

3. THE SYNTHESIS & SPECTROSCOPIC CHARACTERISATION OF METAL CARBONYL COMPLEXES

PRE-LABORATORY WORK

On a separate sheet write the following:

- the experiment title and the date the experiment will be carried out
- a brief statement of the experiment to be performed
- a brief plan of the experimental procedure

You must complete the pre-laboratory work and have it signed by a demonstrator before starting the experiment. Hand in the pre-laboratory work with your write-up. Failure to do so will result in a loss of marks.

SAFETY DATA

2,2'- Bipyridine	TOXIC, IRRITANT	
Chromium complex	TOXIC	
Cyclohexane	FLAMMABLE	Put residues in waste solvents. Avoid flames.
Dichloromethane (DCM)	TOXIC, IRRITANT	Put residues in waste solvents. Use in fume cupboard
Diethyl ether	FLAMMABLE	Put residues in waste solvents. Avoid flames. Use in fume cupboard
Diethylene triamine (Dien)	TOXIC, CORROSIVE	
Ethanol	FLAMMABLE	Put residues in waste solvents. Avoid flames.
<i>p</i> -Fluorobenzenediazonium tetrafluoroborate	TOXIC	Keep in the fridge
<i>n</i> -Hexane	FLAMMABLE, IRRITANT	Put residues in waste solvents. Avoid flames. Use in fume cupboard
Mesitylene molybdenum tricarbonyl	TOXIC	Put residues in waste solvents. Keep away from flames.
Molybdenum hexacarbonyl	TOXIC	
Triphenylphosphine	IRRITANT	
Toluene	FLAMMABLE, HARMFUL	Put residues in waste solvents. Keep away from flames.

INTRODUCTION

This experiment introduces you to the synthesis of low-valent transition metal complexes and to the use of spectroscopy to investigate metal carbonyl derivatives. You will carry out reactions under an inert atmosphere and use IR spectroscopy, in combination with NMR and ESR (electron spin resonance) spectroscopy, to deduce geometric structure and investigate π -bonding between metals and ligands.

Many metal carbonyl complexes are unstable in solution in air. Their reactions are usually carried out in a fume cupboard (particularly if CO gas is evolved during a reaction) and under nitrogen or argon.

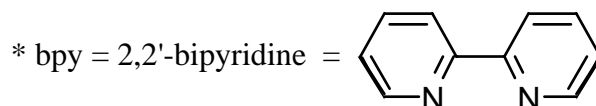
Metal carbonyl derivatives are particularly well-suited for IR spectroscopic studies because the carbonyl ligands give rise to CO stretching frequencies, ν_{CO} , in the so-called 'carbonyl' region (2200-1700 cm^{-1}) of the spectrum, which is comparatively free from other absorptions. NMR spectroscopy is useful for investigating diamagnetic complexes containing spin-active nuclei (^1H , ^{13}C , ^{31}P , ^{19}F , etc.), and ESR spectroscopy is similarly useful for studying paramagnetic complexes.

PART I – THE MOLECULAR STRUCTURES OF CHROMIUM & MOLYBDENUM

CARBONYL COMPLEXES

Part Ia – The Structures of $[\text{Mo}(\text{CO})_4(\text{bpy})]^*$ & $[\text{Mo}(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2]$

Octahedral compounds of the general formula $[\text{M}(\text{CO})_4\text{L}_2]$ (M = metal, L = monodentate ligand, L_2 = bidentate ligand) may exist as *cis* and/or *trans* isomers. However, the number of carbonyl stretching frequencies observed in the IR spectrum will differ for the different structures. In this experiment you will prepare $[\text{Mo}(\text{CO})_4(\text{bpy})]$ and compare its IR spectrum with that of $[\text{Mo}(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2]$.



Experimental

N.B. Use the apparatus shown in Fig 3.1 to carry out syntheses 1, 3 and 4 (where you need to heat a reaction mixture under reflux and under nitrogen). Synthesis 2 is carried out at room temperature, in the open laboratory.

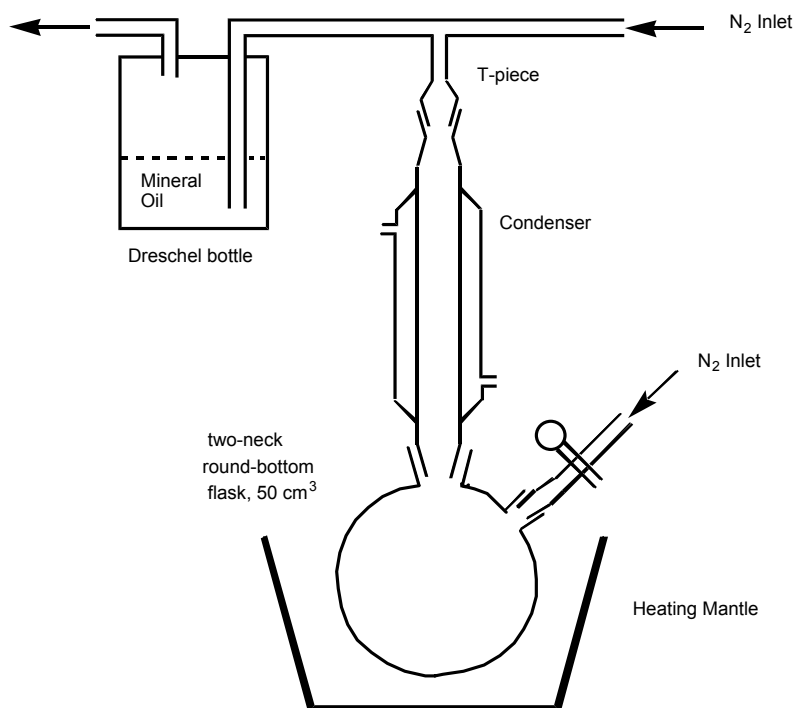


Figure 3.1 Experimental apparatus for syntheses 1, 3 and 4.

Synthesis 1 – Preparation of $[\text{Mo}(\text{CO})_4(\text{bpy})]$

Bubble nitrogen through toluene (25 ml) for 5 min and then add $[\text{Mo}(\text{CO})_6]$ (0.6 g, 2.3 mmol) and 2,2'-bipyridine (0.4 g, 2.6 mmol). Heat the mixture for 1.5 hours under reflux, in an atmosphere of nitrogen. Allow the mixture to cool to room temperature and collect the crystalline product on a sintered glass funnel. Wash the product well with *n*-hexane and dry it in air. Record the mass of $[\text{Mo}(\text{CO})_4(\text{bpy})]$ and the percentage yield based on $[\text{Mo}(\text{CO})_6]$.

Spectroscopy

Record the IR spectrum of $[\text{Mo}(\text{CO})_4(\text{bpy})]$ in DCM in the region $2200\text{-}1700\text{ cm}^{-1}$ using the FTIR spectrometer and the CaF_2 solution cells (which may be obtained from the technicians). You will be shown how to use the spectrometer and cells but you should consult a Demonstrator IMMEDIATELY if you encounter problems.

N.B. $[\text{Mo}(\text{CO})_6]$ reacts with $\text{P}(\text{OPh})_3$ at $100\text{-}120^\circ\text{C}$ (in a high boiling solvent) to give both isomers of $[\text{Mo}(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2]$. You will not carry out this reaction yourself; the IR carbonyl spectrum of the dominant (>90%) isomer is shown in Fig 3.2 (at the end of this experiment).

The Relationship Between IR Spectra & Molecular Structure

Table 3.1 lists the number of carbonyl stretching frequencies, $\nu_{(\text{CO})}$, for complexes of the general formula $[\text{M}(\text{CO})_{6-x}\text{L}_x]$ ($x = 1\text{-}5$). The Table is derived using group theory (Level 3 lecture course on Symmetry Properties in Inorganic Compounds).

Geometry	Number of CO stretching frequencies
$[M(CO)_5L]$	3
<i>cis</i> - $[M(CO)_4L_2]$	4
<i>trans</i> - $[M(CO)_4L_2]$	1
<i>fac</i> - $[M(CO)_3L_3]$	2
<i>mer</i> - $[M(CO)_3L_3]$	3
<i>cis</i> - $[M(CO)_2L_4]$	2
<i>trans</i> - $[M(CO)_2L_4]$	1
$[M(CO)L_5]$	1

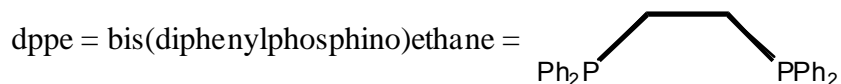
Table 3.1 Expected number of carbonyl stretching frequencies, $\nu_{(CO)}$, for complexes of the general formula $[M(CO)_{6-x}L_x]$ ($x = 1-5$).

Questions

Answer questions (i) to (iv) provided on a separate sheet.

Part Ib – One-Electron Oxidation of $[Cr(CO)_2(dppe)_2]$ ($dppe = Ph_2PCH_2CH_2PPh_2$)

Many neutral, diamagnetic metal carbonyl derivatives undergo one-electron oxidation to paramagnetic monocations. For example, $[Fe(CO)_3(PPh_3)_2][PF_6]$ is readily prepared from $[Fe(CO)_3(PPh_3)_2]$ and $AgPF_6$. When derivatives of $[Cr(CO)_6]$ undergo such oxidation reactions isomerisation is often also observed. You will use IR, NMR and ESR spectroscopy to investigate the oxidative isomerisation of $[Cr(CO)_2(dppe)_2]$.



Experimental

N.B. This part of the experiment is carried out in the open laboratory, without the need for nitrogen. The one-electron oxidant is $[N_2C_6H_4F-p][BF_4]$, a thermally stable arenediazonium salt (which is stored in the fridge).

Synthesis 2 – Preparation of Complex A

In a conical flask, suspend $[Cr(CO)_2(dppe)_2]$ (0.10 g, 0.11 mmol) in DCM (10 ml). Add solid $[N_2C_6H_4F-p][BF_4]$ (30 mg, 0.14 mmol) and stir the mixture for 10 min (using a magnetic stirring bar). Filter the mixture, through a filter paper, into a second conical flask and then add hexane (ca. 30 ml) to the filtrate to precipitate the product (A). Collect the precipitate on a sintered glass funnel, wash it with diethyl ether, and dry it in air. Record the mass and percentage yield of the product.

Spectroscopy

Record the IR spectra (in DCM, in the region $2200-1700\text{ cm}^{-1}$) of $[Cr(CO)_2(dppe)_2]$ and the oxidation product (A). The ESR spectrum of (A) is shown in Fig 3.4.

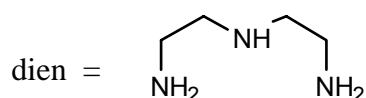
Questions

Answer questions (v) to (vi) provided on a separate sheet.

PART II – THE EFFECTS OF LIGANDS ON THE CARBONYL STRETCHING

FREQUENCIES OF *fac*-[Mo(CO)₃L₃]

The direct reaction of [Mo(CO)₆] with a ligand, L, often leads to a mixture of substitution products, e.g. [Mo(CO)₅L], *cis*- and *trans*-[Mo(CO)₄L₂], etc. However, syntheses may be devised in which the constitution and geometry of the starting material determine the constitution and geometry of the product. A convenient method for selectively preparing *fac*-[Mo(CO)₃L₃] is to react L with [Mo(CO)₃(η-arene)] in which the arene, for example 1,3,5-trimethylbenzene (C₆Me₃H₃, mesitylene), is a six-electron ligand π-bonded to the metal. In this part of the experiment you will react [Mo(CO)₃(η-C₆Me₃H₃)] with (i) diethylenetriamine (dien, see below), and (ii) PPh₃, to form *fac*-[Mo(CO)₃(dien)] and *fac*-[Mo(CO)₃(PPh₃)₃] respectively.



Experimental

Synthesis 3 – Preparation of *fac*-[Mo(CO)₃(Dien)]

Bubble nitrogen through *n*-hexane (25 ml) for 5 min and then add crushed [Mo(CO)₃(η-C₆Me₃H₃)] (0.2 g, 0.67 mmol) and liquid dien (0.3 ml and no more! USE THE GRADUATED SYRINGE SUPPLIED). Heat the mixture under reflux for 20 min. Cool the mixture, discard the mother liquors, and wash the precipitate onto a sintered glass funnel using Purite water. Thoroughly wash the solid sequentially with water, ethanol and diethyl ether and then dry it in air. The product should be a dry powder. If it is not, repeat the washing and drying sequence. Record the mass and percentage yield of the product, *fac*-[Mo(CO)₃(dien)].

Synthesis 4 – Preparation of *fac*-[Mo(CO)₃(PPh₃)₃]

Bubble nitrogen through cyclohexane (30 ml) for 5 min and then add crushed [Mo(CO)₃(η-C₆Me₃H₃)] (0.2 g, 0.67 mmol) and solid PPh₃ (1.0 g, 3.82 mmol). Heat the mixture under reflux for 30 min and then filter the precipitate onto a sintered glass funnel. Wash the product thoroughly with diethyl ether and then dry it in air. Record the mass and percentage yield of the product, *fac*-[Mo(CO)₃(PPh₃)₃].

Spectroscopy

Record the IR spectra of *fac*-[Mo(CO)₃(dien)] and *fac*-[Mo(CO)₃(PPh₃)₃] as Nujol® mulls, in the region 2200-1700 cm⁻¹. (Make sure you use the correct NaCl plates for the dien complex).

Questions

Answer questions (vii) to (ix) provided on a separate sheet.

SOURCES OF INFORMATION

F.A. Cotton, G. Wilkinson and P.L. Gaus. *Basic Inorganic Chemistry*, 3rd. Edn., Chapter 28.

F.A. Cotton and G. Wilkinson. *Advanced Inorganic Chemistry*, 5th Edn., Chapter 22.

N.N. Greenwood and A. Earnshaw. *The Chemistry of the Elements*, Section 8.9.1.

J.E. Huheey, E.A. Keiter and R.L. Keiter. *Inorganic Chemistry*, 4th. Edn., Chapter 15.

D.F. Shriver, P.W. Atkins and C.H. Langford. *Inorganic Chemistry*, 2nd. Edn., Section 16.3.

SPECTRA

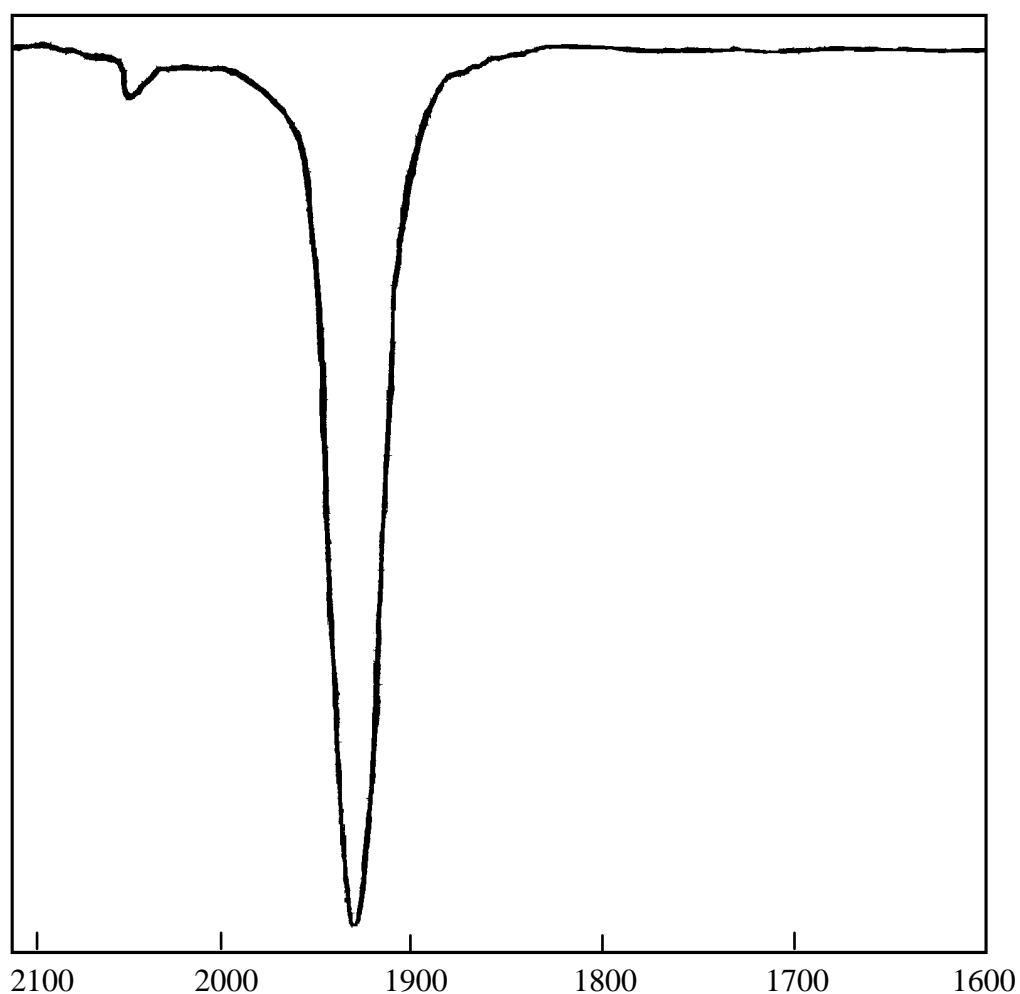


Figure 3.2 The IR spectrum of $[\text{Mo}(\text{CO})_4\{\text{P}(\text{OPh})_3\}_2]$ in CHCl_3 (units are cm^{-1}).

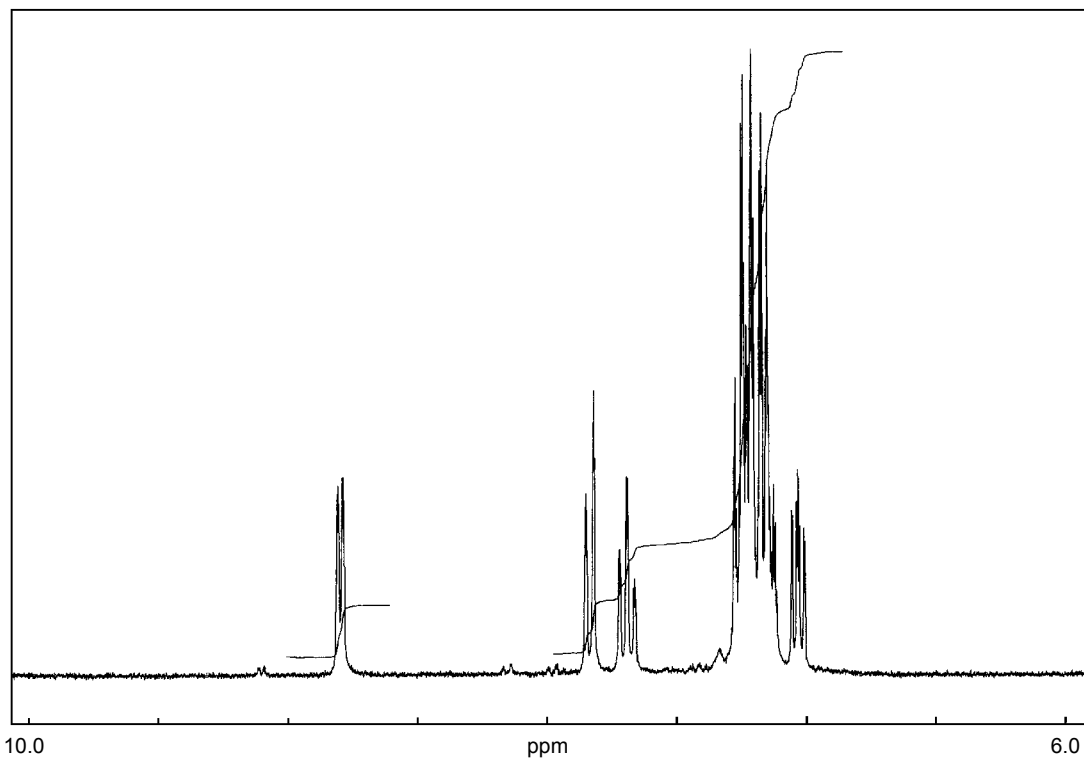


Figure 3.3 The ^1H NMR spectrum of $[\text{Mo}(\text{CO})_3(\text{PPh}_3)(\text{bpy})]$ in CD_2Cl_2 .

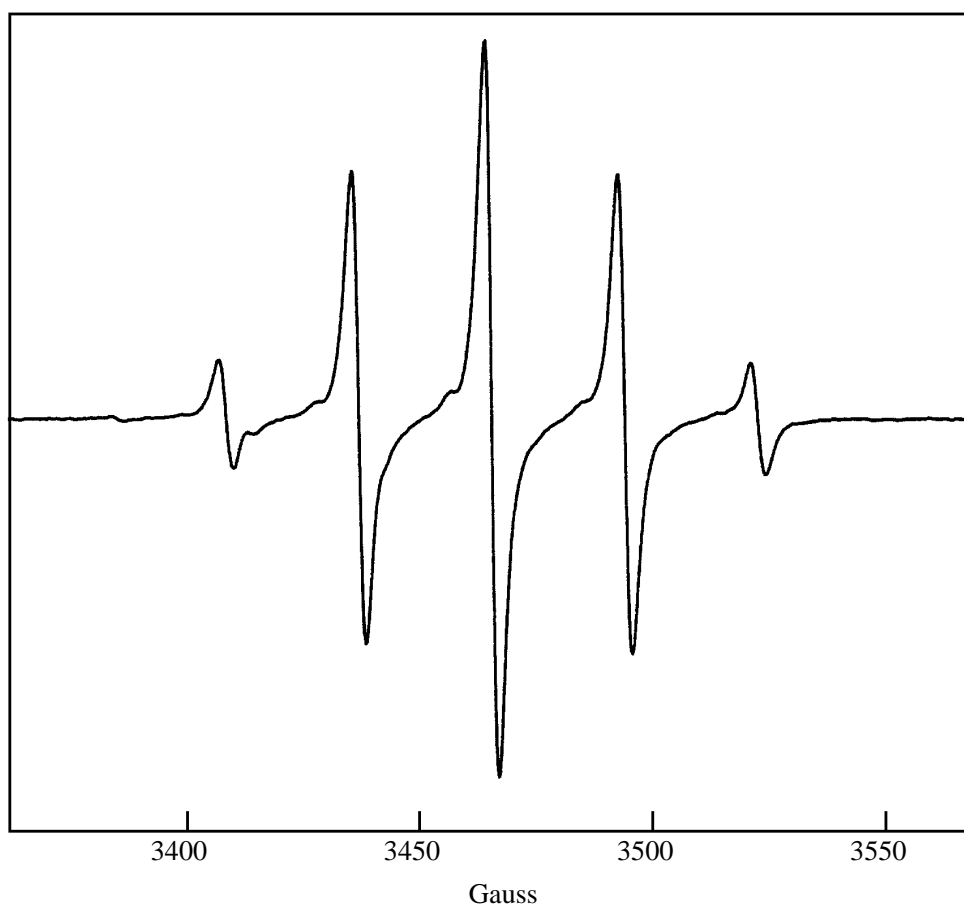


Figure 3.4 The ESR spectrum of $\text{trans-}[\text{Cr}(\text{CO})_2(\text{dppe})_2]^+$ in DCM.

SAFETY INFORMATION SHEET

3. THE SYNTHESIS & SPECTROSCOPIC CHARACTERISATION OF METAL CARBONYL COMPLEXES

This information must be read before the experiment is attempted. You are required to sign the declaration at the bottom of the page and have this countersigned by a Demonstrator before commencing the practical. Do not sign this form until you are satisfied that you appreciate the risks associated with all aspects of the experiment.

2,2'- Bipyridine	TOXIC, IRRITANT	
Chromium complex	TOXIC	
Cyclohexane	FLAMMABLE	Put residues in waste solvents. Avoid flames.
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Molybdenum hexacarbonyl	TOXIC	
Triphenyl phosphine	IRRITANT	
Toluene	FLAMMABLE, HARMFUL	Put residues in waste solvents. Keep away from flames.

I have read the risk assessment and will comply with these procedures.

Name (Please print)	Group	Date
Signature	Demonstrator's Signature	

CAREFULLY TEAR THIS SHEET FROM YOUR LABORATORY MANUAL AND HAND IT TO A DEMONSTRATOR

