adamantane-like cage structures.



Special Safety Precautions

1. Trimethylaluminium is highly flammable and reacts violently with water.
2. 2,6-Diisopropylaniline is toxic.
3. Alumazene and its intermediates are very sensitive to oxidation by traces of oxygen, which is manifested by brown discoloration. Use of nitrogen of 99.999% purity or a deoxygenation column is advisable.

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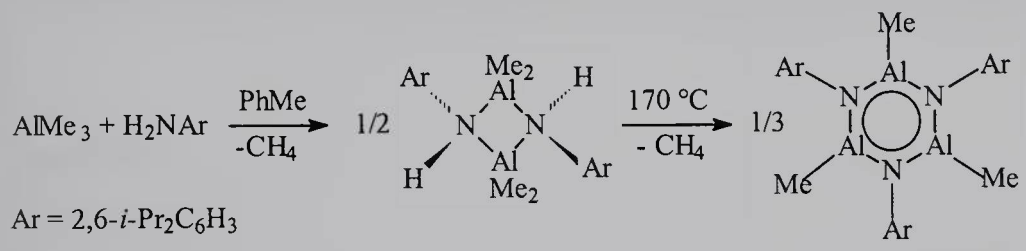
4.26.1 Experimental

A combination of standard Schlenk flask, syringe/septum/cannula, and dry-box techniques is employed in this preparation. Distil 2,6-diisopropylaniline (90%, Aldrich) from KOH under vacuum and collect the colourless fraction of b.p. 115–117 °C/0.01 Torr. Dissolve 2,6-diisopropylaniline (4.9 cm^3, 26 mmol) in 50 cm^3 of dry toluene in a 250 cm^3 round-bottomed Schlenk flask equipped with a Teflon valve. With magnetic stirring add trimethylaluminium (13 cm^3, 26 mmol, 2 M solution in toluene or hexanes) dropwise by syringe at a room temperature. Under a nitrogen flow, fit the reaction flask with a reflux condenser connected to an oil bubbler and reflux the reaction mixture for one day on an oil bath (120 °C). Observe a slow evolution of gas. When the gas evolution ceases, remove 40 ml of solvents under vacuum and place the flask in a −30 °C freezer. During the first 30 minutes, check the tightness of the Teflon valve as its needle contracts on cooling and the valve may open.

Colourless crystals form usually over a period of two days. Isolate them by removing the mother liquor by a Teflon cannula or a syringe while maintaining low temperature with an acetone/liquid nitrogen cold bath. Discard the mother liquor by pouring it slowly into acetone. Wash the crystals by adding and removing a small amount of cold hexane by a syringe. Then dry the solid under vacuum for 30 minutes, fill the reaction flask with nitrogen and slowly heat with an oil bath up to 170 °C. The solid melts above 130 °C and gas evolution is observed in an oil bubbler. After approximately one hour the liquid solidifies.



The reaction flask is evacuated and transferred into a dry box. Weigh the resulting product and calculate the reaction yield (usually 50%). Prepare samples for melting point and mass spectrometric measurements by placing a small amount of the product into capillaries and seal them with Apiezon wax. Flame-seal the capillaries outside the box with a small gas torch. Record the IR spectrum in a KBr pellet prepared with a mini press. Measure ^1H and ^{13}C NMR spectra in C_6D_6 or CD_2Cl_2.

^{13}C NMR (C_6D_6) δ −16.13 (AlMe), 23.53 (CH_3), 30.19 (CH), 122.86, 123.43, 142.57, 143.55. MS (70 eV) 651 (M^+, 85%), 636 ($M-CH_3^+$, 100%), 595, 435, 419, 216, 203, 162, 57, 43. IR (KBr, cm^-) ν 3059 w, 2960 vs, 2923 m, 2867 s, 1588 w, 1458 m, 1429 s, 1383 w, 1363 w, 1317 m, 1237 s, 1186 vs, 1108 m, 1042 m, 957 w, 916 vs, 869 m, 794 s, 729 m, 677 w, 644 m, 437 m.

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4.27
Preparation of $[Bu_4N][B_3H_8]$ and the Formation of $RuH[B_3H_8](CO)(PPh_3)_2$

Anthony F. Hill and J. Derek Woollins

Boron hydrides are often considered to be very reactive and explosive materials. In this experiment you will prepare a boron hydride anion and its ruthenium complex. Both compounds are quite air stable.

Special Safety Precautions

This experiment involves the use of standard solvents which represent normal hazards as well as the *in situ* generation of diborane. You must adhere to the instructions closely to avoid the possibility of fire hazards. Carry out the first stage of the reaction in a fume cupboard behind a safety screen.

4.27.1
Experimental

a) $[Bu_4N][B_3H_8]$

In a dry box (or a nitrogen atmosphere), 8.50 g (0.225 mol) of powdered sodium tetrahydroborate is slurried with 125 cm^3 of anhydrous diglyme in a 500 cm^3 three-necked flask. The flask is fitted with a 125 cm^3 pressure-compensating dropping funnel whose tip is extended below the surface of the mixture. The third neck is connected to a bubbler containing a benzene-amine (4-picoline was used) mixture to scrub the gaseous boranes evolving from the reaction as minor products. During assembly, a gentle stream of dry nitrogen is maintained through the apparatus to minimize the possible entrance of air into the system. After rapidly transferring a solution of iodine into the funnel (11.3 g, 40.0 mmol in 50 cm^3 of dry diglyme), the entire reaction system is purged with nitrogen for about 10 minutes and the reaction flask is placed in a previously heated oil bath whose temperature is adjusted to 98–102 °C before the addition of iodine. After the nitrogen flow is stopped, the iodine solution is added dropwise during a period of 75–90 minutes to the hot, vigorously stirred reaction mixture. The hydrogen gas produced passes through the bubbler. The reac-

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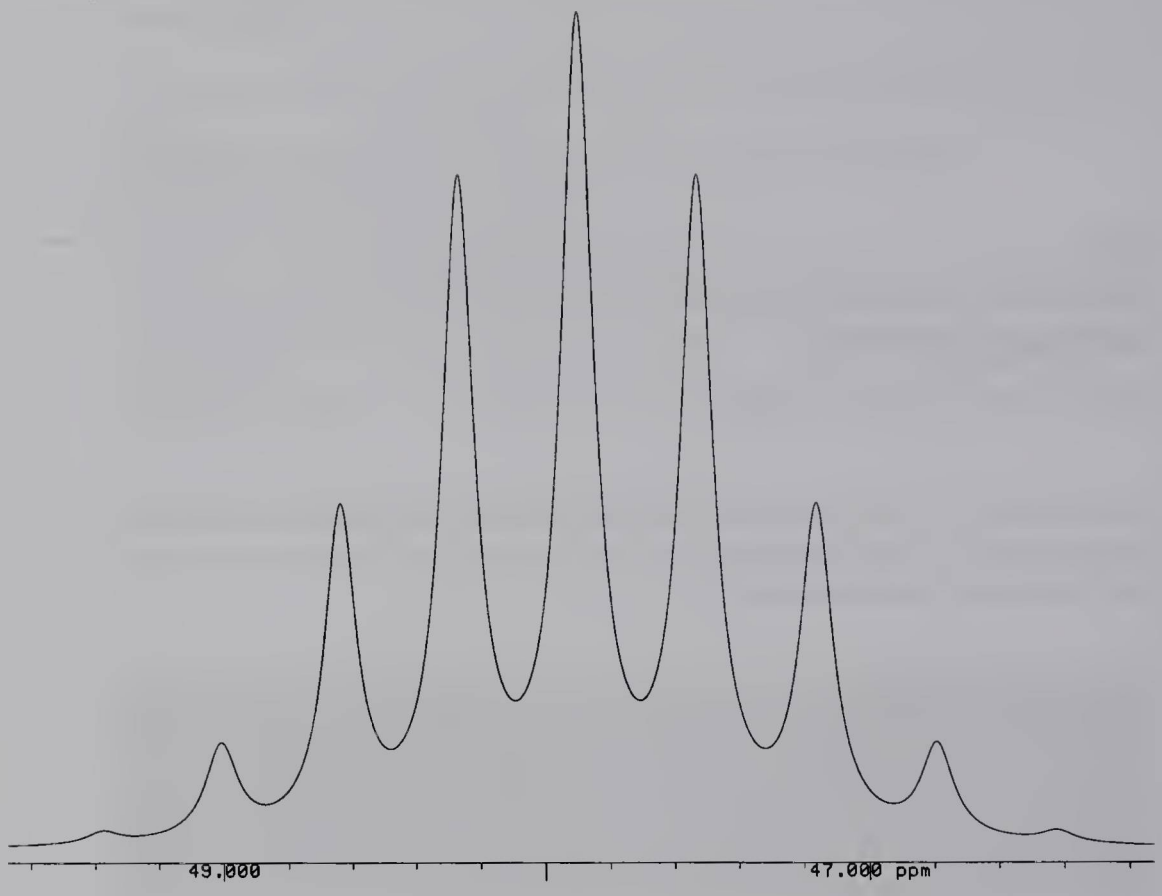

Fig. 4.27-1 ^{11}B NMR spectrum (86.6 MHz, CD_2Cl_2) of the B_3H_8 anion.

tion mixture is stirred for two more hours while the temperature is maintained at about 95 °C. The volume is then reduced to 80 ml by passing dry nitrogen over the warmed reaction mixture at 50 °C, or alternatively by pumping. The cooled mixture, together with washings of 50 ml of water, is transferred to a 2 l beaker. About 500 ml of saturated aqueous tetra-*n*-butylammonium iodide is added slowly with vigorous stirring until no more precipitation takes place. The white precipitate is filtered on a Büchner funnel, washed with water (about 450 ml) and dried under vacuum. (Octahydrotriborate(–1) may be precipitated without removal of diglyme, a lower yield of the crude product being obtained).

A portion of the crude salt (ca. 2 g) is dissolved in 15–20 ml of dichloromethane, filtered and reprecipitated by adding 200 cm^3 of diethyl ether. The precipitate is dried *in vacuo*. Record your yield and the IR spectrum of the crude and purified product. The ^{11}B NMR spectrum of the B_3H_8 anion is shown in Figure 4.27-1.

b) $[RuH(B_3H_8)(CO)(PPh_3)_2]$

A mixture of $[RuClH(CO)(PPh_3)_3]$ (1.00 g, 1.05 mmol, see c) and $[nBu_4N][B_3H_8]$ (0.30 g, 1.05 mmol) in dichloromethane (30 cm^3) is stirred for 2 h. Ethanol (15 cm^3) is added and the suspension filtered through Kieselguhr to remove $[nBu_4N]Cl$. The

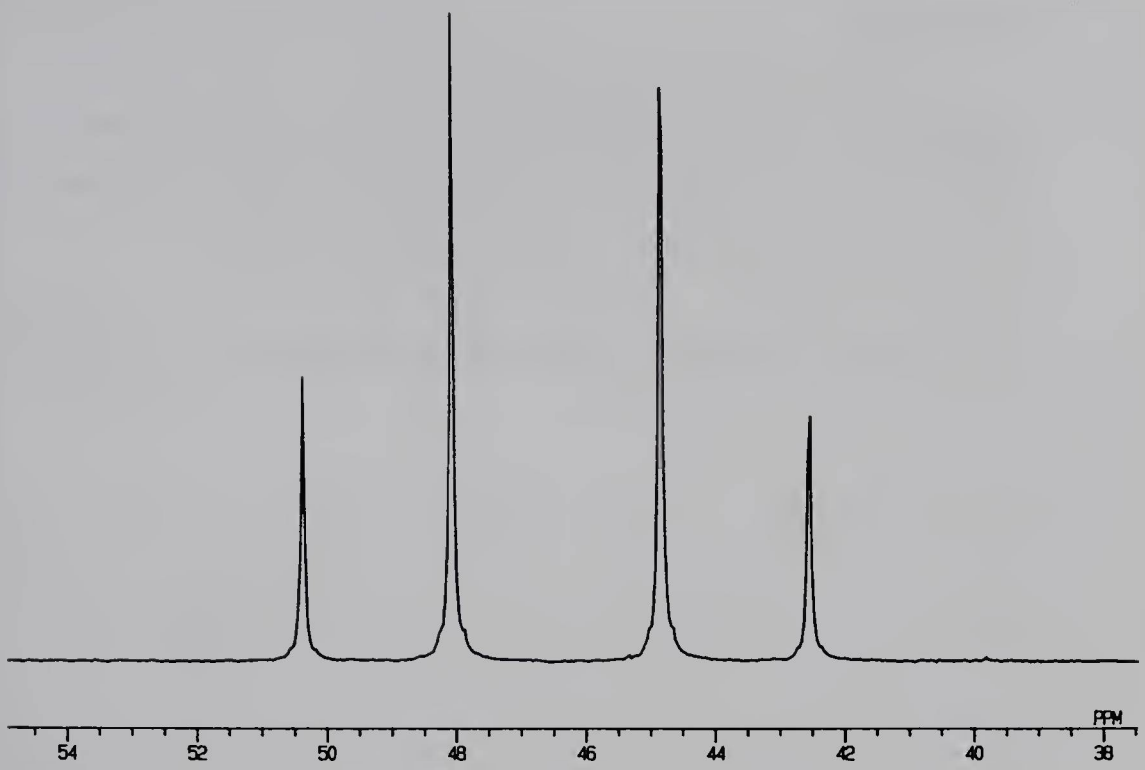

Fig. 4.27–2 ^{31}P-{^1H}NMR spectrum (at 109.3 MHz) of $RuH(B_3H_8)CO(PPh_3)_2$.

filtrate is concentrated to ca. 50 cm^3 and the product, $[RuH(B_3H_8)(CO)(PPh_3)_2]$, isolated by filtration, washed with ethanol (10 cm^3) and recrystallised from a mixture of dichloromethane and ethanol.

Your characterisation of the complex should include yield, melting point, infrared (Nujol mull, 4000–600 cm^{-1}) and ^1H NMR ($CDCl_3$, 60 MHz) spectra. Figure 4.27-2 shows the ^{31}P NMR spectrum and you should use these data to identify the stereochemistry at the ruthenium centre and rationalise this with reference to the Skeletal Electron Pair theory.

N. B.: A stock of the ruthenium complex may be prepared as described below.

c) $[RuClH(CO)PPh_3)_3]$

A suspension of commercial $RuCl_3 \cdot xH_2O$ (3.00 g) and triphenylphosphine (23.0 g) in 2-methoxyethanol (350 cm^3) is heated under reflux for 48 hours. The suspension is then allowed to cool and stirred at room temperature for 3–5 hours to complete precipitation of the product. The product is then isolated by filtration and washed with ethanol (2 × 50 cm^3) and petrol (2 × 50 cm^3) and dried *in vacuo*. Yield ca. 9 g depending on quality of $RuCl_3 \cdot xH_2O$. The colour of the sample varies from pale yellow to pale pink, but this is not important.

N. B.: A smaller scale preparation is also provided on p. 196.

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4.28
Vacuum Line Techniques: Preparation of SiF_4 and $SiF_4(C_5H_5N)_2$

J. Derek Woollins

Before starting this experiment, read these instructions carefully, then read them again in front of the vacuum line which you intend to use, identifying the parts referred to in Figure 4.28-1 and their function in the experiment.

Make sure that the vacuum line is clean (and remember that you are responsible for cleaning it when you have finished your experiment).

It is very important that the line should be free of leaks (sources of these are badly greased taps and joints, particularly the spherical joints). Check that all the taps and ground glass joints are free from streaks. Use Apiezon-M grease sparingly, there should be no grease in the tap-barrel bore. To test the line, evacuate it, isolate it from the pump and watch for an increase in pressure over a period of about 5 minutes (manometer).

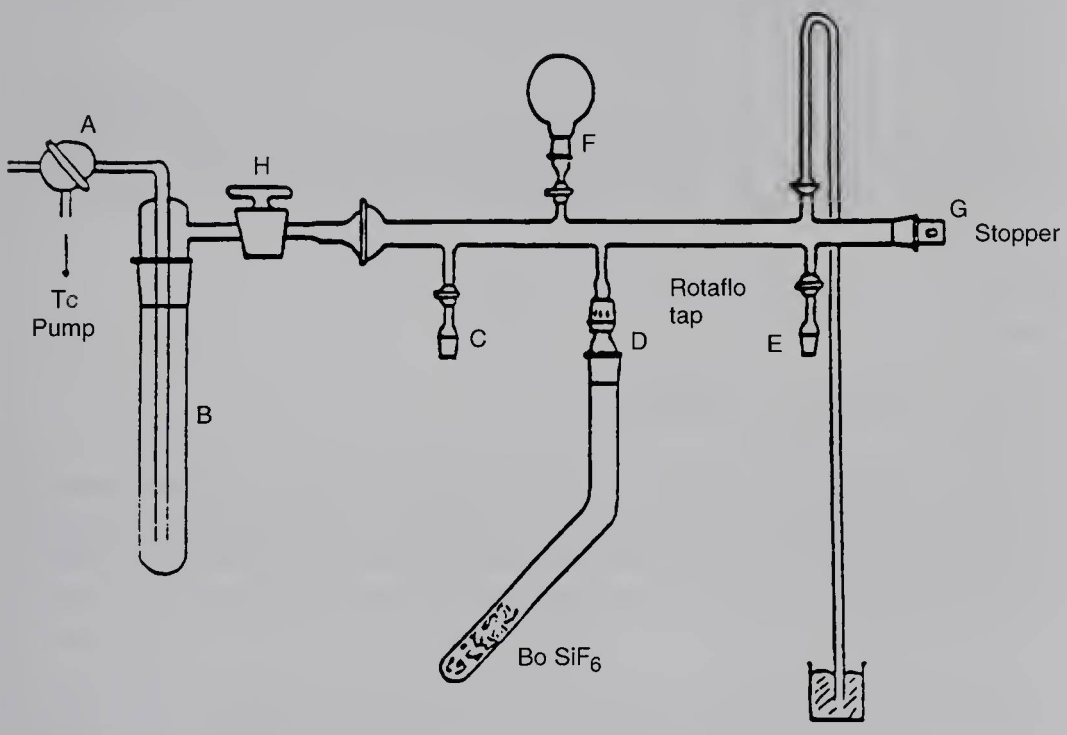

Fig. 4.28-1 Vacuum line apparatus.

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Make sure that you keep the Dewar flask around trap B (Fig. 4.28-1) topped up with liquid nitrogen throughout the experiment. Both the Dewar flask and the gas-storage flask must be taped.

At *no stage* in the experiment should you leave solid SiF_4 in a vessel with a closed tap unless it is surrounded by liquid nitrogen since it is a gas at room temperature.

Never let air into the vacuum line while the Dewar flask surrounds trap B, otherwise you will condense liquid oxygen with consequent dangers of explosion. When you have finished, isolate the line with tap H, turn off the pump and let air into it *via* tap A, let air into trap B *via* tap A and immetiately remove the Dewar surrounding trap B. Ease the trap B off at the joint and place it in a fume cupboard. Use a tisssue to hold the *top* of trap B as it will still be very cold.

Carry out part b) and, if possible, part c) in one day. Keep the SiF_4 which has not been used in the storage bulb overnight (if necessary) to carry out part d) on the following day.

Special Safety Precautions

1. Read and note the introductions to this experiment.
2. Both pyridine and silicon tetrafluoride are toxic materials; avoid inhaling their vapours. If you do inhale either, inform a demonstrator. Rest and keep warm, breathe fresh air. Take milk of magnesia after SiF_4 inhalation.
3. Special hazards which may arise in this experiment include tap blockage, overheating the pyridine, condensation of liquid oxygen into the main or smaller traps, escape of SiF_4 or pyridine, a build up of the SiF_4 pressure (caused by the premature removal of the Dewar flasks while taps are closed).
4. The Dewar flasks which you use must all be protected with insulating tape or metal containers. Be *especially careful* when you *clamp* them; it is better to use a supporting ring at the base and a loose clamp as a top support.

4.28.1 Experimental

a) Barium Hexafluorosilicate ($BaSiF_6$)

Barium chloride dihydrate (25 g, 0.1 mol) is dissolved in 70 cm^3 of water. Aqueous H_2SiF_6 (30%) is added until precipitation is complete, this requires about 40 cm^3 of the solution. The freshly precipitated white barium hexafluorosilicate is filtered and washed thoroughly until free from chloride. The product is dried in an oven at 110 °C and then in a desiccator over phosphorus(V) oxide. Yield is nearly 100%.

b) SiF_4

Place dry $Ba[SiF_6]$ (5.0 g) in the bent-tube provided at the PTFE Rotaflo tap equipped socket D. Attach two smaller tubes at sockets C and E and a 500 cm^3 gas storage flask at socket F (this *must* be protected with tape). Evacuate the whole assembly after ensuring that all connections, taps, etc. are properly greased.

Test for leaks with the manometer. Isolate the vacuum line from the pump and heat the $Ba[SiF_6]$ with a Bunsen burner (start heating at the top of the $Ba[SiF_6]$ to avoid this being blown into the line) until there is a pressure of about 10 mm (1 cm) of crude SiF_4 in the line. Stop heating, slowly pump this crude SiF_4 (contaminated with HF and fluorosilicic acid) into the main trap B (this is of course cooled with liquid nitrogen throughout). Isolate the line again (tap H) and cool the small tube at E, using a small Dewar flask almost full of liquid nitrogen, *cool only the bottom 3–4 cm*. Open tap E. This is to condense the SiF_4 in the next stage. Now heat the $Ba[SiF_6]$ to just *below* the softening point of the glass until no more SiF_4 is evolved. Cool the small tube at C with liquid nitrogen in the same way as that at E, then open tap C, remove the small Dewar surrounding the vessel E and allow some 4/5 of the SiF_4 to sublime from E into C. Isolate C from the vacuum line, keeping it cold with liquid nitrogen. Keeping tap E open, immediately pump the crude residue from E into the main trap. Isolate the line by closing tap H. Open tap C, remove the Dewar around the tube at C, and allow the pure SiF_4 to vapourise from C into the evacuated gas storage bulb F. Isolate F from the line. The gas can now be slowly drawn from this as required for the two experiments below. Open tap H and pump any remaining SiF_4 from the line into the trap. Slowly open taps C and E to also pump any remaining SiF_4 into the trap. Close taps C, D and E. After it has cooled, remove the bent tube.

c) Infrared Spectrum of SiF_4

Attach an infrared gas cell (NaCl windows) to the vacuum line at E and evacuate it for five minutes. Allow SiF_4 to enter the cell from the storage bulb until a pressure of about 10 cm is attained in the cell. Isolate the cell *and* the storage bulb and pump out the line. Measure the infrared spectrum over the range 2500–625 cm^{-1}, and then run another spectrum after pumping out most of the gas from the cell in order to measure ν_3 accurately (this will also give the cell "blank"). Using a 10 cm long cell with polythene windows, measure the infrared spectrum of approximately 1 cm pressure of SiF_4 over the region 625–250 cm^{-1}. To compensate for the absorption of the polythene windows place two polythene discs cemented together with Apiezon-M grease in the reference beam. Pump all the SiF_4 out of the cells before letting air in. Give a complete assignment of all the bands observed from 2500–250 cm^{-1}.

d) $SiF_4 \cdot py_2$

Place ca. 4 cm^3 of dried pyridine, some 3A molecular sieves (check that these are new) and a very small PTFE stir bar in a small tube and attach it to the line at E.

Attach a calcium chloride drying tube to D (leave tap of D closed). Freeze the pyridine in liquid nitrogen and evacuate E. Then close tap E and allow the pyridine to warm up to room temperature. With the tap still closed, refreeze the pyridine and re-evacuate by opening tap E. Isolate E from the line and evacuate the tube C. Condense SiF_4 into C by cooling the tube in liquid nitrogen (cover only the bottom 3–4 cm) and opening the storage bulb F. Quickly evacuate the line to remove any traces of uncondensed SiF_4 and again isolate the line. Now distil the dry pyridine onto the solid SiF_4 in C, moving the stir bar with an external magnet. If the pyridine does not distill under hand heat only from E, you have a leak in the line and must rectify this after turning off tap E. In this event, pump out the line again, rectify the leak, again evacuate the line and repeat the degassing of the pyridine. Never warm the pyridine other than with your hand. Allow the mixture in C to warm up *very slowly*. The tap C must be open to the manometer during this process. If the reaction becomes too violent, cool again with liquid nitrogen. When the mixture has attained room temperature, pump off al the excess pyridine into the main trap B, close H, close the tap at C, let *dry* air (via a calcium chloride drying tube at D) into the vacuum line. Remove the tube at C containing the adduct and immediately stopper it. Transfer it to a dry bag and run the IR spectrum. Turn the pump and line off as directed. Measure the spectrum of pyridine (POISON!) as a thin film between KBr plates over the same region. Make sure that you make this film up in the fume cupboard. Clean the plates afterwards in the fume cupbaord when you have finished. Comment on the spectrum of the adduct. Hand in a sealed sample of the adduct with your report.

At the end of the experiment (or the session), remove the Dewar, let air via A into the trap, allow the bent tube to cool and then remove the tubes form C, D and E. (There should only be slight resistance – you do not need to let the line up to air.) Remove the trap and place in a fume cupboard. Let air into the pump and switch off at mains. Let air into the line via tap H. Clean and return "quick-fit" tubes and magnetic stir bars to vacuum line. Keep NaCl cells in desiccator. Ba residues should be place in a fume cupboard in a marked container.

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4.29
Amino- and Nitrotetrazoles: Nitrogen-rich Heterocycles

Davin G. Piercey and Thomas M. Klapötke

Tetrazoles are five-membered heterocyclic rings containing four nitrogen atoms, one carbon atom and two degrees of unsaturation. This class of compounds boasts some of the highest nitrogen percentages of all organic compounds and at the same time most tetrazoles have high positive heats of formation, while possessing high thermal stabilities. These characteristics, along with the ease of synthetically tailoring the properties of tetrazole-containing compounds, have led to the application of various tetrazole compounds in all areas of energetic materials: propellants, explosives and pyrotechnics.

5-Aminotetrazole is synthesised by the diazotisation of aminoguanidine to guanyl azide, followed by cyclisation to 5-aminotetrazole, via a modified procedure similar to Thiele's first historic synthesis of this compound in 1892. Sodium nitrotetrazolate was synthesised in a Sandmeyer reaction from aminotetrazole using copper nitrite. 5-Aminotetrazole has applications in gas-generating and propellant compositions, and sodium nitrotetrazolate is a useful precursor to the primary explosive heavy metal nitrotetrazolates.

Special Safety Precautions

Caution: Explosion hazard!

The acidic copper salt of 5-nitrotetrazole produced is a powerful primary explosive when dry. When dry it is sensitive to flame, impact and static electricity. Care should be taken to ensure that it remains in the Buchner funnel only as long as is necessary to produce a damp solid filter-cake and does not begin to dry out. Excessive friction or force on the wet material should be avoided and a plastic as opposed to a metal spatula should be used to remove the filter-cake from the funnel.

The sodium 5-nitrotetrazolate obtained is harmless to handle in the hydrated form produced in this experiment, but it should not be heated in the dry form as loss of the hydration waters produces the extremely sensitive explosive anhydrous material. The recrystallisation must be monitored closely to ensure it does not boil dry. Ensure that the vessel used for recrystallisation is sufficient for at least 1 cm depth of liquid, as too thin layers of liquid can boil dry in a very localised

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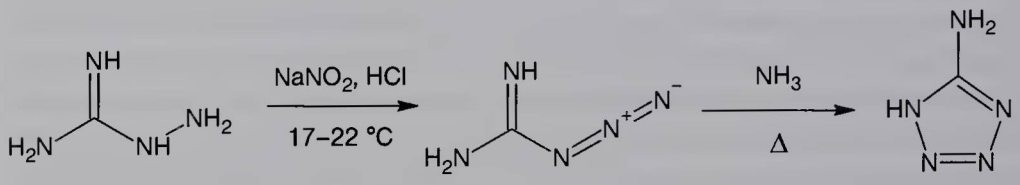
area, producing loud but harmless detonations. A steam bath is the preferred heat source for these recrystallisations.

During the diazotisation of 5-aminotetrazole to 5-nitrotetrazole, small amounts of toxic nitrous oxides are given off. The procedure should be conducted in a fume hood.

4.29.1 Experimental

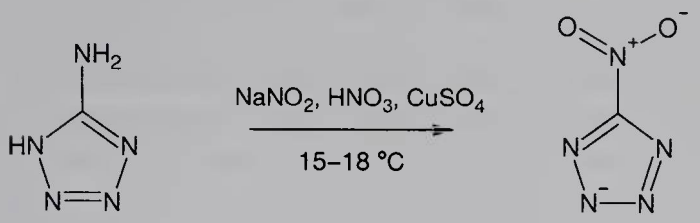
a) 5-Aminotetrazole ($CN_5H_3 \cdot H_2O$)



In a 125 cm^3 Erlenmeyer flask, 8 g of aminoguanidine bicarbonate is slurried with 11.5 cm^3 of distilled water, then 10.2 cm^3 of 37% hydrochloric acid are added in small portions (2–3 ml) while magnetically stirring the flask to keep the mixture from foaming. The solution is allowed to stir for 15 minutes. A thermometer is inserted in the flask and the flask is placed in an ice–water bath and allowed to cool to 15 °C. A solution of 4.33 g of sodium nitrite in 9 ml of water is then added dropwise by hand from a Pasteur pipette while maintaining the temperature at 17–22 °C. If near the end of the addition of nitrite solution the aminoguanidine solution begins to turn yellow, the addition of nitrite is ceased as all the aminoguanidine has reacted. After addition, the reaction mixture is stirred at 20 °C for 20 minutes, then 5.4 ml of 28% aqueous ammonia are added all at once, stirred for 5 minutes and then the solution is transferred to a 150 cm^3 round-bottomed flask equipped with a heating mantle, stirrer bar and reflux condenser and brought to the beginning of reflux and is held there for 2 hours. Upon completion of the reflux, while the solution is still hot, the pH is adjusted to 4 using hydrochloric acid and ammonia solution. The solution is then transferred to a 125 cm^3 Erlenmeyer flask fitted with a thermometer and slowly cooled to 10 °C during which time 5-aminotetrazole crystallises. (*Note:* The solution may supersaturate; if crystals have not appeared by 40 °C, the interior of the flask should be scratched with a glass rod until crystallisation occurs). The supernatant is then carefully decanted, squeezing out as much liquid as possible from the crystalline mass with a rubber spatula, and 15 cm^3 of distilled water are added to the crystals and the mix is heated to 45 °C, held there for 5 minutes and then allowed to cool to 10 °C. The crystals are filtered using a Buchner funnel and are washed with a few small portions of ice-cold distilled water.

Calculate the yield of 5-aminotetrazole monohydrate and measure its IR spectrum (Nujol mull, KBr plates) and NMR spectrum.

b) Sodium 5-Nitrotetrazolate Dehydrate



A solution of 5.2 g of sodium nitrite and 2.75 g of copper(II) sulfate pentahydrate in 15 cm^3 of distilled water is prepared in a 200 cm^3 three-necked round-bottomed flask equipped with a stirrer bar, addition funnel and thermometer (Fig. 4.29-1). The remaining neck is left open to the atmosphere. This solution is cooled to 5 °C in an ice bath and the addition funnel is charged with a solution of 2.57 g of aminotetrazole monohydrate, 0.05 g of copper(II) sulfate pentahydrate and 3.2 cm^3 of 70% nitric acid in 30 cm^3 of distilled water. The acidic aminotetrazole solution is added to the dark-green copper nitrite solution over the course of 2–3 hours, keeping the temperature between 15 and 18 °C. After addition, the reaction mixture is stirred for 30 minutes in the ice bath, followed by the dropwise addition of a solution of 3.5 ml of 70% nitric acid in 1.5 ml of distilled water with cooling and stirring. After this addition, the reaction mixture is allowed to stir for 30 minutes while warming up to room temperature. The mixture is then vacuum filtered using a Buchner funnel and the green filter-cake of acid copper nitrotetrazolate is washed with 15 cm^3 of distilled water, then 15 cm^3 of 1.8 M nitric acid, followed by three washes with 15 cm^3 of distilled water. The filter-cake is allowed to dry in the funnel for around 3 minutes (not longer!) and it is carefully (avoiding excessive friction of the acid nitrotetrazolate between the spatula and the Buchner funnel!) removed with a plastic spatula and

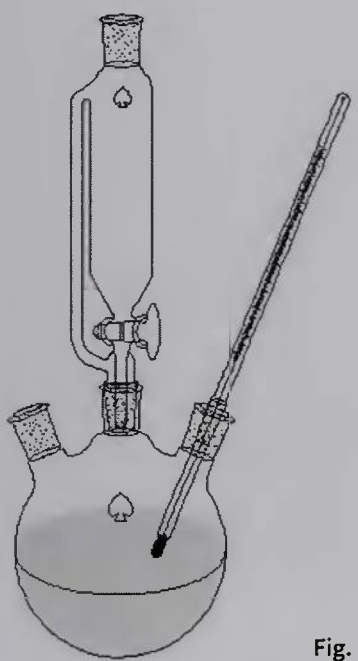


Fig. 4.29-1 Glassware for the Sandmeyer reaction on aminotetrazole.

transferred to a 150 cm^3 beaker containing 30 ml of distilled water. The suspension is stirred rapidly magnetically and 50% sodium hydroxide solution is added until the pH reaches 9. Copper hydroxide precipitates and the solution is heated and stirred at 70 °C for 45 minutes. While still hot, the solution is filtered through a Buchner funnel packed with Celite to remove black copper oxide. The precipitate is washed with two 5 ml portions of distilled water. The filtrate is treated with concentrated nitric acid until the pH reaches 6 and then the solution is evaporated to half its volume on a rotovap with a bath temperature of 60 °C. The solution is then transferred to a crystallisation dish and water is allowed to evaporate off completely over several days. When dry, the crystals are dissolved in hot acetone and filtered to remove sodium nitrate and the filtrate is allowed to evaporate, leaving crystals of sodium 5-nitrotetrazolate dihydrate. Recrystallise from acetone paying attention to the Special Safety Precautions.

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4.30
Ammonium 5-Nitro-1*H*-Tetrazolate-Hemihydrate

Franz Xaver Steemann and Thomas M. Klapötke

The ammonium salt of 5-nitro-1*H*-tetrazole is useful in the preparation of various energetic compounds, e.g. NTNAP, containing the 5-nitro-1*H*-tetrazole moiety, which can be introduced by nucleophilic substitution.

5-Amino-1*H*-tetrazole is first converted to the explosive diazonium salt, which forms, under copper catalysis, the copper complex of 5-nitro-1*H*-tetrazole. This complex is next converted into 5-nitro-1*H*-tetrazole, which reacts with ammonia to form ammonium 5-nitro-1*H*-tetrazolate hemihydrate.

Special Safety Precautions

1. The reactions should be carried out in polyethylene (PE) beakers.
2. Sulfuric acid is corrosive.
3. Copper(II) sulfate pentahydrate is harmful and hazardous to the environment.
4. Sodium nitrite is an oxidant, toxic if ingested and hazardous to the environment.
5. Gaseous ammonia is toxic and flammable and should only be handled in a well-ventilated fume hood.
6. The intermediately formed green copper complex of 5-nitro-1*H*-tetrazolate is explosive when dry and therefore should be kept wet at all times!
7. 5-Nitro-1*H*-tetrazole can react rapidly with carbon or reducing agents, especially if heated. The addition of decolourising carbon should therefore take place at temperatures below 50 °C and the resulting suspension should not be stirred longer than about 10 minutes.
8. Protective clothing and safety eyeware should be worn at all times.

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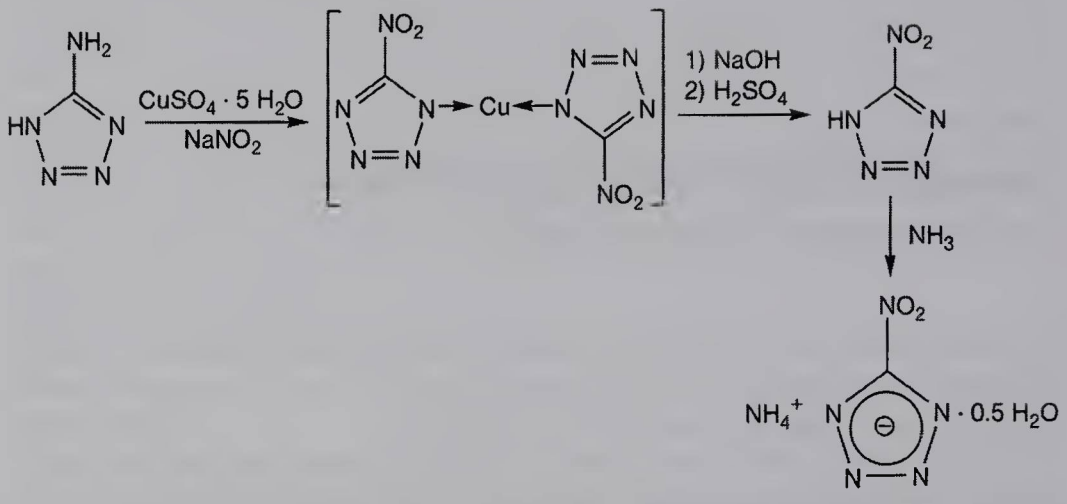
4.30.1
Experimental

Ammonium 5-Nitro-1*H*-Tetrazolate Hemihydrate



5-Amino-1*H*-tetrazole (8.5 g, 305 mmol) is dissolved in a solution of copper(II) sulfate pentahydrate (two spatulas) in water (140 cm^3) by adding concentrated sulfuric acid (5.6 cm^3, 105 mmol). Copper(II) sulfate pentahydrate (11.1 g, 45 mmol) and sodium nitrite (21.1 g, 305 mmol) are dissolved in water (60 cm^3) in a PE beaker on an ice bath and the acidified 5-amino-1*H*-tetrazole solution is added dropwise (ca. 30 minutes) while maintaining ice cooling. Gas evolution and precipitation of the green copper complex of 5-nitro-1*H*-tetrazolate are observed.

The ice bath is removed and sodium hydroxide solution (2.7 M, 80 cm^3) is added. The suspension is then heated on a water bath at 78 °C for 1 hour. Precipitation of copper hydroxide is observed. The suspension is filtered through wet packed Celite and the filtrate is acidified with concentrated sulfuric acid (3.2 cm^3, 60 mmol). Decolourising carbon is added to the warm acidified filtrate and the suspension is stirred for 10 minutes. Gas evolution is observed.

The suspension is filtered through wet packed Celite and the filtrate is again acidified with concentrated sulfuric acid (3.2 cm^3, 60 mmol) and then extracted with ethyl acetate (10 × 50 cm^3). The organic layer is dried with magnesium sulfate and concentrated to *ca.* 200–250 cm^3. Gaseous ammonia is bubbled through the organic layer (Fig. 4.30-1) and the precipitated colourless solid is filtered off. This procedure is repeated until no more solid is obtained. The colourless solid can be recrystallised from methanol to yield 7.1 g (50 %) ammonium 5-nitro-1*H*-tetrazolate-hemihydrate.

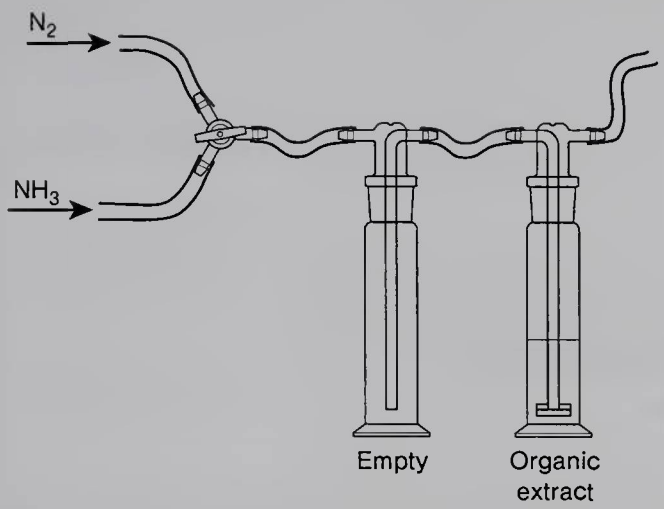


Fig. 4.30-1 Setup for reacting 5-nitro-1*H*-tetrazole with ammonia.

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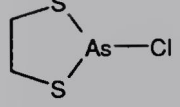
4.31
Arsenium Cations: Carbene Analogues

Neil Burford and Trenton M. Parks

Carbenes and their analogues represent important synthetic building blocks in that they are small, simple molecules with coordinatively unsaturated sites and high reactivity. The phosphorus analogues (phosphenium cations) have been known since the 1970's, but the first arsenium cations were only recently identified. This project involves the preparation of a chloroarsolidine (**1**), which is the starting material for quantitative production of the arsolidinium (**2**) gallate. The reaction involves heterolytic cleavage of the covalent As–Cl bond using a Lewis acid to give the ionic salt. In addition, the novel arsolidine-arsolidinium complex (**3**) is prepared and all three compounds are characterised by their melting point and IR and NMR spectroscopic features.



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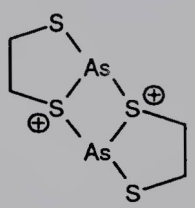
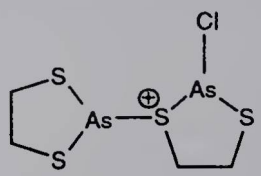


(2)



(3)

Special Safety Precautions

Operations should be performed in a fume cupboard.

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4.31.1 Experimental

a) 2-Chloro-cyclo-1,3-dithia-2-arsapentane 1[1)]

Chemicals required

1,2-Ethanedithiol	Due to the pungent odour of ethanedithiol, all procedures should be performed in an efficient fume cupboard. The apparatus should be rinsed with bleach following the procedure.
Arsenic trichloride	*Intensely poisonous!* Latex gloves are not effective protection against this compound. The most effective protection is to avoid contact. Arsenic trichloride is slowly hydrolysed in air.
Carbon tetrachloride	Poisonous and carcinogenic. Must be dried over P_2O_5.

Apparatus required

50 cm^3 two-neck round-bottomed flask with stoppers, 50 cm^3 pressure-equalising dropping funnel, stir motor and stir bar, source of dry nitrogen.

Procedure

Under an atmosphere of dry nitrogen, 1.4 g of 1,2-ethanedithiol in 5 ml of CCl_4 is added dropwise over a period of 5 minutes to a stirred solution of 2.7 g of $AsCl_3$ in 10 cm^3 of CCl_4. The reaction self-cooling and is accompanied by the liberation of HCl gas. The solution is stirred for 30 minutes, then stoppered and placed in the freezer (–20 °C) to promote crystallisation of the product. The cold supernatant liquid is decanted from the crystals and the remainder of the solvent is removed *in vacuo*. Typical yields: 80–90%. M.p.: 38.5–39 °C. The FT-IR spectrum is shown in Figure 4.31-1a. NMR (CD_2Cl_2): ^1H, 3.74 ppm, multiplet; ^{13}C, 44.6 ppm.

b) Bis(1,3-dithia-2-arsolidinium Tetrachlorogallate), [2] $[GaCl_4]_2$

Chemicals required

Gallium trichloride	Extremely moisture sensitive. Purified by vacuum sublimation onto a water cooled finger.
2-Chloro-*cyclo*-1,3-dithia-2-arsapentane	From part a), exposed to dynamic vacuum (10^{-3} Torr) for at least 30 minutes. Slowly hydrolyses in air.
Methylene chloride	Dried over CaH_2, P_2O_5, and CaH_2; degassed by freeze-pump-thaw.

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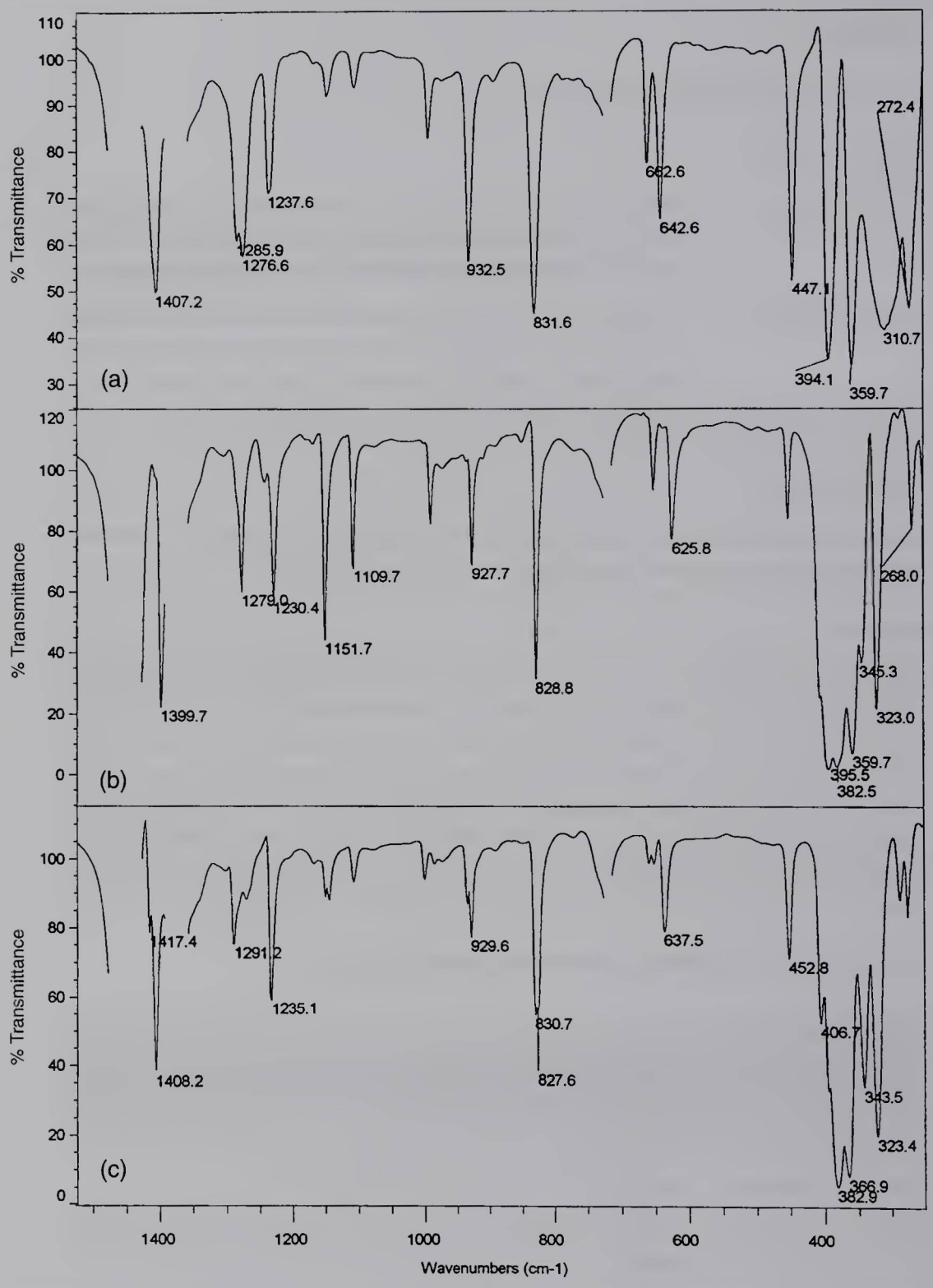

Fig. 4.31-1 FT-IR spectra obtained as Nujol mulls between CsI plates on a Nicolet 510P spectrometer, Nujol regions have been blanked. a) 2-chloro-cyclo-1,3-dithia-2-arsapentane (**1**). b) Bis(1,3-dithia-2-arsolidinium tetrachlorogallate), [**2**][$GaCl_4$]$_2$. c) 2-chloro-cyclo-1,3-dithia-2-arsapentane-1,3-dithia-2-arsolidinium tetrachlorogallate, [**3**][$GaCl_4$].

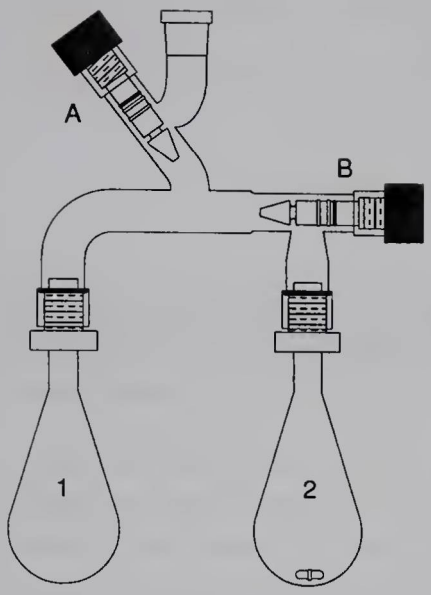

Fig. 4.31-2 Dual compartment vacuum reactor.

Apparatus required

Dual compartment (100 cm^3 each) reactor with two Teflon stopcocks (A and B) and FETFE O-rings, featuring demountable compartments separated by stopcock B (Fig. 4.31-2), a modification of the standard H-tube reaction vessel.

Teflon coated magnetic stir bar, stirring motor, evacuated glass solvent bulb containing dry and degassed CH_2Cl_2, dry box (N_2), vacuum line.

Procedure

The product and $GaCl_3$ are extremely moisture sensitive and must be handled, stored and manipulated under vacuum or in an inert atmosphere (dry box). The reaction is performed in a dual compartment reaction vessel, which is evacuated and flame dried (Bunsen) under dynamic vacuum before use. The starting materials, 0.50 g of 2-chloro-*cyclo*-1,3-dithia-2- arsapentane and 0.45 g of $GaCl_3$, are introduced into separate compartments in the dry box, and a stir bar is included with the $GaCl_3$ (compartment 2). The sealed unit is removed from the dry box and evacuated (do not evacuate for long periods, as $GaCl_3$ is volatile). Methylene chloride solvent is static vacuum distilled onto each of the reactants (L15 ml each) by cooling each compartment, in turn, with liquid nitrogen ($GaCl_3$ first). At room temperature, the solution of 2-chloro-*cyclo*-1,3-dithia-2-arsapentane is poured slowly (15 minutes) into the stirred solution of $GaCl_3$ giving an instantaneous bright yellow reaction mixture. After stirring for 15 minutes, $\approx 75\%$ of the solvent is distilled from the solution by cooling empty compartment 1. Solid or oil may be observed at this time. Stopcock B is closed and the solid or oily material is redissolved by warming the bulb under the hot water tap ($\approx 65\ ^\circ C$), accompanied by vigorous shaking. On slow cooling to room temperature, a yellow crystalline solid is formed. The solution is decanted from the crystals, and they are washed by cold spot (liquid nitrogen cotton swabs) back-distil-

lation. The solvent is entirely removed from the vessel *in vacuo* and the crystalline material is isolated and manipulated in the dry box.

Typical yields: 80–90%. M.p.: 94–95.5 °C. The FT-IR spectrum is shown in Figure 4.31-1b, NMR (CD_2Cl_2): ^1H, 4.06 ppm; ^{13}C, 45.8 ppm.

c) 2-Chloro-cyclo-1,3-dithia-2-arsapentane-1,3-dithia-2-arsolidinium Tetrachlorogallate, [3][$GaCl_4$]

Using the same materials and procedures described in part b), slowly add a solution of 0.45 g of $GaCl_3$ in 15 cm^3 of CH_2Cl_2 to a stirred solution of 1.0 g of 2-chloro-*cyclo*-1,3-dithia-2-arsapentane in 15 ml of CH_2Cl_2. A yellow solution is initially formed and produces a pale yellow precipitate during the addition. The majority of the solvent (A75%) is removed *in vacuo* depositing more of the product, then the remainder of the supernatant solution is decanted from the precipitate, which is washed by cold spot (liquid nitrogen cotton swabs) back-distillation. The prodcut can be recrystallised from hot methylene chloride as described in part b).

Typical yields: 80–90%. M.p.: 116–117 °C. The FT-IR spectrum is shown in Figure 4.31-1c. NMR (CD_2Cl_2): ^1H, 3.90 ppm; ^{13}C, 45.0 ppm.

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4.32
Preparation and Structure of the Acetyl Chloride-Antimony Pentachloride Complex

Peter N. Gates

Reaction of a Lewis acid of the type MX_n (e.g. M = B, Al, Sb, etc.; X = Cl, Br) with acid halides, RCOX (R = alkyl, aryl, etc.), usually produces a 1:1 complex $RCOX \cdot MX_n$. The structure of such complexes depends on the particular acid halide and Lewis acid but is usually of one of two types.

$$\begin{matrix} CH_3 \\ X \end{matrix}\!\!>\!C{=}O \rightarrow MX_n \quad \text{or} \quad [CH_3{-}C{\equiv}O]^+[MX_{n+1}]^-$$

(1) (2)

An example of type **1** is the 1:1 complex formed between $TiCl_4$ and CH_3COCl which has the structure $\begin{matrix} CH_3 \\ Cl \end{matrix}\!\!>\!C{=}O \rightarrow TiCl_4$. Reaction between CH_3COF and BF_3 produces a complex of type **2**, $CH_3C{\equiv}O^+BF_4^-$.

A very quick and convenient distinction between such structural types can be made by infra-red spectroscopy and relies on the characteristic group frequencies of carbon–oxygen bonds. In the parent acid halide the vibrational mode which corresponds mainly to the stretching of the CO bond lies in the region of 1800 cm^{-1}. In a complex of type **1**, a polarisation of electron density in the carbonyl bond would be predicted with a consequent reduction in the stretching force constant and hence the vibrational frequency. Such reductions have been observed in many Lewis acid complexes of carbonyl containing molecules. In a type **2** complex, where the formal bond order increases to 3, an increase in the CO force constant would be predicted with a consequent increase in the vibrational frequency (CH_3CO^+ is isoelectronic with CH_3CN).

In this experiment, the object is to determine the structure of the complex formed between CH_3COCl and $SbCl_5$. The complex is very sensitive to hydrolysis and must be prepared and handled under anhydrous conditions.

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Special Safety Precautions

1. Antimony pentachloride is corrosive and toxic by inhalation and skin contact. Apart from the dry bag, always use in a fume cupboard.
2. Carbon tetrachloride is toxic by inhalation and skin contact.
3. Acetyl chloride is corrosive and toxic by inhalation and skin contact. Keep away from sources of ignition.
4. The product is moisture sensitive and will hydrolyse to HCl and ethanoic acid in moist air.

4.32.1 Experimental

Both reactants and the product are sensitive to hydrolysis and all operations should be carried out in a dry bag. You are provided with a sealed ampoule containing a known amount (ca. 5 g) of $SbCl_5$. This should be opened in the dry bag by making a small nick with a glass knife in the constriction of the ampoule and carefully breaking the neck. Pour the $SbCl_5$ into CCl_4 (15 cm^3) contained in a dropping funnel fitted with a silica gel drying tube. Calculate the stoichiometric quantity of CH_3COCl required for a 1:1 molar ratio with the $SbCl_5$ you have used and place this in a 100 cm^3 B24 round-bottomed flask together with 20 cm^3 of CCl_4. Remove the dropping funnel from the dry bag and fit it to the round-bottomed flask *via* a connector with a side-arm. The apparatus should be protected from the atmosphere by attachment of a silica gel drying tube to the side-arm. Add the solution of $SbCl_5$ in CCl_4 dropwise, slowly with constant shaking (or stirring with a magnetic stir bar). When the addition is complete, the white solid may be filtered off as follows: connect a

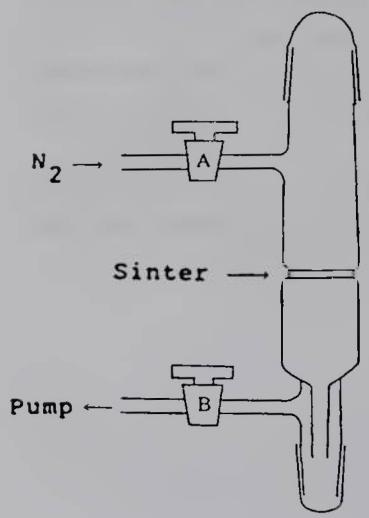

Fig. 4.32-1 Closed suction filter.

100 cm^3 flask to the lower end of the closed sintered filter (Fig. 4.32-1) and connect the filter (via tap B) to an oil pump protected by a liquid nitrogen trap. (Consult a demonstrator).

With tap A on the filter closed, quickly remove the side-arm connector from the reaction vessel, replace it with the top end of the closed filter, invert the apparatus and open tap B. Wash the white solid on the filter twice with 10 cm^3 portions of CCl_4. (This should be done quickly with minimum exposure to the atmosphere. To release the vacuum in the filter, dry nitrogen may be admitted through tap A.) Suck the product dry on the filter. When most of the CCl_4 has been removed from the product, rapidly replace the lower flask (as above when washing) with an empty one and continue pumping. When the product is dry, close tap B on the filter, detach from the suction and remove the closed apparatus to the dry bag. Transfer the white solid to a dry sample tube and seal it thoroughly with parafilm.

While the complex is drying, record the infrared spectrum of CH_3COCl as a neat liquid: place several drops of CH_3COCl on a KBr plate and cover with another plate to give a thin liquid film. Record the spectrum over the range 4000–1200 cm^{-1}. The infra-red spectrum of the complex should be obtained by preparing a sample in the dry bag as follows: remove a small quantity of the white solid from the sample tube and place it on the KBr plate. Then add a *small* amount of Nujol (liquid paraffin) and cover it with another plate. Rub the two plates together to obtain an even dispersion of the complex in the Nujol and quickly record the infra-red spectrum over the range 2500–1200 cm^{-1} (consult a demonstrator).

If Raman facilities are available, a low-frequency spectrum is also instructive. Place a small amount (about 1 cm depth) of the sample in a melting point capillary tube, seal the end with plasticine and remove from the dry bag. Record a Raman spectrum over the range 100–400 cm^{-1} (consult a demonstrator). Alternatively, a Raman spectrum may be supplied. On this basis, suggest a structure for the complex, assigning the major bands in the infra-red and Raman spectra.

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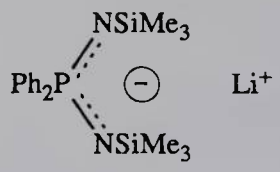
4.33
Preparation and Some Reactions of the Folded $P_2N_4S_2$ Ring

Tristram Chivers, Daniel D. Doxsee, and Robert W. Hilts

The eight-membered ring in 1,5-$R_4P_2N_4S_2$ (R = aryl, alkyl) has a folded structure (**1**) with a cross-ring S-S bond of ca. 2.5 Å. This inorganic heterocycle is a hybrid of S_4N_4 and the well known cyclophosphazenes. It undergoes a wide range of reactions based on the sulfur or nitrogen centres. For example, oxidative addition with halogens gives S,S′-dihalo derivatives, while the interactions with Lewis or Brønsted acids produces N-bonded adducts with retention of the S–S bond. The $P_2N_4S_2$ ring in **1** exhibits a versatile coordination chemistry and the following bonding modes have been established: η^1-N, η^2-S,S′, η^2-N,S-μ-S′. The reaction of **1** (R = Ph) with organolithium reagents produces the adducts $Li[Ph_4P_2N_4S_2R]$ (R = alkyl, aryl), which serve as a source of $Ph_4P_2N_4S_2R^-$ anions in the formation of η^1-S bonded complexes with late transition metals. The folded rings (**1**) exhibit ^{31}P NMR chemical shifts at anomalously low fields (110–140 ppm) compared to cyclophosphazenes as a result of the transannular S–S interaction. Consequently, ^{31}P NMR spectroscopy provides a diagnostic probe for the loss or retention of the S–S bond in reactions of **1**.

In this experiment, you will prepare **1** (R = Ph) from $Li[Ph_2P(NSiMe_3)_2]$ (**2**) and investigate the reactions of this inorganic heterocycle with bromine and with a Brønsted acid. The phosphorus-nitrogen-silicon reagent (**2**) has a monomeric structure and may be used for the preparation of P-N heterocycles containing lanthanide or actinide metals.

1



2

Note: If necessary, in view of time limitations, this experiment can be subdivided into parts a) and b) only or, if $Li[Ph_2P(NSiMe_3)_2]$ is provided, parts b) to d) only. The second option avoids delays imposed by the lengthy reflux necessary for the Staudinger reaction (Eq. 1).

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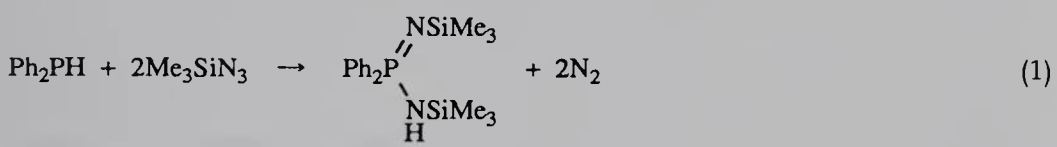
Special Safety Precautions

1. Chlorodiphenylphosphine (Ph_2PCl) is a noxious, acrid liquid which reacts readily with moist air. It should be stored in a Schlenk vessel under a nitrogen atmosphere and transferred in a fume cupboard. Spillages should be destroyed with an aqueous solution of sodium hypochlorite.
2. Liquid bromine and thionyl chloride ($SOCl_2$) are highly toxic and extremely corrosive liquids. These reagents must be handled with protective gloves inside a fume cupboard.
3. Organolithium reagents are likely to combust spontaneously on contact with air. These reagents must be transferred from 'sure-seal' bottles by using a calibrated syringe after a needle has been inserted through the septum of the container. Spillages should be destroyed with *n*-butanol.
4. Trimethylsilyl azide (Me_3SiN_3) is a highly flammable and poisonous liquid. It also must be handled with gloves in the fume cupboard.

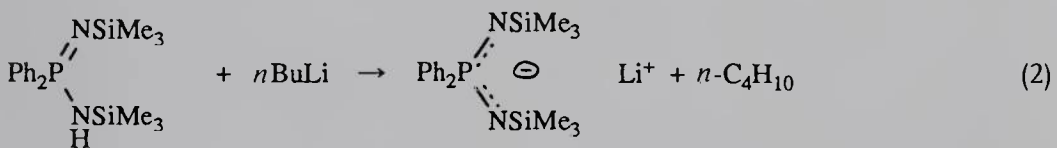
4.33.1 Experimental

a) $Li[Ph_2P(NSiMe_3)_2]$ (2)

The preparation of the lithium reagent (**2**) involves the two steps in Eqs. (1) and (2).



(1)



(2)

The procedure for Eq. (1) is a modification of that described by Paciorek and Kratzer.

Under an atmosphere of nitrogen, heat a mixture of Me_3SiN_3 (3.63 g, 31.5 mmol) and Ph_2PH (2.75 g, 15 mmol) in a 100 cm^3 side-arm (Schlenk) flask fitted with a reflux condenser at 140 °C for 24 hours. While still at 140 °C, apply a dynamic vacuum for at least 2 hours to remove any residual Me_3SiN_3. Cool the flask to room temperature and record the yield of your product. This procedure will give 3–4 g of $[Ph_2P(NHSiMe_3)(NSiMe_3)]$ as a colourless liquid. Obtain the infrared spectrum of the product on KBr plates. Look for a strong N-H band at ca. 2900 cm^{-1}. Record and interpret the ^1H NMR

spectrum in $CDCl_3$. ^{31}P NMR ($CDCl_3$): singlet at 0.2 ppm (with reference to 85% H_3PO_4).

$Ph_2P(NSiMe_3)[N(H)SiMe_3]$ (6.07 g, 16.9 mmol) is transferred via cannula to a 250 cm^3 side-arm (Schlenk) flask fitted with a septum and equipped with a magnetic stir bar. The flask should be previously evacuated and back-flushed with N_2 gas several times. Approximately 75 ml of dry hexanes are added to the flask, which is then placed in an ice-water bath. After about 10 minutes, an equimolar amount of *n*BuLi in hexanes (calculate the required volume based on the known concentration of this solution) is added dropwise via syringe (20 minutes) with stirring. The ice-water bath is then removed and the mixture is stirred until it reaches

room temperature. The septum is then replaced (be sure N_2 gas is flowing into the vessel through the side-arm) with a reflux condenser equipped with a tap adapter which has N_2 gas flowing through it. With the tap adapter open and the side-arm tap closed, the mixture is heated at reflux for one hour by using a heating mantle. The mixture is then allowed to cool to room temperature, the condenser is replaced with a septum and the flask is placed in a freezer (ca. –20 °C) for 2–3 hours. This results in the formation of white crystals. The residual supernatant liquid is decanted with a cannula and discarded. The white crystals of $Li[Ph_2P(NSiMe_3)_2]$ (4.80 g, 13.1 mmol) (78% yield) are dried under vacuum. The product can be handled in air for short periods, but it should be stored under an atmosphere of dry nitrogen. Record and interpret the ^1H NMR spectrum of your product in $CDCl_3$. ^{31}P NMR (in CH_2Cl_2): singlet at 16.5 ppm (referenced to 85% H_3PO_4).

b) 1,5-$Ph_4P_2N_4S_2$ (1, R = Ph)

A colourless solution of freshly distilled $SOCl_2$ (0.97 g, 8.16 mmol) in dry CH_2Cl_2 (100 cm^3) cooled in an ice bath at 0 °C is added dropwise (ca. 15 minutes), by cannula, to a rapidly stirred solution of $Li[Ph_2P(NSiMe_3)_2]$ (3.0 g, 8.16 mmol) in dry CH_2Cl_2 (200 cm^3) at 0 °C in a 500 cm^3 side-arm (Schlenk) flask. During the addition, the solution should change from colourless to yellow. The ice bath is removed and the mixture is stirred under N_2 for 18 hours. The solvent is removed under vacuum and then acetonitrile (30 cm^3) is added to the pale yellow residue. The resulting yellow suspension is stored overnight in the freezer at ca. –20 °C. The yellow supernatant solution is discarded and the cream coloured solid is dissolved in 25 cm^3 of CH_2Cl_2 to give a cloudy, colourless solution. The precipitated LiCl is removed by using a filter cannula and the filtrate is taken to dryness under vacuum. The residue is washed with hexane (30 ml) and then dried under dynamic vacuum for 2 hours to give 1,5-$[Ph_4P_2N_4S_2]$ (1.20 g, 2.45 mmol) as a white crystalline solid. Yield: 60%. The product can be handled in air for short periods, but it is slowly hydrolysed upon exposure to moist air for several weeks. Obtain a $^{31}P\{^1H\}$ NMR spectrum for your product in toluene. If your sample is contaminated with phosphorus containing by-products, it can be purified by recrystallisation from CH_2Cl_2/hexane at 0 °C. Record the infrared spectrum of your product as a Nujol mull and compare it with the literature values. Obtain the mass spectrum of your product and identify the parent ion. Provide an explanation of the unusually long S-S bond in **1**.

c) 1,5-$Ph_4P_2N_4S_2Br_2$ (3)

Note: In view of the moisture sensitivity of 1,5-$Ph_4P_2N_4S_2Br_2$, all samples of **3** must be handled in an inert atmosphere.

Liquid bromine (1.0 g, 0.6 mmol) is added dropwise by syringe to a stirred solution of 1,5-[$Ph_4P_2N_4S_2$] (0.30 g, 0.6 mmol) in dry dichloromethane (15 cm^3) in a 100 cm^3 Schlenk flask. (The syringe should be washed with hexanes immediately after use.) The resulting yellow solution is stirred for 30 minutes and then cooled to –20 °C to produce yellow moisture-sensitive crystals of 1,5-$Ph_4P_2N_4S_2Br_2$ (0.33 g, 0.5 mmol). Yield: 83%. Record and interpret the $^{31}P\{^1H\}$ NMR spectrum of your product in $CDCl_3$. Is your product contaminated with unreacted 1,5-$Ph_4P_2N_4S_2$? Record the infrared spectrum of your product as a Nujol mull and compare it with the literature values. Where would you expect the S-Br stretching vibration to occur?

d) Reaction of 1,5-$Ph_4P_2N_4S_2$ with $HBF_4 \cdot Et_2O$

A colourless solution of $HBF_4 \cdot Et_2O$ (0.19 g, 1.2 mmol) in 8 cm^3 of dry dichloromethane is added dropwise, over 30 minutes, by cannula, to a stirred solution of 1,5-[$Ph_4P_2N_4S_2$] (0.51 g, 1.0 mmol) in 25 cm^3 of dichloromethane in a 100 cm^3 Schlenk flask. Stir the mixture for 16 hours at 23 °C, and then filter the slightly cloudy solution and remove the solvent under vacuum. Dry hexane (50 ml) is added to the pale yellow residue and the mixture is rapidly stirred. Discard the supernatant solution and dry the colourless precipitate of 1,5-[$Ph_4P_2N_4S_2H$]BF_4 (0.43 g, 0.74 mmol) under dynamic vacuum. Record the $^{31}P\{^1H\}$ NMR spectrum of your product in $CDCl_3$ and propose a structure for the protonated derivative on the basis of the data that you obtain.

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4.34
Sulfur-Nitrogen Heterocycles and $[SNBr_{0.4}]_x$ Polymer

J. Derek Woollins

As a result of investigations begun over a hundred years ago, there is an extensive chemistry of inorganic sulfur-nitrogen compounds. Many of these compounds have remarkable chemical properties as well as unusual structures and bonding. Most recently, polymeric sulfur nitride, $(SN)_x$, has been found to be a one-dimensional conductor and a superconductor at low temperature. In this experiment, you will prepare three examples of SN heterocycles: $[S_3N_2Cl]Cl$, $(NSCl)_3$ and $[S_4N_3]Cl$, as well as the doped polymer $[SNBr_{0.4}]_x$. The first two are useful intermediates in the formation other SN compounds whilst the third is an example of a 10π aromatic system.

Special Safety Precautions

1. Sulfur monochloride (S_2Cl_2) is corrosive and very toxic by inhalation. *Always* use in a fume cupboard. Spillages should be treated with solid sodium bicarbonate followed by copious amounts of water.
2. Sulfur dichloride (SCl_2), which is produced and collected in the liquid nitrogen cold trap during the preparation of $(NSCl)_3$, is corrosive. After removal from the vacuum line, clamp the trap at the back of the fume cupboard and allow to warm to room temperature. Add *dropwise* aqueous sodium bicarbonate. The *treated* material can be washed down the drain.
3. Chlorine gas is toxic. The whole cylinder should be securely clamped inside a fume cupboard. If in any doubt whatsoever about safe operation of the cylinder, consult a demonstrator.
4. Carbon tetrachloride is toxic by inhalation or contact.
5. All of the sulfur-nitrogen compounds prepared in this experiment, except $[S_4N_3]Cl$, should be regarded as air and moisture sensitive and thus likely to hydrolyse to HCl and SO_2 if exposed to the atmosphere.

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6. The residue from the preparation of $[S_3N_2Cl]Cl$ must be destroyed. You should slowly tip the contents onto solid sodium bicarbonate in a fume cupboard. Very slowly add water and allow to stand.
7. Make sure that you carefully grease all joints with silicone.

4.34.1 Experimental

a) $[S_3N_2Cl]Cl$

In a fume cupboard, ammonium chloride (8.0 g), sulfur (4.0 g) and sulfur monochloride (24 cm^3; *care*) are placed in a dry 50 cm^3 B24 neck round-bottomed flask. The flask is fitted with a B24 straight walled condenser and a calcium chloride drying tube. The joints should be throughly greased with silicone grease. The mixture is heated to *gentle* reflux (isomantle). Deep red crystals of the product should sublime out of the reaction into the lower end of the condenser within 15–20 minutes. You should try to keep the heating to a minimum and it is often helpful to lag the top of the flask with glass wool insulation. Gentle refluxing is maintained for 6–8 hours, or overnight if necessary – do not attempt to restart the reaction with product in the condenser since the product is often washed back into the reaction by the refluxing S_2Cl_2. The reaction is allowed to cool and the $[S_3N_2Cl]Cl$ removed as follows.

A thoroughly dried, preweighed B24 Schlenk tube is prepared and securely clamped with N_2 flowing through it. The condenser containing $[S_3N_2Cl]Cl$ is rapidly transferred over (less than 5 seconds!). With continuous and steady N_2 flow, the $CaCl_2$ tube is removed and the product gently scraped into the Schlenk tube using a long handled spatula. The condenser is then returned to the reaction vessel and the Schlenk tube is stoppered (carefully grease the stopper with silicone grease). It may be necessary to pump on the product for a few minutes to remove traces of S_2Cl_2.

A second batch of $[S_3N_2]Cl$ (to be used in the synthesis of $[S_4N_3]Cl$) is prepared by addition of a further 10 ml of S_2Cl_2 to the reaction which is then refluxed as before.

Calculate the yield of your first crop of product and measure its IR spectrum (glove bag, Nujol mull, NaCl plates). Seal up a small sample in an ampoule.

b) $(NSCl)_3$

Using the first crop of $[S_3N_2Cl]Cl$, transfer the condenser to the top of a B24 Schlenk tube as before. With N_2 flow, remove the drying tube and connect the condenser to a scrubber unit. Turn off the N_2 and connect the apparatus to a Cl_2 cylinder (ask a demonstrator before using the chlorine cylinder). Pass Cl_2 gently through the system. The $[S_3N_2Cl]Cl$ will rapidly react and the product should be washed down into the Schlenk tube by the SCl_2 that is formed. Usually 5 minutes of slow Cl_2 flow is sufficient. Turn off the Cl_2 cylinder and pump away the SCl_2. If the product is still orange

coloured, repeat the chlorination. Measure the IR spectrum (glove bag, NaCl and polythene plates, 1100–200 cm^{-1}) and seal some of your sample in a glass ampoule.

c) $[S_4N_3]Cl$

Use the $[S_3N_2Cl]Cl$ from your second crop. You may have to rescale the reaction.

$[S_3N_2Cl]Cl$ (0.4 g) is refluxed in dry CCl_4 (20 cm^3) and S_2Cl_2 (12 cm^3) under N_2 for 5 hours or until all of the dark solid has been converted to a bright yellow precipitate. Cool the reaction, filter off the product (in air on a sintered funnel) wash it with 3×5 cm^3 of CCl_4. Discard your CCl_4/S_2Cl_2 waste into the container provided (see point 1 of the Special Safety Precautions).

Measure the IR spectrum (Nujol mull, KBr plates, 1200–200 cm^{-1}). Measure the UV spectrum (400–200 nm) in *conc.* HCl (*Care:* if you spill any acid in the spectrometer, report it the demonstrator immediately). You should accurately weigh your sample so that you can report extinction coefficients. As a guide to the concentration required, the strongest band has $\varepsilon = 10000–15000$ dm^3 mol^{-1} cm^{-1}. There is no need to seal your product up as it is not particularly air sensitive. The ^{15}N NMR spectrum of 100% ^{15}N labelled $[S_4N_3]Cl$ is given in Figure 4.34-1.

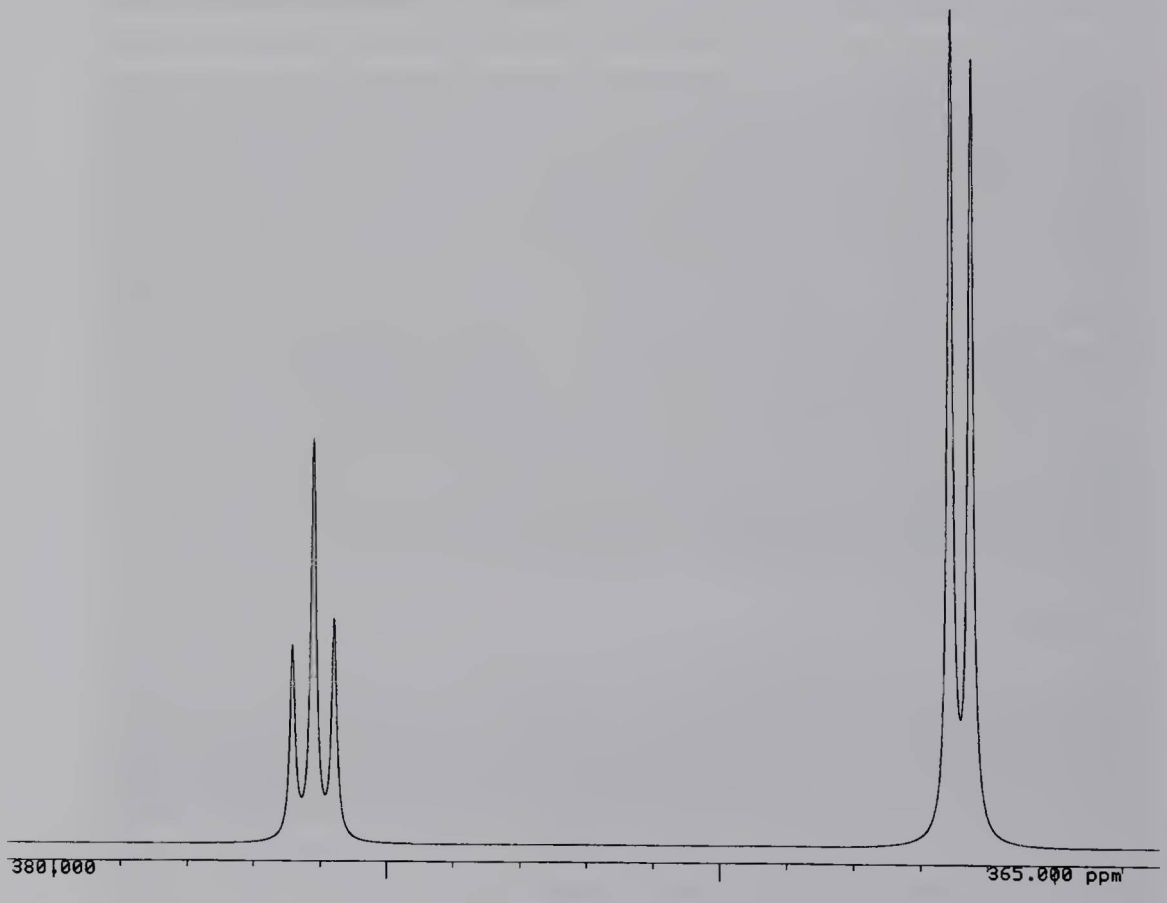

Fig. 4.34-1 ^{15}N NMR of 100% ^{15}N labelled $[S_4N_3]Cl$ in conc. HCl at 27.36 MHz.

d) $[SNBr_{0.4}]_x$

$(NSCl)_3$ (1.34 g) is dissolved in 35 cm^3 of dry CH_2Cl_2 under N_2. The reaction is cooled to −60 °C and Me_3SiBr (2.2 cm^3) is *slowly* added. After stirring for 15 minutes, the reaction is allowed to warm to room temperature and the resulting precipitate filtered, washed with CH_2Cl_2 (2 × 10 ml) and dried *in vacuo*.

Record the IR spectrum of your product and compare it with that in the literature. Prepare a pressed disc using the IR press and measure the conductivity of your solid sample. The properties of $(SN)_x$ and its halogenated derivatives have been reviewed by Labes *et al.*

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4.35
Selenium-Nitrogen and Tellurium-Nitrogen Compounds

Herbert W. Roesky and Judith Gindl

In the last ten decades, a large number of sulfur-nitrogen compounds could be obtained, but only a few selenium-nitrogen and tellurium-nitrogen compounds are known. Most are unstable and some of them decompose with explosion. Another problem is the lack of suitable stable precursors for the selenium- and tellurium-nitrogen chemistry. In this experiment you will find that some stable selenium-nitrogen and tellurium-nitrogen compounds ($Se[N(SiMe_3)_2]_2$, $Te[N(SiMe_3)_2]_2$, $Se[(NCMe_3(SiMe_3)]_2$ and $Te[NCMe_3(SiMe_3)]_2$) are useful precursors for preparing new compounds with Se–N and Te–N bonds. $Se(NCMe_3)_2SnCl_4$ is a stable selenodiimide. $(ClTeNSN)_3N$ and $(FTeNSN)_3N$ are tellurium nitrides that are stable at room temperature. Most of the known tellurium nitrides are very explosive. All compounds described have been characterised by X-ray structural analysis.

Special Safety Precautions

1. Most of the selenium and tellurium compounds are toxic. $Se[N(SiMe_3)_2]_2$, $Se[NCMe_3(SiMe_3)]_2$, $Te[N(SiMe_3)_2]_2$ and $Te[NCMe_3(SiMe_3)]_2$ are relatively volatile. All preparations should be carried out in a well ventilated fume cupboard.
2. All compounds are air and moisture sensitive. Therefore, experimental manipulations should only be performed under an atmosphere of dry nitrogen gas in Schlenk apparatus or in a dry box.
3. Butyllithium reacts violently with H_2O, the solutions should only be handled under dry nitrogen gas.
4. $(ClTeNSN)_3N$ may decompose violently when heated over 207 °C. $(FTeNSN)_3N$ may explode at room temperature when exposed to mechanical strain.

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4.35.1 Experimental

a) $Se[N(SiMe_3)_2]_2$

$LiN(SiMe_3)_2$ (3.08 g) is dissolved in 40 cm^3 of dry *n*-hexane. The solution is cooled to −78 °C and Se_2Cl_2 (2.11 g) is slowly added. The resulting yellow solution is stirred for 1 hour and then allowed to warm up to room temperature. It is further stirred for 12 hours, the solution is filtered and the volatiles are removed *in vacuo* by using a liquid nitrogen trap system. The orange residue is sublimed at 30–40 °C under dynamic vacuum (<0.1 torr), which yields 2.75 g (75%) of the yellow crystalline product having a melting point of 64–65 °C.

Measure the ^1H NMR spectrum (dry box, CCl_4 as solvent, $SiMe_4$ as reference). ^1H NMR: δ 0.27 (s). Mass spectrum (EI) [*m/z* (^{80}Se peaks, %)]: 400 (M^+).

b) $Te[N(SiMe_3)_2]_2$

A solution of $LiN(SiMe_3)_2$ (1.10 g) in dry *n*-hexane is cooled to −78 °C, then $TeCl_4$ (0.51 g), dissolved in toluene, is added slowly. The reaction mixture is stirred for 1 hour at −78 °C and after being allowed to warm up to room temperature, it is further stirred for 12 hours. The solution is filtered and the volatiles are removed *in vacuo* using a liquid nitrogen trap system. Sublimation of the residue at 30–40 °C under dynamic vacuum (<0.1 Torr) gives 0.43 g of the product. In order to obtain analytically pure product, the orange crystals are sublimed once again, now melting at 69–71 °C.

Measure the ^1H NMR spectrum (dry box, CCl_4 as solvent, $SiMe_4$ as reference). ^1H NMR: δ 0.24 (s). Mass spectrum (EI) [*m/z* (^{130}Te peaks, %)]: 450 (M^+).

c) $Se[NCMe_3(SiMe_3)]_2$

To a solution of $HNCMe_3(SiMe_3)$ (3.08 g) in 40 cm^3 dry *n*-hexane are added 16 cm^3 of a 1.6 M *n*BuLi/hexane solution at 0 °C. The solution is stirred for a few hours at room temperature, then cooled to −78 °C and Se_2Cl_2 (3.0 g) is slowly added. After allowing it to warm up to room temperature, the solution is stirred further for 12 hours then filtered through Celite. The volatiles are removed *in vacuo* using a liquid nitrogen trap system. The orange residue is sublimed at 40–50 °C under vacuum (0.1 Torr). Sublimation gives 3.2 g (65%) yellow crystals, melting at 72–73 °C. Further sublimation gives colorless crystals.

Measure the ^1H NMR spectrum (dry box, CCl_4 as solvent, $SiMe_4$ as reference) and the ^{77}Se NMR spectrum ($CDCl_3$ as solvent, $SeMe_2$ as reference). ^1H NMR: δ 0.35 (s, $SiMe_3$), 1.45 (s, CMe_3). ^{77}Se NMR: δ 1071 (s). Mass spectrum (EI) [*m/z* (^{80}Se peaks, %)]: 368 (M^+, 100).

d) $Te[NCMe_3(SiMe_3)]_2$

To a solution of $HNCMe_3(SiMe_3)$ (3.18 g) in 40 cm^3 dry *n*-hexane are slowly added 16 ml of a 15% *sec*BuLi/cyclohexane solution at 0 °C. The solution is stirred for a few hours, then cooled to –78 °C and $TeCl_4$ (1.47 g), dissolved in toluene, is added slowly. After allowing to warm up to room temperature, the solution is stirred for 12 hours and filtered through Celite. The volatiles are removed *in vacuo* using a liquid nitrogen trap system. The crude product is purified by sublimation at 40–50 °C under dynamic vacuum (<0.1 Torr). The bright yellow product (0.81 g; 35%) melts at 67–70 °C.

Measure the ^1H NMR spectrum (dry box, CCl_4 as solvent, $SiMe_4$ as reference) and the ^{125}Te NMR spectrum ($CDCl_3$ as solvent, $TeMe_2$ as reference). ^1H NMR: δ 0.35 (s, $SiMe_3$), 1.47 (s, CMe_3). ^{125}Te NMR: δ 1742 (s). Mass spectrum (EI) [*m/z* (^{130}Te peaks, %)]: 418 (M^+).

e) $Se(NCMe_3)_2SnCl_4$

To a solution of $Se[NCMe_3(SiMe_3)]_2$ (2.16 g) from part c) in 20 ml dry CH_2Cl_2 is added $SnCl_4$ (3.03 g) in 10 ml CH_2Cl_2 and the reaction mixture is stirred for 3 d at room temperature.

The green precipitate is separated by filtration and the residue redissolved in 500 ml dry THF. Insoluble by-products are separated by filtration and the solvent is removed *in vacuo*. A yellow product remains (0.87 g, 31%), decomposing at 142 °C.

Alternatively, the following procedure can be employed. To a suspension of $SeCl_4$ (0.55 g) in 20 ml dry diethyl ether is slowly added H_2NCMe_3 (1.1 g). The solution is filtered, the solvent removed *in vacuo* and the residue dissolved in 8 cm^3 dry CH_2Cl_2. To this solution is added dropwise $SnCl_4$ (0.65 g) in 10 cm^3 CH_2Cl_2 at room temperature. The immediately formed yellow solid is filtered off, dissolved in 200 ml dry THF and red by-products removed by filtration. After removing the solvent *in vacuo*, 0.35 g (29%) of the product remain, decomposing at 141 °C.

Measure the ^1H NMR spectrum (dry box, $(CD_3)_2SO$ as solvent, $SiMe_4$ as reference) and the ^{77}Se NMR spectrum ($(CH_3)_2SO$ as solvent, $SeMe_2$ as reference). The product is not stable in this solvent, the measurements must be performed immediately. ^1H NMR: δ 1.57 (s). ^{77}Se NMR: δ 1392.0 (s).

f) $(ClTeNSN)_3N$

3.50 g $TeCl_4$ are dissolved in 120 cm^3 of dry toluene. A solution of 3.10 g $S(NSiMe_3)_2$ in 40 ml dry toluene is slowly added at 0 °C. The yellow precipitate is separated by filtration, washed with dry $CHCl_3$ and dried *in vacuo* to give 2.2 g (74%) of the product, decomposing at 207 °C.

Measure the IR spectrum (dry box, Nujol mull, KBr plates).

IR [cm^{-1}]: 1120 (vs sh), 1090 (s), 1060 (vs sh), 680 (s), 570 (s), 520 (s).

g) $(FTeNSN)_3N$

A solution of $S(NSiMe_3)_2$ (1.04 g) in 30 cm^3 ether is slowly added to a suspension of TeF_4 (0.94 g) in 30 ml dry ether and the reaction mixture is stirred for 8 hours. The red solid is filtered off, redissolved in dry pyridine/toluene (3:1) and allowed to crystallise at –10 °C, giving 0.50 g (51%) of the product after drying *in vacuo*. It decomposes at 112 °C.

Measure the ^{19}F NMR spectrum (pyridine/C_6D_6 as solvent, $CFCl_3$ as reference) and the ^{125}Te NMR spectrum (pyridine/C_6D_6 as solvent, $TeMe_2$ as reference). ^{19}F NMR: δ –42.6 (s). ^{125}Te NMR: δ 1157.

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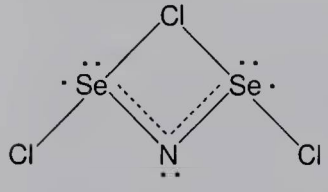
4.36
Nitride Chlorides of Selenium(III) and Selenium(IV): Se_2NCl_3 and Se_2NCl_5

Kurt Dehnicke

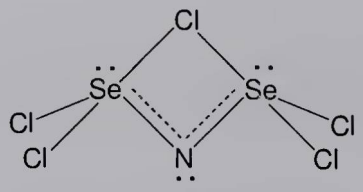
Special Safety Precautions

1. The nitride chlorides of selenium and their derivatives as well as the starting materials are moisture sensitive. All operations must be carried out under dry nitrogen.
2. Never use a larger quantity of tris(trimethylsilyl)amine as it is described in the procedure of synthesis, since explosive selenium nitride, Se_4N_4, is formed as a by-product (yellow solid).
3. The nitride chlorides of selenium may be handled only at room temperature. Heating them, particularly in an open flame, causes explosions.
4. The solvents dichloromethane and acetonitrile are toxic by inhalation or contact. Use a fume cupboard.

The nitride chlorides of selenium are highly reactive compounds which can be used as reagents for the preparation of other selenium nitride compounds. They can easily be prepared from selenium tetrachloride with tris(trimethylsilyl)amine in dichloromethane and acetonitrile suspensions, respectively, in good yields. Both nitride chlorides have molecular structures like dividers with almost planar Se_2NCl four-membered rings:



$Se^{III}{}_2NCl_3$



$Se^{IV}{}_2NCl_5$

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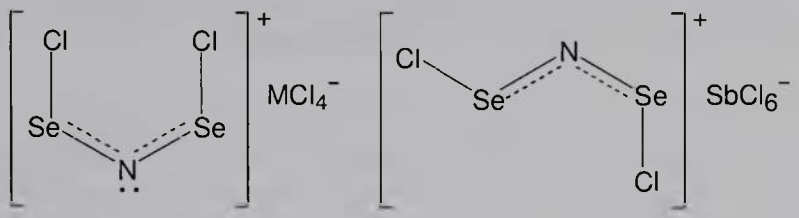
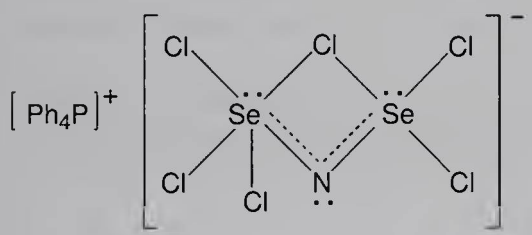
With respect to the non-bonding electrons and the lone pairs at the selenium atoms, respectively, these atoms have distorted Ψ-trigonal bipyramidal environments.

Se_2NCl_3 reacts with the Lewis-acids $GaCl_3$ and $FeCl_3$ to give the U-shaped cations $[Se_2NCl_2]^+[MCl_4]^-$ (M = Ga, Fe), whereas with $SbCl_5$ the corresponding S-shaped cation is formed:



From Se_2NCl_5 a cationic derivative is known, too: $[Se_2NCl_4]^+[AsF_6]^-$, which is easily obtained from $[SeCl_3]^+[AsF_6]^-$ and $N(SiMe_3)_3$.

According to the higher Lewis-acidity of Se^{IV} compared with Se^{III}, Se_2NCl_5 also reacts as a Lewis-base with tetraphenylphosphonium chloride to give the anionic species $[Se_2NCl_6]^-$. Interestingly, its structure is asymmetric in that it has two selenium atoms with different co-ordination numbers (ψ-octahedral and ψ-trigonal bipyramidal, respectively), the Se_2NCl four-membered ring being retained:



Thus, the amphoteric Lewis acid/base character of Se_2NCl_5 makes it possible to compare the bonding and structural features of the series:

	$[Se_2NCl_4]^+$	$[Se_2NCl_5]$	$[Se_2NCl_6]^-$
Se-N/pm (on average)	175.1	176.5	177.1
Se-N-Se/°	117.6	115.8	114.8

The differences are relatively small; however, they show the expected trends: the smaller the bond angle SeNSe, the longer the bond lengths SeN. These trends correspond also with respect to the changing of the charge. In all cases the SeN bond lengths are close to double bonds; the expected value of a Se-N single bond is 186 pm.

4.36.1
Experimental

a) Se_2NCl_3

A solution of freshly distilled tris(trimethylsilyl)amine (2.2 g, 9.4 mmol) in dichloromethane (20 cm^3) is added dropwise to a suspension of selenium tetrachloride (4.1 g, 18.7 mmol) in dichloromethane (30 cm^3) and stirred (magnetic stirrer).

Caution: Never change the order of the reagents; during the reaction $SeCl_4$ must always be in excess! The reaction mixture is than refluxed for 12 hours, filtered to remove small amounts of unreacted $SeCl_4$, and after concentration to 10 cm^3 cooled to 5 °C. The red crystals are separated by filtration, washed with a little cold CH_2Cl_2 and dried in vacuum (yield 1.5 g, 57%, based on $SeCl_4$, m.p. 69 °C). The chlorine formed by the reaction

$$2\ SeCl_4 + N(SiMe_3)_3 \rightarrow Se_2NCl_3 + 3\ ClSiMe_3 + Cl_2 \qquad (1)$$

reacts with part of the tris(trimethylsilyl)amine. An improvement in the yield strived for by the addition of larger quantities of amine is not advisable since explosive by-products are formed.

Measure its IR spectrum (glove bag, Nujol mull, KBr or CsBr plates) and compare it with the literature data.

Measure the ^{77}Se NMR spectrum in CH_2Cl_2 and/or CH_3CN solution. Give an explanation why the compound is diamagnetic, although there are two single electrons.

b) Se_2NCl_5

The procedure of synthesis is similar to that for Se_2NCl_3, except for the reaction temperature. Follow the precautions mentioned above.

$$2\ SeCl_4 + N(SiMe_3)_3 \rightarrow Se_2NCl_5 + 3\ ClSiMe_3 \qquad (2)$$

A solution of freshly distilled tris(trimethylsilyl)amine (2.03 g, 8.67 mmol) in dichloromethane (9 ml) is added dropwise at 0 °C to a suspension of selenium tetrachloride (3.83 g, 17.35 mmol) in dichloromethane (15 ml) and stirred (magnetic stirrer) at 0 °C for 8 hours. After filtration, the pale pink powder of Se_2NCl_5 is washed with CH_2Cl_2 and dried in vacuum (yield 2.84 g, 94%, based on $SeCl_4$). The compound is somewhat light-sensitive.

Measure its IR spectrum (glove bag, Nujol mull, KBr or CsBr plates) and compare it with the literature data.

Measure its ^{77}Se NMR spectrum in CH_2Cl_2 and/or CH_3CN solution and compare the data with those of Se_2NCl_3 (see above). Use other dry solvents with and without donor properties (for example THF, 1,4-dioxane, $CHCl_3$, $ClCH_2CH_2Cl$) and compare the results.

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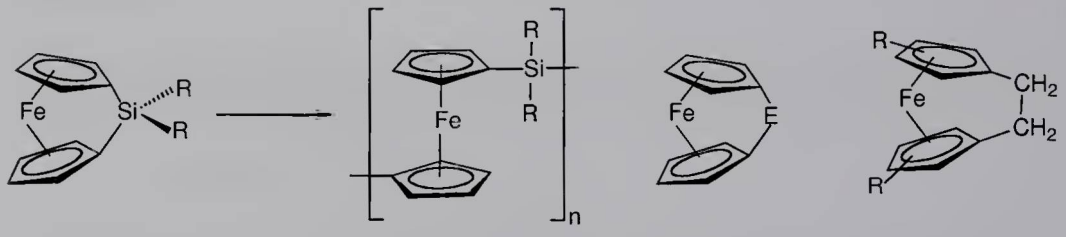
4.37
The Synthesis and Ring-Opening Polymerisation Behaviour of a [1]Silaferrocenophane

Ian Manners

Transition metal-containing polymers have attracted considerable attention. These materials offer the potential for combining the interesting and possibly useful properties of metals (e.g. redox, catalytic, electrical, magnetic) with the processability normally found for organic polymers. However, there are few examples of well-characterised, transition metal-containing polymers, due in part to the synthetic challenge of obtaining these compounds.

One route that has been used successfully to obtain these materials is ring-opening polymerisation (ROP). High molecular weight poly(ferrocenylsilanes) (**2**) were first obtained by the thermally-induced ROP of the strained [1]silaferrocenophanes (**1**) in 1992. Since then, anionic and transition metal-catalysed ROP synthetic routes have been successfully applied to obtain a variety of high molecular weight polymers and copolymers from other strained [1]- (e.g., **3**) and [2]ferrocenophanes (e.g., **4**). This section outlines the synthesis and polymerisation of one of these monomers.



1 **2** **3** **4**

E = GeR_2, PPh, S R = H, Me

Special Safety Precautions

Handling of the commercially available solutions of *n*-butyllithium in hexanes requires inert gas (argon or dinitrogen). Both *n*-butyllithium and the resulting product(s) are pyrophoric.

4.37.1 Experimental

a) Synthesis of (1,1′-Ferrocenediyl)dimethylsilane

Transfer 5.0 g of ferrocene into a dry, 250 cm^3 three-necked round-bottomed flask, which is being continuously flushed with N_2 gas. Add 100 cm^3 of hexanes and 3.8 cm^3 of 1,1,1′,1′-tetramethylethylenediamine (TMEDA) to the flask. Place a rubber septum in one neck. Using a syringe, transfer 34 cm^3 of a 1.6 M *n*-butyllithium solution (in hexanes) to the flask through the septum. Stir the mixture overnight under a slow flow of N_2.

Stop stirring the contents of the flask and allow the solid to settle. Using a cannula, transfer as much of the supernatant as possible into a separate, dry 250 cm^3 flask which has been purged with N_2. Using a syringe, add 100 cm^3 of fresh hexanes to wash the solid. Remove the supernatant as before. Finally, add 100 cm^3 of fresh hexanes to the solid.

Cool the contents of the flask to –10 °C. Add 4.2 cm^3 of dichlorodimethylsilane *dropwise* via a syringe to the stirred contents of the flask, maintaining the temperature at –10 °C during the addition. Maintain the temperature between –10 and –5 °C for 30 minutes after the addition is complete and then remove the cooling bath and allow the flask to warm up to room temperature. Remove the solvent under high vacuum and dry the product in this way for several hours (overnight, if necessary – *be sure to check the liquid nitrogen traps before leaving*).

Refill the flask with N_2 gas and insert a sublimation cold finger into one of the necks of the flask. Adjust the cooling water temperature to 5–10 °C and evacuate the flask. Leave the apparatus under high vacuum overnight (*be sure to check the liquid nitrogen traps before leaving*), allowing the red–orange product to sublime on to the cold finger.

Next morning, refill the flask with N_2 gas and transfer the apparatus to an N_2 glove-bag. Scrape the product into a clean, dry 100 cm^3 round-bottomed flask. Obtain a ^1H NMR spectrum in degassed C_6D_6.

If there are significant amounts of impurities (what might these be?) evident in the NMR spectrum of the sample, recrystallise the product at –20 °C overnight. Decant the mother liquor under N_2 using a cannula (*do not* discard the mother liquor; reduce the volume of solvent under vacuum and attempt another recrystallisation at –20 °C to obtain more of the product). Wash the crystals with cold (–78 °C), fresh hexanes to remove trace amounts of ferrocene and TMEDA and then dry the solid under high vacuum (about 20–30 minutes). Obtain a ^1H NMR spectrum in degassed C_6D_6, to confirm the purity of the product.

b) Transition Metal-catalyzed ROP of (1,1′-Ferrocenediyl)dimethylsilane

Under N_2, dissolve 0.5 g of the monomer in 5 cm^3 of dry tetrahydrofuran (THF). Add a few spatula tips of $PtCl_2$ and leave the reaction mixture stirring for a few hours at room temperature. Filter this solution (if necessary) and then add it dropwise to

100 cm^3 of hexanes with stirring. Filter off the polymer and dry it under vacuum. Obtain a ^1H NMR spectrum in C_6D_6 and also a gel permeation chromatogram of the polymer.

To cast a film, dissolve 0.4 g of polymer in 1 cm^3 of THF. Place this solution on a film-casting plate and allow the solvent to evaporate. Carefully remove the film from the plate. To oxidise the polymer film, dip it into a hexanes solution of I_2. Carefully wash the film with hexanes. To reduce the film, dip it into a solution of hydrazine in methanol.

c) Thermal ROP of (1,1′-Ferrocenediyl)dimethylsilane

Under N_2, transfer 0.3 g of the monomer into a polymerisation tube. Seal it under vacuum. Heat the tube in an oven at 120–130 °C. During this period, the monomer will melt and then the contents of the tube will be seen to solidify. Remove the tube immediately. Carefully crack open the tube and dissolve the contents in THF. Filter (if necessary) and precipitate the polymer in 100 cm^3 of hexanes. Filter the polymer and dry it under vacuum. Obtain a ^1H NMR spectrum in C_6D_6 and also a gel permeation chromatogram of the polymer.

c) Characterisation

Compare and contrast:

1. the ^1H NMR spectra obtained for the monomer and both samples of polymer;
2. the weight-average molecular weight (M_w), the number-average molecular weight (M_n) and the polydispersity index (PDI = M_w/M_n) obtained from the gel permeation chromatograms.

Acknowledgements

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Inorganic chemistry is one of the first subjects any chemistry student learns. This classic book, now in its third edition, has been revised, restructured and updated to help students learn to develop their laboratory and reporting skills.

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J. Derek Woollins obtained his PhD from the University of East Anglia (UK) under the supervision of Andrew Thomson and Roger Grinter. He carried out postdoctoral work with Bill Cullen (UBC, Vancouver), Barnett Rosenberg (MSU, Michigan) and Norman Greenwood (Leeds, England) before being appointed as a lecturer at Imperial College London. After 12 years at Imperial College he moved to Loughborough as the Chair in Inorganic Chemistry where he stayed for five years before moving to St. Andrews as the Chair in Synthetic Chemistry in 1999. He is currently Head of the School of Chemistry in St. Andrews.

He has played a major part in the development of P-Se heterocyles, synthesising the new reagent [Ph(Se)PSe2P(Se)Ph]. This compound is now commercially available and known as 'Woollins Reagent'. He has published over 440 research papers in main group chemistry and two books.

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