

PHYSICO-CHEMICAL STUDIES ON
ORGANO-TRANSITION METAL COMPLEXES

by
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ABSTRACT

After a short preface, in which the object of the work reported in this dissertation is explained, the chemistry of bis- π -cyclopentadienyl compounds of transition metals, other than pure metallocenes, is briefly reviewed.

The preparations of the new pseudo-halide complexes, $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{N}_3)_2$, ($\text{M} = \text{Mo}, \text{W}$), $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OR})\text{CN}$, ($\text{R} = \text{C}_2\text{H}_5, \text{CH}_3$), $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)(\text{CN})\text{H}]\text{PF}_6$, $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{NCS})_2$, ($\text{M} = \text{Mo}, \text{W}$), a complex of proposed formula, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})(\text{SCN})$ and $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})\text{Cl}$ are reported and these have been characterised by analysis and various physical measurements. Other reactions and attempts to form related complexes are also discussed. The cyano-complex $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}$ is hygroscopic and this has been shown by the use of infra-red spectroscopy and deuterium oxide. The bonding of the thiocyanato complexes is discussed in the light of infra-red spectra, ultra-violet spectra and other data and the evidence suggests that all the complexes except one, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})(\text{SCN})$, contain only N-bonded thiocyanate groups. The products of oxidation by nitric of all complexes have been investigated and a paramagnetic salt, $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})\text{Cl}]\text{PF}_6$, has been characterised. Other paramagnetic products were either, not stable enough or, obtained pure enough for complete characterisation but their nature is discussed. The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{MCl}_2$, ($\text{M} = \text{Mo}, \text{W}$), with cyanates gave hygroscopic products having the formula, $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{OCONH}_2)_2$, formed by hydrolysis of cyanate. However a hygroscopic cyanato complex, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCN})_2 \cdot \sim 1\text{H}_2\text{O}$ is also reported.

The novel pentafluorophenyl hydrido complexes, $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MH}(\text{C}_6\text{F}_5)$, ($\text{M} = \text{Mo}, \text{W}$), are described. Both complexes have been characterised by analysis, proton magnetic resonance spectra, mass spectra, molecular weight measurements and infra-red spectra. The fluorine magnetic resonance spectra of the molybdenum complex is also reported. The results indicate the presence of a sterically hindered pentafluorophenyl group, attached to the metal, which has non equivalent orthofluorine atoms and one of these fluorine atoms interacts with the metal hydrogen causing a splitting of the metal hydride nuclear resonance signal. Both complexes react with carbon tetrachloride to give the complexes

$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MCl}(\text{C}_6\text{F}_5)$ and these complexes oxidise to give cations that can be isolated as the salts, $[(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MCl}(\text{C}_6\text{F}_5)]\text{PF}_6$. These salts in solution, at room temperature, have well resolved electron spin resonance spectra showing ligand and metal hyperfine splitting. A related bromo-complex $[(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WBr}(\text{C}_6\text{F}_5)]\text{PF}_6$ is mentioned and its electron spin resonance spectrum reported.

The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{MCl}_2$, ($\text{M} = \text{Mo}, \text{W}$), with LiC_6H_5 gave unstable products that are discussed in the light of analytical, mass spectral, proton magnetic resonance and infra-red spectral results.

The new complexes $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{NHC}_6\text{H}_4\text{Y})$, ($\text{M} = \text{Mo}, \text{W}$, $\text{Y} = \text{S}$; $\text{M} = \text{Mo}$, $\text{Y} = \text{O}$), $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_{14}\text{H}_8)$, $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{O}_2\text{C}_5\text{H}_7)\text{Cl}\cdot\text{H}_2\text{O}$, $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{O}_2\text{C}_5\text{H}_7)]\text{BF}_4$, and $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{OCOR})_2$, ($\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{CF}_3, \text{C}_6\text{H}_5$), have been prepared and characterised by analysis and physical techniques. Chemical reactions of some of these complexes are discussed and, in particular, the reactions of iodine and nitric acid.

The reaction of alkyl halides with sulphur ligand complexes of tungsten and molybdenum are reported. The complexes $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{RX}$, ($\text{R} = \text{CH}_2\text{C}_6\text{H}_5$, $\text{X} = \text{Cl}, \text{PF}_6$; $\text{R} = \text{CH}_2\text{CHCH}_2$, $\text{X} = \text{Br}, \text{PF}_6$; and $\text{R} = \text{CH}_3$, $\text{X} = \text{I}, \text{PF}_6$), and a related complex $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{HgCl}_2$ have been prepared. The complex $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_6\text{H}_5)_2$ was shown to give $(\pi\text{-C}_5\text{H}_5)_2\text{MoI}_2$ by reaction with CH_3I but, in a similar reaction, $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SCH}_3)_2$ gave the new complex, $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}(\text{CH}_3)_2)\text{I}]\text{I}$. The related salt, $[(\pi\text{-C}_5\text{H}_5)_2\text{MoS}(\text{CH}_3)_2\text{Br}]\text{PF}_6$, reacted with LiCl to give $(\pi\text{-C}_5\text{H}_5)_2\text{MoClBr}$ and this, on oxidation gave the salt $[(\pi\text{-C}_5\text{H}_5)_2\text{MoClBr}]\text{PF}_6$ as the major product.

Oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ by nitric acid gave the paramagnetic complex $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)]\text{PF}_6$, which was characterised, and related oxidation products of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ and $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ are discussed.

Electron spin resonance spectra, in solution, of the isolable paramagnetic compounds mentioned above, mixed halide complexes formed by exchange in strong acids and unstable species formed by electrolytic oxidation are reported. The trends in the isotropic $\langle g \rangle$ and a parameters are discussed in a general manner. Frozen solution spectra of some complexes are also recorded.

The work reported in this thesis was carried out in the Inorganic Chemistry Laboratory, South Parks Road, Oxford, during the tenure of an S.R.C. Research Studentship from October 1966 to December 1968, under the supervision of Dr. M.L.H. Green. All the work is my own unless stated to the contrary, and it has not been submitted for any degree in this or any other University.

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Preface

The compounds $(\pi\text{-C}_5\text{H}_5)_2\text{MH}_2$ ($\text{M} = \text{Mo}, \text{W}$) were prepared by Green et al. (A1). These compounds were shown by Cooper and Green (A2) to be readily convertible into the species $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$ ($\text{X} = \text{Cl}, \text{Br}$). The latter cations gave electron spin resonance (E.S.R.) spectra in solution.

It was, therefore, decided to vary the ligand X in $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2$ and also to form, if possible, cations of the type $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$ so that a series of complexes could be obtained which might give E.S.R. spectra. The preparation of such compounds would also be of interest since the chemistry of W and Mo in intermediate oxidation states is not well known and the bis- π -cyclopentadienyl system appears to stabilise such states.

Such a project was carried out for one year by the author as a Part II project in which several interesting sulphur and oxygen species were obtained (A3) but no E.S.R. spectra of interest. This thesis describes a continuation of this work in which many more new compounds are characterised and also E.S.R. spectra are recorded and discussed.

Chapter I

INTRODUCTION

Bis- π -cyclopentadienyl compounds $(\pi\text{-C}_5\text{H}_5)_2\text{M}$ are known for all first row transition metals and for some of the second and third row transition elements, namely, Zr, Ru, Rh, Os, Ir and Pt (dimeric in some cases) (A4). It is of interest that, although $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}$ has not been prepared, a compound $(\pi\text{-(C}_6\text{H}_5)_5\text{C}_5)_2\text{Mo}$ has been reported (A5).

However in this survey, only the chemistry of bis- π -cyclopentadienyl compounds with other ligands directly attached to the metal will be discussed. These fall into four general classes: A) halides and pseudo-halide derivatives, B) hydride, hydrocarbon and fluorocarbon derivatives, C) compounds with other organic ligands, D) miscellaneous complexes with inorganic ligands.

A. Halides, pseudo-halides and related oxy derivatives

The bis- π -cyclopentadienyl transition metal halides prepared up to 1965 have been well reviewed by Cooper (A6). Cooper also gives details of methods of preparation which can also be found in a review (A7).

The known compounds are listed in Table 1 (other complexes, e.g. $(\pi\text{-C}_5\text{H}_5)_2\text{M}^+\text{X}^-$ (M = Co, Rh), being basically ionic, are omitted). The new halides made since Cooper's review are of the less common elements, Zr, Hf and Nb. The chief methods of preparation involve the reaction of $\text{C}_5\text{H}_5\text{Na}$, $\text{C}_5\text{H}_5\text{MgX}$ or $\text{C}_5\text{H}_5\text{Li}$ with metal halides (e.g. A8); the reaction of halogenated solvents (e.g. A2, A31) or free halogens (e.g. A2) on metal hydrides or metallocenes; the reduction of higher bis- π -cyclopentadienyl halides to lower halides (e.g. A13) or the exchange of halogen (e.g. A8). The halides

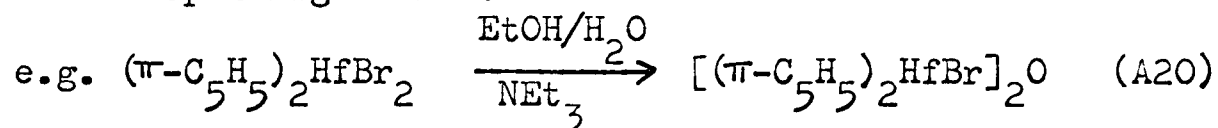
are generally thermally stable and most melt or decompose in the range 200-300°C.

The readiness of the halides to undergo hydrolysis varies. Group IVA metals are hydrolysed by water but are fairly stable to hydrolysis by atmospheric moisture. Niobium and tantalum halides are readily hydrolysed and must be handled in a dry atmosphere. Molybdenum and tungsten halides are not readily hydrolysed and are insoluble in cold water.

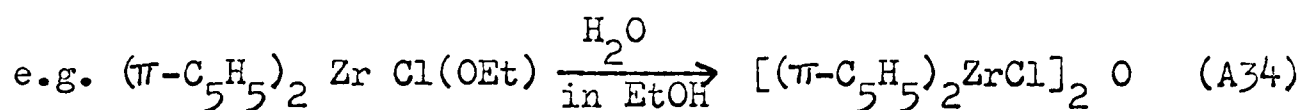
The monohalides of titanium and vanadium are oxidised by air but other species are all fairly stable to oxidation.

The dihalides, $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2$ (M = Ti, Zr, Mo, W), have been the usual precursors in the preparation of the compounds listed in Tables 2, 3 and 4.

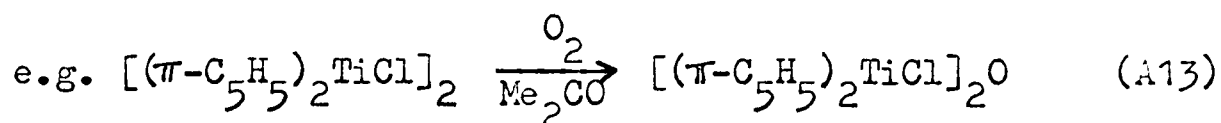
Oxy- or hydroxy-halogeno compounds have usually been made by hydrolysis of the corresponding halide.



or by hydrolysis of similar complexes:



Oxidation of lower halides has also given oxy species:

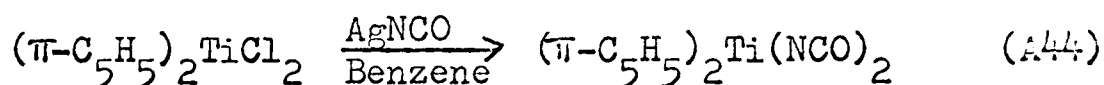
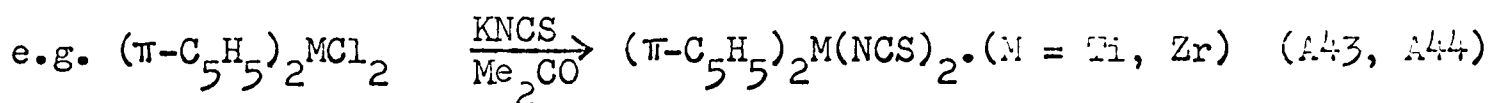


Further oxy bridging of the bis- π -cyclopentadienyl system can give rise to titanoxane polymers.

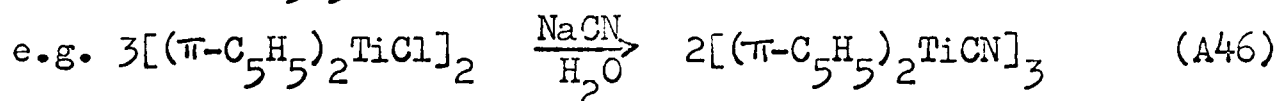
The hydroxy species $(\pi\text{-C}_5\text{H}_5)_2\text{TiBr(OH)}$, $(\pi\text{-C}_5\text{H}_5)_2\text{ZrBr(OH)} \cdot 2\text{H}_2\text{O}$, and $(\pi\text{-C}_5\text{H}_5)_2\text{ZrI(OH)} \cdot 3\text{H}_2\text{O}$ have been obtained from aqueous solutions of the

respective cations, $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{OH})^+$. The Zr monomers form the dimeric oxy species when recovered from acetone solution. The niobium hydroxy complexes, $(\pi\text{-C}_5\text{H}_5)_2\text{Nb}(\text{OH})\text{X}_2$, are the usual products obtained from the reaction of $\text{C}_5\text{H}_5\text{Na}$ and NbCl_5 unless care is taken to prevent hydrolysis of $(\pi\text{-C}_5\text{H}_5)_2\text{NbX}_3$.

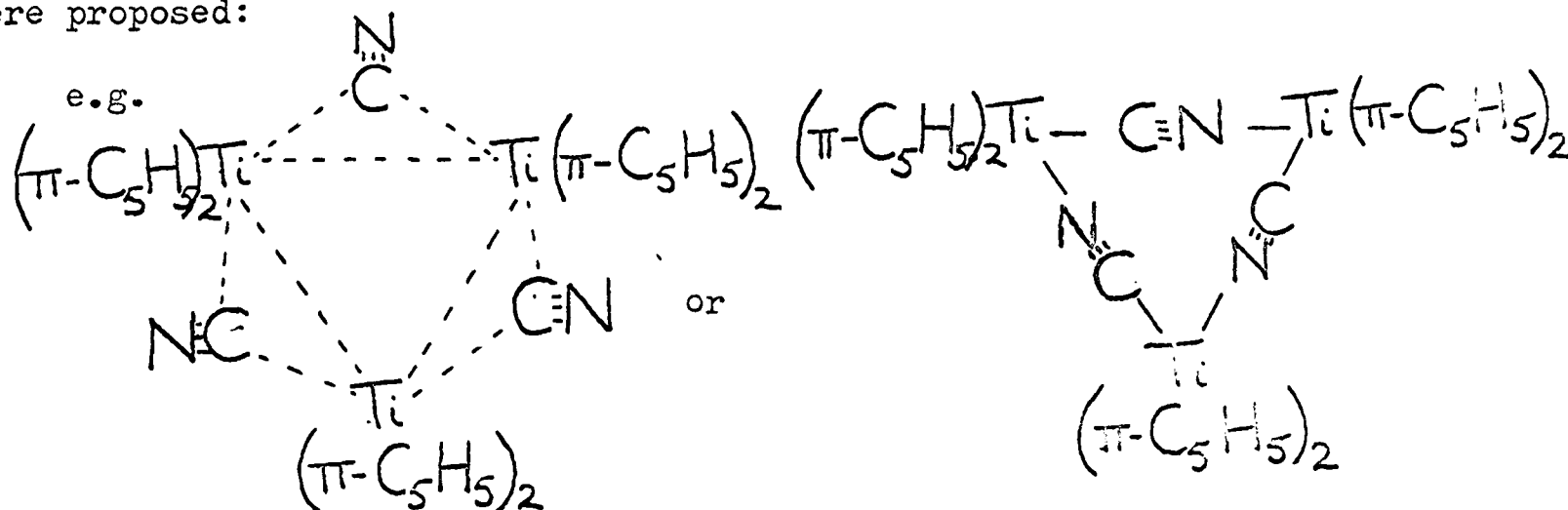
Pseudo halide complexes have been reported for Ti and Zr. They have all been prepared by nucleophilic displacement of halide ligands by pseudo-halide ligands.



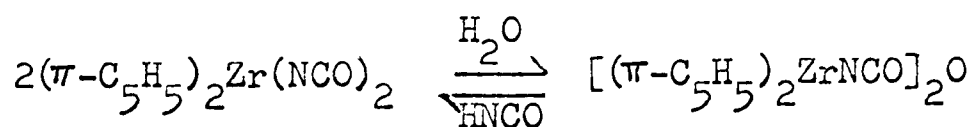
The mono pseudo-halide derivatives of Ti have been prepared from aqueous solutions of $[(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}]_2$



The mono pseudo-halide derivatives with CN or NCS ligands were postulated to be trimeric on the basis of magnetic studies and bridged structures were proposed:

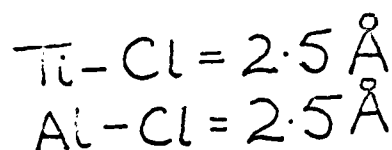
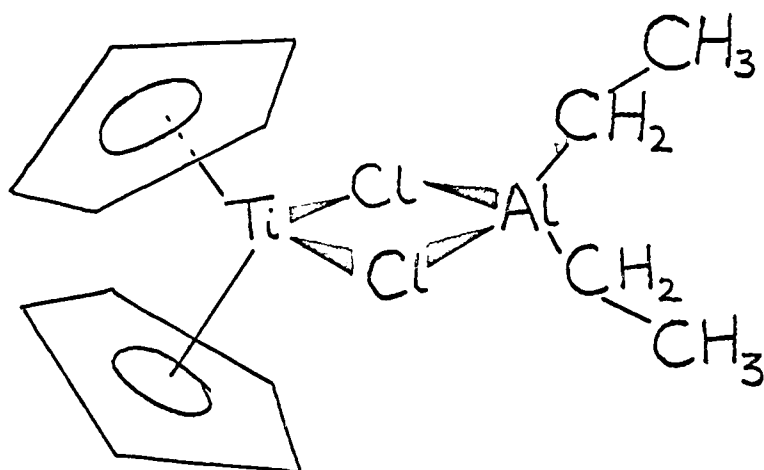


The cyanato complex of Zr is readily hydrolysed to give the oxy-dimer (A44):



Infra-red evidence for the NCS and NCSe compounds of Ti and Zr indicate N-bonding to the metal (A44, A45). N-bonding was also proposed for $(\pi\text{-C}_5\text{H}_5)_2\text{M(NCO)}_2$ (A44).

Ziegler catalysts for the polymerisation of olefins, especially ethylene, include the system $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2/\text{AlR}_3$. Complexes obtained from the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ with aluminium ethyls include $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2\text{Al}(\text{C}_2\text{H}_5)_2$ for which the structure has been determined by X-ray diffraction (A143).



Solutions of this complex and similar complexes will polymerise olefins. E.S.R. spectra of such complexes in solution have been studied (A40, A41).

The structure of $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ has been determined by electron diffraction (A10).

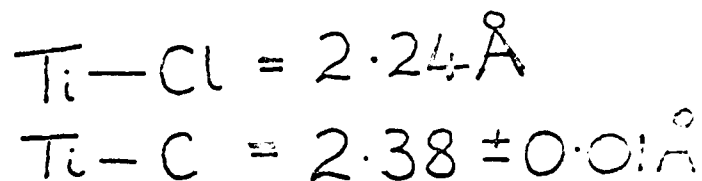
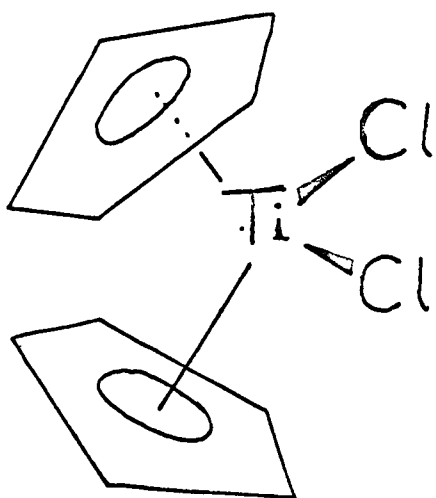


Table 1

BIS- π -CYCLOPENTADIENYL HALIDE, PSEUDO-HALIDE AND RELATED OXY COMPLEXES OF TRANSITION METALS

Compound	Colour	Melting or decomp. point °C	Reference	Comments
$(\pi-C_5H_5)_2TiF_2$	yellow	d > 250	A8, A9	Electron diff. structure A10
$(\pi-C_5H_5)_2TiCl_2$	red	289d	A8, A11	
$(\pi-C_5H_5)_2TiBr_2$	red	309-310d	A8, A11	
$(\pi-C_5H_5)_2TiI_2$	purple	317-318d	A8, A11	
$[(\pi-C_5H_5)_2TiCl]_2$	green/violet brown	279-282d	A12, A13, A14	Magnetic susceptibility at variable temp. A15. ESR A142.
$[(\pi-C_5H_5)_2TiBr]_2$	brown-red	250-260d	A12	
$(\pi-C_5H_5)_2TiI$	black-brown	290	A12	
$(\pi-C_5H_5)_2ZrCl_2$	colourless	248	A16, A17	
$(\pi-C_5H_5)_2ZrBr_2$	colourless	260d	A8, A17	
$(\pi-C_5H_5)_2ZrI_2$	yellow	300	A17, A18	
$(\pi-C_5H_5)_2HfCl_2$	colourless	236	A19, A37	
$(\pi-C_5H_5)_2HfBr_2$		266.5-268.5	A20	
$(\pi-C_5H_5)_2VCl_2$	pale green	d250	A8	E.S.R. A21 more stable in solution
$(\pi-C_5H_5)_2VBr_2$	dark green	d in solid state	A8	
$(\pi-C_5H_5)_2VCl$	blue	206-207	A22, A23, A24	

Table 1 - continued

Compound	Colour	Melting or decomp. point °C	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{VBr}$	dark blue	221-222	A23	
$(\pi\text{-C}_5\text{H}_5)_2\text{VI}$	dark green	214-215	A23	
$(\pi\text{-C}_5\text{H}_5)_2\text{NbCl}_3$			A25	
$(\pi\text{-C}_5\text{H}_5)_2\text{NbBr}_3$	red-brown	d260	A8	
$(\pi\text{-C}_5\text{H}_5)_2\text{NbI}_3$	violet	> 300	A26	
$(\pi\text{-C}_5\text{H}_5)_2\text{NbI}_2\text{Cl}$	dark red	145	A27	
$(\pi\text{-C}_5\text{H}_5)_2\text{NbI}_2$	black	155d	A26	paramagnetic
$(\pi\text{-C}_5\text{H}_5)_2\text{TaCl}_3$			A28	little data given
$(\pi\text{-C}_5\text{H}_5)_2\text{TaBr}_3$	rust	280d	A8	very easily hydrolysed
$(\pi\text{-C}_5\text{H}_5)_2\text{CrBr}$	dark blue	> 285	A29, A30	
$(\pi\text{-C}_5\text{H}_5)_2\text{CrI}$	yellow	d150	A31	
$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^+$	brown	d150 (as PF_6^-)	A32, A2	basically ionic $\rightarrow (\pi\text{-C}_5\text{H}_5)_2\text{Cr}^+$
$(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2^+$	purple	d150 "	A2	obtained as salts of PF_6^- , PtCl_6^{2-} or bihalide anions.
$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$	green	d270	A32, A2	
$(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2$	dark green	d250	A2	
$(\pi\text{-C}_5\text{H}_5)_2\text{MoI}_2$	dark green	d230	A2	

Table 1 - continued

Compound	Colour	Melting or decomp. point °C	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$	orange-brown	d150 (as PF_6^-)	A32, A2	obtained as salts of PF_6^- , PtCl_6^{2-} or bihalide anions
$(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2^+$	brown	d150 "	A2	
$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$	green	d250	A2	ionic $\rightarrow (\pi\text{-C}_5\text{H}_5)\text{ReCl}_2^+$
$(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2$	green	d250	A2	
$(\pi\text{-C}_5\text{H}_5)_2\text{WI}_2$	green	d250	A2	
$(\pi\text{-C}_5\text{H}_5)_2\text{ReCl}_3$	maroon	d150	A2	
$(\pi\text{-C}_5\text{H}_5)_2\text{ReBr}_3$	maroon	d150	A2	several related polymeric species (A13)
$(\pi\text{-C}_5\text{H}_5)_2\text{ReI}_3$	green	d150	A2	
$[(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}]_2\text{O}$	orange	240d	A13, A33	
$[(\pi\text{-C}_5\text{H}_5)_2\text{TiBr}]_2\text{O}$	orange-red	240d	A18, A33	
$[(\pi\text{-C}_5\text{H}_5)_2\text{TiI}]_2\text{O}$	red		A18	
$(\pi\text{-C}_5\text{H}_5)_2\text{TiBr(OH)} \cdot \text{H}_2\text{O}$	orange		A8	
$[(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}]_2\text{O}$		270-280	A34, A35	
$[(\pi\text{-C}_5\text{H}_5)_2\text{ZrBr}]_2\text{O}$			A35, A18	
$(\pi\text{-C}_5\text{H}_5)_2\text{ZrBr(OH)} \cdot 2\text{H}_2\text{O}$	colourless		A18	
$(\pi\text{-C}_5\text{H}_5)_2\text{ZrI(OH)} \cdot 3\text{H}_2\text{O}$	colourless		A18	

Table 1 - continued

Compound	Colour	Melting or decomp. point °C	Reference	Comments
$(\pi-C_5H_5)_2Zr(OH)_2$	white	d250	A36	
$[(\pi-C_5H_5)_2HfCl]_2O$		265-269d	A18, A37	
$[(\pi-C_5H_5)_2HfBr]_2O$		267-282	A20	
$(\pi-C_5H_5)_2NbCl_2(OH)$	yellow		A25, A27	Other species, $(\pi-C_5H_5)_2NbCl_x$ (OH) _y , reported (A25)
$(\pi-C_5H_5)_2NbBr_2(OH)$	orange-red		A8	
$(\pi-C_5H_5)_2NbOCl$	white	192	A27	
$(\pi-C_5H_5)_2TiCl_2Al(C_2H_5)_2$	blue	126-130	A38, A39	E.S.R. A40, A41
$(\pi-C_5H_5)_2TiCl_2Al(C_2H_5)Cl$	blue	88-92	A38, A39	Similar species known. X-ray structure A143
$(\pi-C_5H_5)_2Ti(N_3)_2$	orange-red	ready decomp.	A42	
$(\pi-C_5H_5)_2Ti(NCS)_2$	red/purple	303-307d	A18, A42, A43 A44	
$(\pi-C_5H_5)_2Ti(NCO)_2$	orange-red		A18, A44	sublimes $160^\circ C/10^{-4}$ mm Hg
$(\pi-C_5H_5)_2Ti(NCSe)_2$	moss green	d140	A45	N-bonded
$[(\pi-C_5H_5)_2TiCN]_3$	purple	d	A46	mass spectrum shows tri- meric formula
$(\pi-C_5H_5)_2TiN_3$	yellow	explodes	A46	unstable, not characterised
$[(\pi-C_5H_5)_2TiNCS]_3$	red-brown	210	A46	
$(\pi-C_5H_5)_2TiNCO$		d	A46	

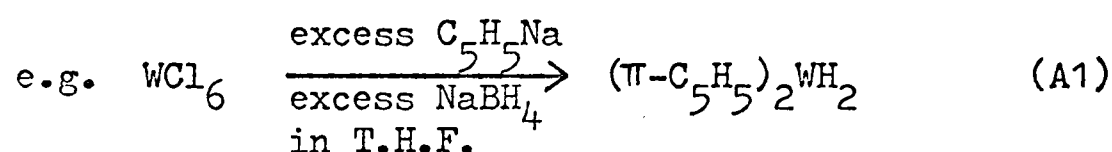
Table 1 -- continued

Compound	Colour	Melting or decomp. point °C	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{NCS})_2$	yellow	260	A18, A44	sublimes $175^\circ/10^{-4}$ mm Hg
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{NCO})_2$	colourless		A44	
$[(\pi\text{-C}_5\text{H}_5)_2\text{TiNCS}]_2\text{O}$	orange	235-238d	A43	
$[(\pi\text{-C}_5\text{H}_5)_2\text{ZrNCO}]_2\text{O}$	colourless		A18, A44	

B. Bis- π -cyclopentadienyl hydrido, hydrocarbon and fluorocarbon complexes

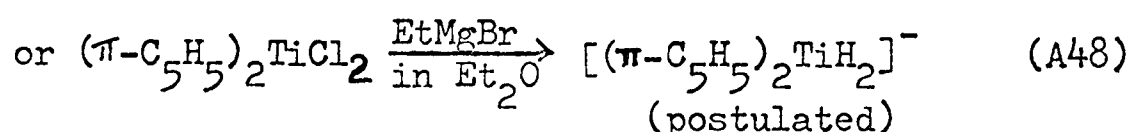
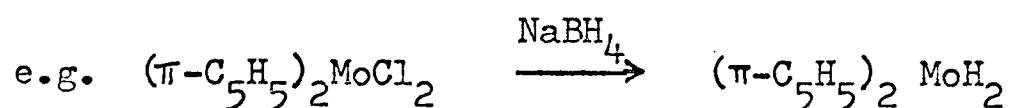
The known complexes are listed in Table 2. Hydride complexes have been the subject of several reviews (A145, A146).

The main method of preparation of bis- π -cyclopentadienyl complexes has been the reaction of C_5H_5Na with metal halides in the presence of a reducing agent, e.g. $NaBH_4$.

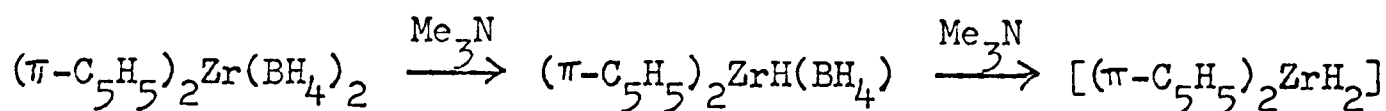


Other methods of preparation include:

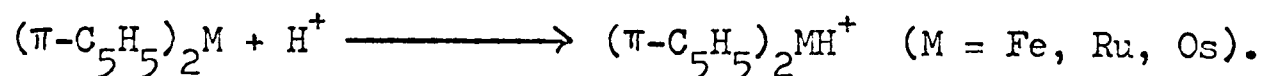
i) reduction of bis- π -cyclopentadienyl halides:



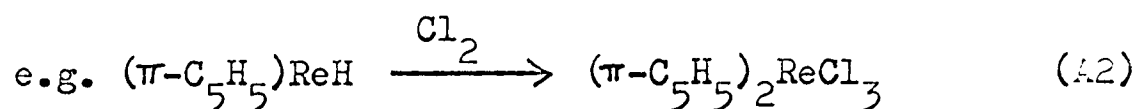
ii) the reaction of base on borohydride derivatives (A50):



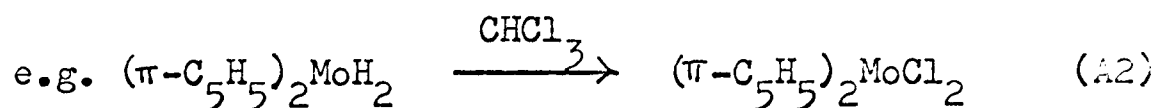
iii) protonation of metallocenes in strong acid media (A56):



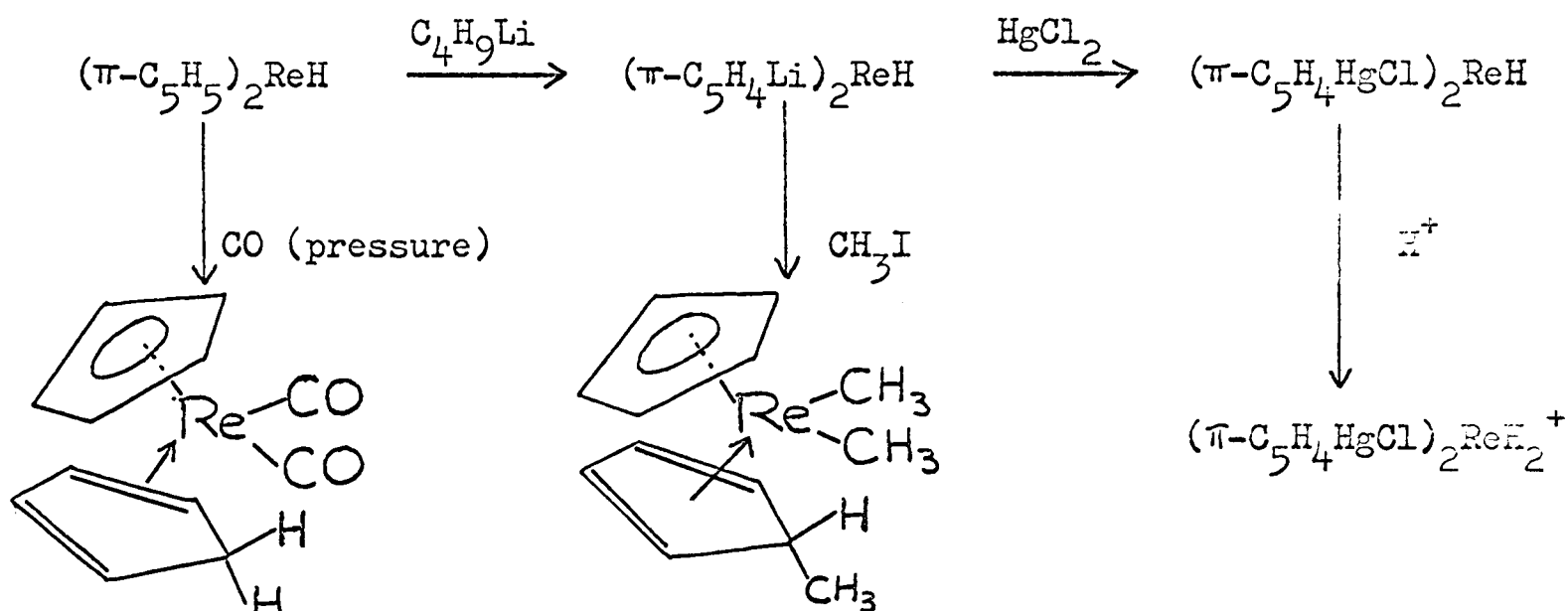
The hydrides are air sensitive compounds. The well characterised, sublimable, neutral hydrides of Re, Mo and W react with free halogens to give halogeno derivatives:



The hydrides of Mo and W also react with halogenated solvents:

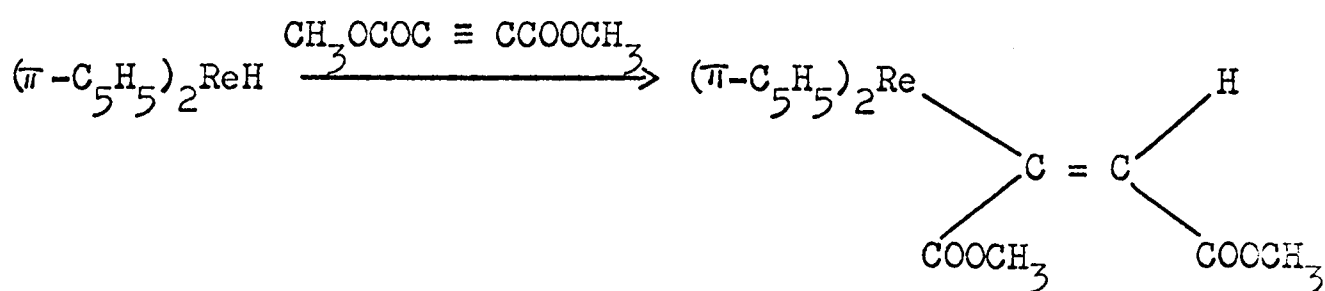


The hydrides of Re and W undergo ring attack by $n\text{-C}_4\text{H}_9\text{Li}$ to give 1,1'-dilithiated species (A147). The lithium derivative of Re shows the following reactions:



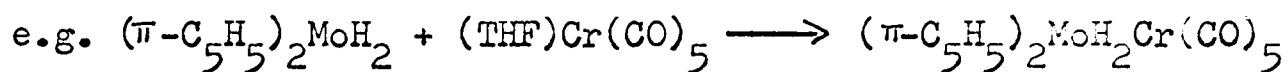
The structure of the product formed by reaction of CH_3I with the dilithiated species has been determined by X-ray analysis (A148). Carbon monoxide on the hydride gives an olefin complex as shown.

The Re-H bond will react with some acetylenes to give a cis addition product which may then be isomerised to the trans product if dimethyl acetylene dicarboxylic acid is used.



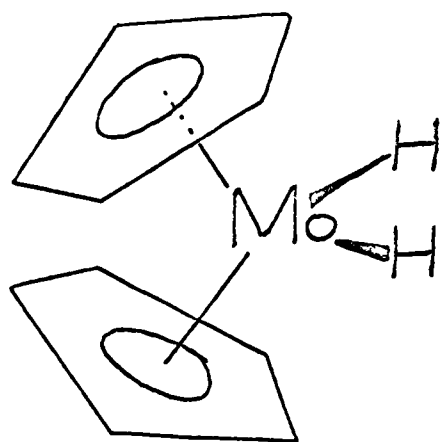
The neutral hydrides of Mo, W and Re are basic and accept protons in

acidic media to give the hydride cations shown in Table 2. They also form addition complexes with BF_3 (A149), group III B alkyls (150) and recently the Mo and W hydrides have been shown to form metal-metal bonds with $\text{M}(\text{CO})_5$ species ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) (151).



The tantalum hydride, $(\pi\text{-C}_5\text{H}_5)_2\text{TaH}_3$ does not show basic properties.

The structure of $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ has been determined by X-ray diffraction (A140) and although the metal-hydrogens cannot be located, as first claimed, (A141) the basic structure is as shown:



$$\text{Av. C-C} = 1.42 \text{ \AA}$$

Theoretical calculations (A152) suggest that for wedge shaped molecules, like the above, with ring-metal-ring angles 135° - 180° , six hybridised metal orbitals are involved in ring bonding and three metal orbitals, pointing away from the rings, are available for ligand bonding. These three orbitals are fully occupied in $(\pi\text{-C}_5\text{H}_5)_2\text{TaH}_3$ but $(\pi\text{-C}_5\text{H}_5)\text{MH}_2$ ($\text{M} = \text{Mo}, \text{W}$) and $(\pi\text{-C}_5\text{H}_5)\text{ReH}$ have lone pairs and this explains the donor properties of the latter three compounds.

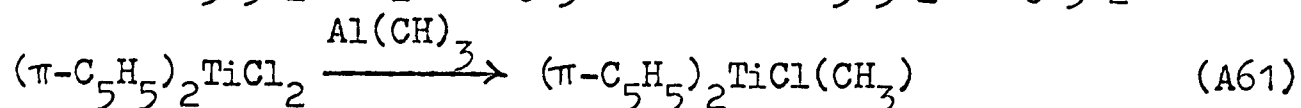
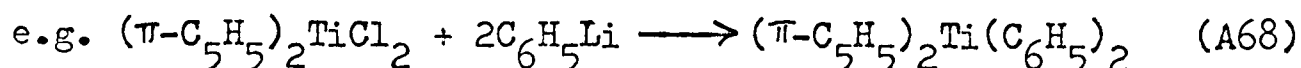
The hydride anion of probable formula $[(\pi\text{-C}_5\text{H}_5)_2\text{TiH}_2]^-$ (or a bridged species) was postulated as an intermediate in nitrogen fixation by the system

$(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2/\text{C}_2\text{H}_5\text{MgBr}$ (A47, A153) but the mechanism proposed has since been rejected (A48).

Borohydride derivatives are known, as listed, and these are prepared from LiBH_4 on bis- π -cyclopentadienyl compounds



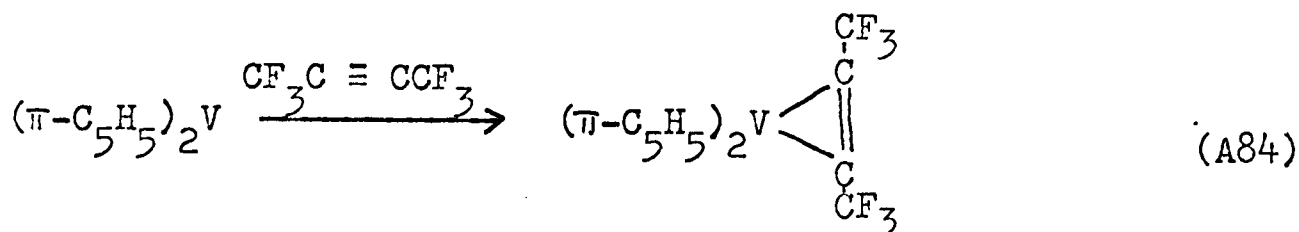
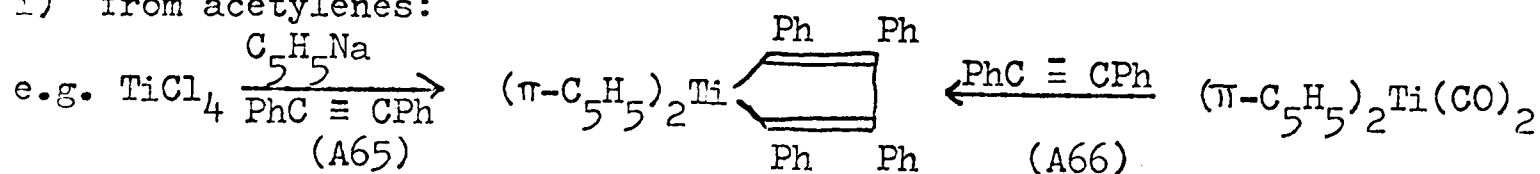
Alkyl, aryl and fluorocarbon complexes are also shown in Table 2. These are generally prepared by the action of RLi , RMgX or R_3Al on the related halogeno complexes



It is to be noted that, while $\text{C}_6\text{F}_5\text{Li}$ gave the bis-pentafluorophenyl complex with $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$, $\text{C}_6\text{F}_5\text{MgBr}$ reacted to give $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{F}_5)\text{Cl}$.

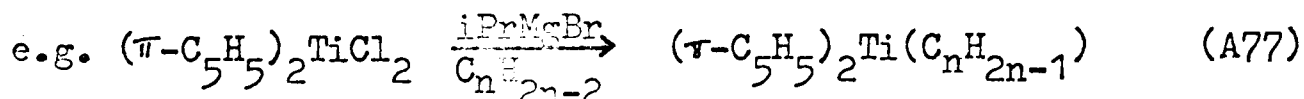
Other methods of preparation include:

i) from acetylenes:

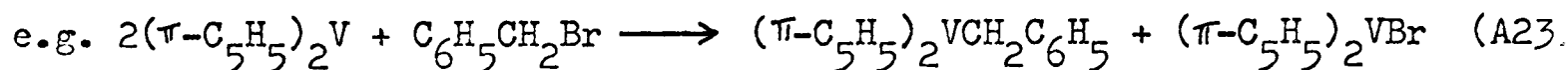


(The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{ReH}$ with acetylenes has been mentioned above.)

ii) from conjugated dienes to give π -allyl complexes:



iii) from alkyl halides:



iv) Tetracyclopentadienyl derivatives have been made for Ti (?), Zr, Hf, Nb, Ta and Mo using $\text{C}_5\text{H}_5\text{Na}$ either on the binary metal halide (e.g. TaCl_5 , NbCl_5 or MoCl_5) or on the bis- π -cyclopentadienyl metal halide (e.g. $(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$). Proton magnetic resonance ($^1\text{H.M.R.}$) indicates that all cyclopentadienyl protons are equivalent in the compounds of Zr and Hf even at low temperatures whereas the $^1\text{H.M.R.}$ spectra of the Nb and Ta compounds (with other evidence) indicate two π - and two σ -bonded cyclopentadienyl rings. The $^1\text{H.M.R.}$ spectrum of the Mo compound indicates one π - and three σ -bonded cyclopentadienyl rings.

In general it is found that the order of stability of complexes is $\text{alkyl} < \text{aryl} < \text{perfluoro-carbon complex}$.

The decomposition of $(\pi\text{-C}_5\text{H}_5)_2\text{TiR}_2$ ($\text{R} = \text{C}_6\text{H}_5$ or CH_3) has been studied under various conditions; both thermally decompose and alkyl radical formation is postulated while $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ is formed which then reacts further with solvents (A62, A63, A70). $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{F}_5)_2$ decomposes thermally with fluorine migration to give $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{F}_5)\text{F}$ (A90).

Table 2

BIS- π -CYCLOPENTADIENYL, HYDRIDO, HYDROCARBON AND FLUOROCARBON COMPLEXES OF TRANSITION METALS

Compound	Colour	Melting or decomp. point	Reference	Comments
$[(\pi-C_5H_5)_2TiH_2]^-$ or $[(\pi-C_5H_5)_2TiH]_2^-$			A47, A48, A49	E.S.R. in solution only
$[(\pi-C_5H_5)_2ZrH_2]^n$	white		A50, A51	H-bridging in polymer
$(\pi-C_5H_5)_2ZrH(BH_4)$	white		A50, A51	low field χ_{ZrH} postulated
$(\pi-C_5H_5)_2TaH_3$	white	187-189d	A1	$\chi_{TaH} = 11.63, 13.02$
$(\pi-C_5H_5)_2MoH_2$	yellow	183-185d	A1, A52	$\chi_{MoH} = 18.76$ X-ray structure A140, A141
$(\pi-C_5H_5)_2MoH_3^+$	light yellow solution		A1, A52	$\chi_{MoH} = 16.08$
$(\pi-C_5H_5)_2WH_2$	yellow	163-165	A1, A52	$\chi_{WH} = 22.3$
$(\pi-C_5H_5)_2WH_3^+$	golden yellow solution	$d > 185$	A1, A52	$\chi_{WH} \sim 16.3$
$(\pi-C_5H_5)_2TcH$	golden yellow	150	A53	$\chi_{TcH} = 17.8$
$(\pi-C_5H_5)_2TcH_2^+$	white salts		A53	$\chi_{TcH} = 19.7$
$(\pi-C_5H_5)_2ReH$	pale yellow	161-162	A54, A55	$\chi_{ReH} \sim 23$
$(\pi-C_5H_5)_2ReH_2^+$	white salts		A54, A55	$\chi_{ReH} = 24.6$
$(\pi-C_5H_5)_2FeH^+$	yellow salts		A56	$\chi_{FeH} = 12.1$
$(\pi-C_5H_5)_2RuH^+$	yellow		A56	solution $\chi_{RuH} = 17.2$

Table 2 .. continued

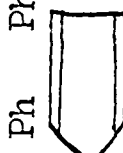
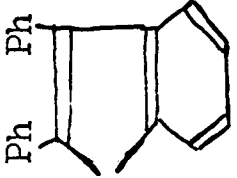
Compound	Colour	Melting or decomp. point	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{OsH}^+$	yellow		A56	solution only
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{BH}_4)$	black-violet		A57	
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{BH}_4)_2$	white	155d	A58	$(\pi\text{-C}_5\text{H}_5)_2\text{Hf}(\text{BH}_4)_2$ (A51)
$(\pi\text{-C}_5\text{H}_5)_2\text{Nb}(\text{BH}_4)\text{Cl}$	red-violet		A59	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$	orange	d > 100	A60, A61	Thermal decomp. studied A62, A63
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}\equiv\text{CC}_6\text{H}_5)_2$	orange	141	A64	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ 	green	150	A65, A66	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ 	dark green	227-228	A67	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$	yellow	146-148	A68	Decomposition studied A69, A70 A62
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{Ar})_2$	maroon	137-139	A68, A71	Ar = p-(CH ₃) ₂ NC ₆ H ₄
	orange yellow	133-134	A68, A71	Ar = p-CH ₃ C ₆ H ₄
	orange yellow	137-139	A68, A71	Ar = m-CH ₃ C ₆ H ₄

Table 2 - continued

Compound	Colour	Melting or decomp. point	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{Ar})_2$	orange	142-143	A71	Ar = $\text{p-CF}_3\text{C}_6\text{H}_4$ Several other less well characterised aryl compounds known & N.M.R. studied A71
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_2\text{Al}(\text{CH}_3)\text{Cl})_2$	dark red		A137	similar complexes reported
$(\pi\text{-C}_5\text{H}_5)_4\text{Ti} (?)$	brown		A72	impure
$(\pi\text{-C}_5\text{H}_5)_2\text{TiRCl}$	orange-red	168-170	A61, A73	R = CH_3
		92-94	A138	R = C_2H_5
	orange	d160	A139	R = C_3H_7
$(\pi\text{-C}_5\text{H}_5)_3\text{Ti}$	deep green	~ 130	A74	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\pi\text{-C}_3\text{H}_5)$	purple/violet	118d	A75	Several other substituted alkyls. ESR A77
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\pi\text{-CH}_3\text{C}_3\text{H}_4)$	blue/violet	96.5-97	A76	$-\left[(\pi\text{-C}_5\text{H}_5)_2\text{TiH}_2\right]^-$ intermediate
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti} \left(\begin{array}{c} \text{Ph} \quad \text{Ph} \\ \diagdown \quad \diagup \\ \text{C} \\ \parallel \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \end{array} \right)$	orange/yellow	215-217	A78	
$[(\pi\text{-C}_5\text{H}_5)_2\text{TiR}_2]^-$			A48	postulated from E.S.R. spectra R = Me, Et, Pr.

Table 2. continued

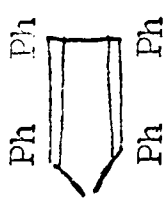
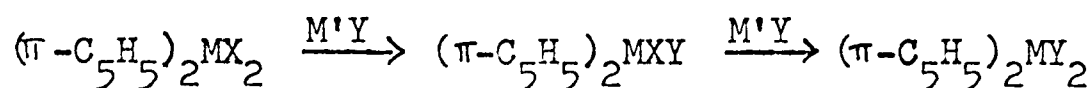
Compound	Colour	Melting or decomp. point	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}$ 	orange	140-170	A79	
$(\text{C}_5\text{H}_5)_4\text{Zr}$			A80	one H resonance in $^1\text{H.M.R.}$
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2\text{Cl}$		d191-193	A87	
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{C}_2\text{H}_5)_2\text{Cl}$	bright yellow	d > 0	A83	
$[(\pi\text{-C}_5\text{H}_5)_2\text{ZrC}_6\text{H}_5]_2\text{O}$		250-260	A35	
$[(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{C}_6\text{H}_4\text{CH}_3)_2]_2\text{O}$		210-224	A35	
$(\text{C}_5\text{H}_5)_4\text{Hf}$		207-208d	A37	one H resonance in $^1\text{H.M.R.}$
$(\pi\text{-C}_5\text{H}_5)_2\text{V} < \begin{array}{c} \text{CR} \\ \parallel \\ \text{CR} \end{array}$	dark green	146-147	A84	R = OCOCH_3
	brown	124-126	A84	R = CF_3
$(\pi\text{-C}_5\text{H}_5)_2\text{VO}=\text{C}(\text{C}_6\text{H}_5)_2$	dark green	159-163	A78	
$(\pi\text{-C}_5\text{H}_5)_2\text{VCH}_3$	grey	d80-100	A23	
$(\pi\text{-C}_5\text{H}_5)_2\text{VCH}_2\text{C}_6\text{H}_5$	blue-black	109	A23	
$(\pi\text{-C}_5\text{H}_5)_2\text{VC}_6\text{H}_5$	black	92	A24	
$(\pi\text{-C}_5\text{H}_5)_2\text{V}(\text{C}_3\text{H}_5)$	brown solution		A75, A85	σ -allyl ?

Table 2 - continued

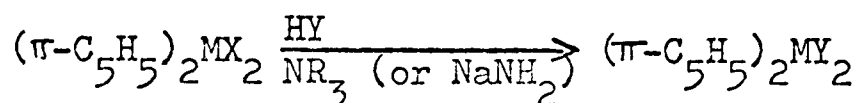
Compound	Colour	Melting or decomp. point	Reference	Comments
$(\pi-C_5H_5)_2Nb(\sigma-C_5H_5)_2$	blue-black	d	A86	H.M.R. evidence for bonding of C_5H_5
$(\pi-C_5H_5)_2Ta(\sigma-C_5H_5)_2$	red-black	d	A86	
$(\pi-C_5H_5)_3Mo(\sigma-C_5H_5)_3$	red-violet	d120	A87	
$(\pi-C_5H_5)_2Mo(NO)CH_3$	brown	d	A88	
$(\pi-C_5H_5)_2Re(CRCICOCCH_3)_3$	dark red	107-108	A89	R = $COOCH_3$ cis
	dark red	151-152	A89	R = $COOCH_3$ trans
	orange brown	161-162	A89	R = H
$(\pi-C_5H_5)_2Ti(C_6F_5)_2$	orange	228-230	A90, A93	
$(\pi-C_5H_5)_2Ti(C_{12}F_8)$		> 230	A91	
$(\pi-C_5H_5)_2Ti(C_6F_5)F$	yellow	d240	A90	
$(\pi-C_5H_5)_2Ti(C_6F_5)Cl$	orange	201-203	A90, A92	
$(\pi-C_5H_5)_2Ti(C_6F_5)OH$	yellow	183-185	A90	
$(\pi-C_5H_5)_2Ti(C_6F_5)OC_2H_5$	yellow	117	A90	
$(\pi-C_5H_5)_2Zr(C_6F_5)_2$	white	219	A36	
$(\pi-C_5H_5)_2Zr(C_6F_5)OH$	white	d > 260	A36	

C. Bis- η -cyclopentadienyl transition metal complexes with other organic ligands

The known complexes are listed in Table 3. The complexes prepared have generally been made by a nucleophilic displacement reaction of the type :

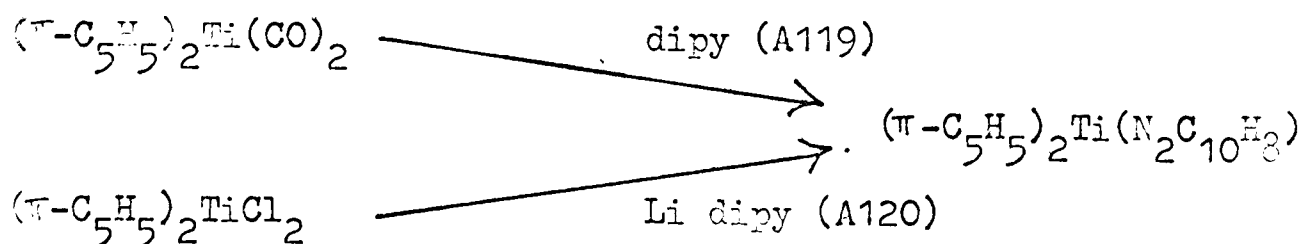
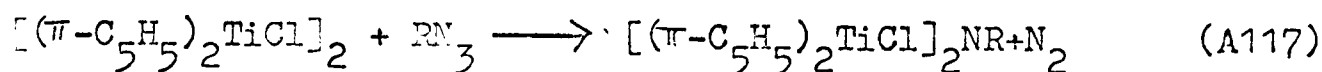
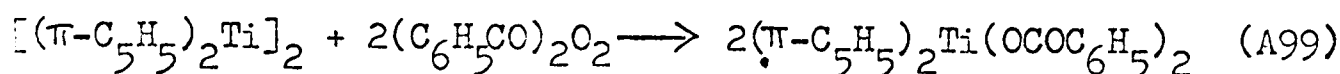
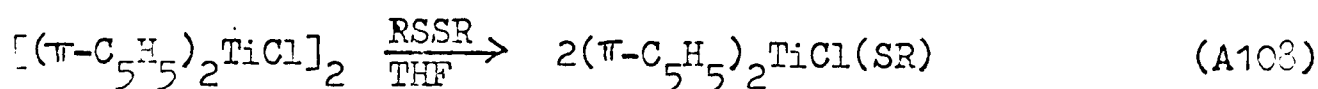
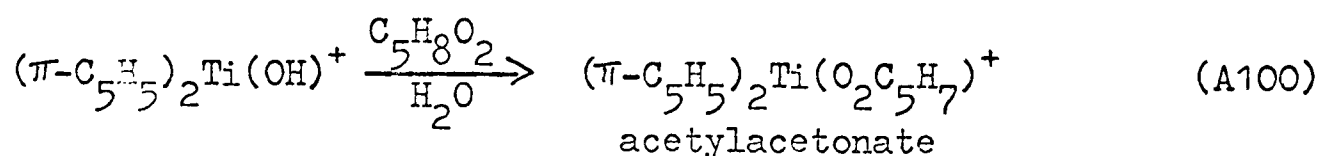


where Y = OCOR, OCSR, OR, SR, PR₂, NR₂ etc. M' = K, Na, Li, Ag, or by the similar reaction :

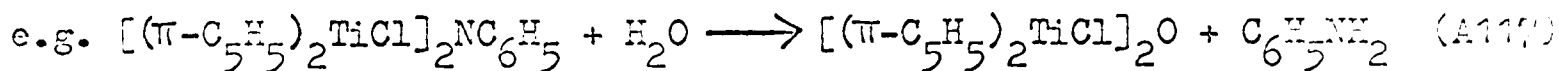


Y = SeR, SR, OR etc.

Other slightly different reactions which have been used include:

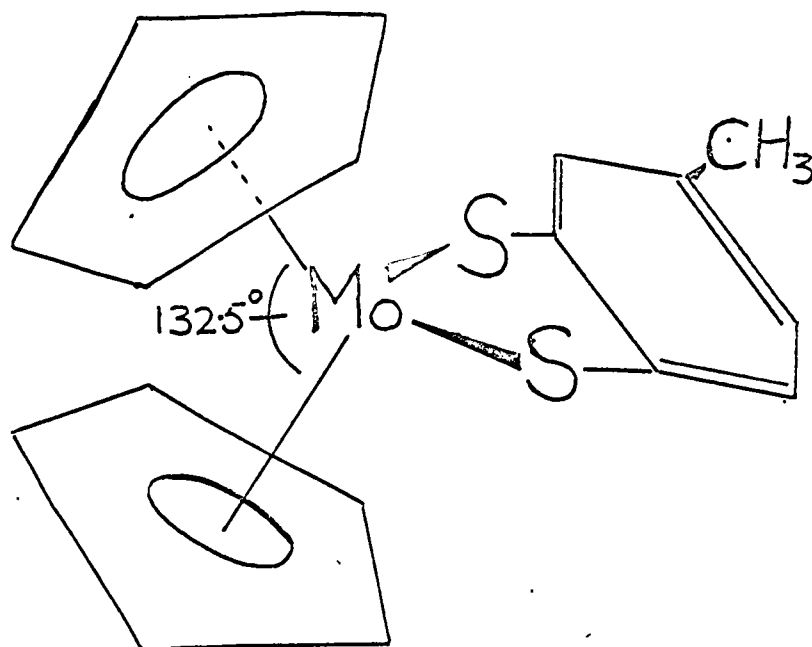


Little further chemical work has been done on these derivatives. It has been shown in some cases that the parent halides can be formed by treatment with the appropriate halo-acid. Controlled hydrolysis in some cases gives oxy-halo-species:



Polymers have been formed from bis- π -cyclopentadienyl acrylates.

The structure of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ has been determined by X-ray diffraction (A125) and is shown below.

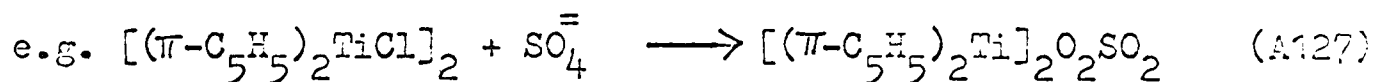


$$\text{Mo-S} = 2.43 \text{ \AA}$$

D. Miscellaneous bis- π -cyclopentadienyl transition metal complexes

Other bis- π -cyclopentadienyl transition metal complexes, primarily with inorganic ligands, are shown in Table 4.

The oxyanion complexes of Ti(IV) and Ti(III) are formed by reaction of solutions of the respective bis- π -cyclopentadienyl halides in water with the oxy anions



(in water as cation)

Table 3.

COMPLEXES OF BIS- π -CYCLOPENTADIENYL TRANSITION METAL SYSTEMS WITH ORGANIC LIGANDS

Compound	Colour	Melting or decomp. point	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OCOR})_2$	orange	127-130d	A94, A99	R = CH_3
	yellow orange	135-150	A94, A95	R = CCH_3CH_2
	orange	177-178.5	A97, A98	R = CF_3
		110-111	A97	R = C_3F_7
	yellow	188-192	A99	R = C_6H_5
$(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{OCOR})$			A96	R = $\text{CH}_2\text{Cl}, \text{CHCl}_2$
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OC}_2\text{H}_5)(\text{OCOR})$				$\text{CCl}_3, \text{CH}_2\text{CH}_3, \text{C}_4\text{H}_9, \text{CH}_2\text{OH}, \text{CH}_2\text{SH}.$
$[(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OCOR})_2\text{O}]$				
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{O}_2\text{C}_5\text{H}_7)^+$				
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OCH}_2\text{CF}_3)_2$	red-brown	47-48	A101	R = $\text{CCH}_3=\text{CH}_2$
$(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{OC}_2\text{H}_5)$	yellow	89-91	A94, A102, A103	R = $\text{CCH}_3=\text{CH}_2$
$(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{OC}_3\text{H}_5)$	orange-yellow	57-58	A94	R = CH_3
				as salt of ClO_4^- , PF_6^- etc. other β -diketonates prepared also

Table 3 - continued

Compound	Colour	Melting or decomp. point	Reference	Comments
$(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OAr})_2$	yellow	142	A105	Ar = C_6H_5
	yellow to red	range of mp.s 120-165	A104	Other compounds
	red-brown	100-103	A104	Ar = o- and p- ClC_6H_4
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{O}_2\text{C}_6\text{H}_4)_2$	red	208-211	A104	o- and p- $\text{CH}_3\text{C}_6\text{H}_4$, o- $\text{NO}_2\text{C}_6\text{H}_4$,
$(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{OC}_6\text{H}_5)$	orange yellow	71-73	A94	p- $\text{C}_6\text{H}_5\text{C}_6\text{H}_4$, 3,5- $(\text{CH}_3)_2\text{C}_6\text{H}_3$
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{SR})_2$	burgundy	194-197	A43, A106, A36 A108	R = CH_3
	dark red	107-110d	A107, A108	R = C_2H_5
	red	88-93	A107	R = n- C_3H_7
	burgundy	200-201	A106, A43, A108	R = C_6H_5
	red		A107, A108	Other complexes R=p- $\text{CH}_3\text{C}_6\text{H}_4$,
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{SCH}_2)_2$	red	d50	A36	p- ClC_6H_4 , $\text{C}_6\text{H}_5\text{CH}_2$, $\text{C}_6\text{H}_5(\text{CH}_2)_2$
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{SC}_2\text{R}_2)_2$	green-black	177-179	A109	R = H
	green	d > 300	A114, A111, A36	R = CN

Table 3. continued

Compound	Colour	Melting or decomp. point	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{SC}_6\text{H}_5\text{R})$	blue-black	222-224	A110	R = H
$(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{SR})$	blue-black	158-160	A110, A36	R = CH_3
		range - 100-180d	A108	R = CH_3 , C_2H_5 C_6H_5 , $\text{C}_6\text{H}_5\text{CH}_2$
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{SeR})_2$	deep green	99-101	A45	R = C_2H_5
	blue-violet	120-122	A45	R = C_6H_5
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{N}(\text{CH}_3)_2)_2$	brown oil	b.p. 120/0.2 mm Hg	A113	
$[(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}]_2\text{NR}$	brown		A117	R = C_6H_5 , p- ClC_6H_4 , poorly characterised
$(\pi\text{-C}_5\text{H}_5)_2\text{TiClNHR}\cdot x\text{NH}_2\text{R}$			A114	R = H, CH_3 - tensimetric studies
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OCOR})$	green	92	A115	R = H
	royal blue		A115	R = CH_3 , $\text{CH}_3(\text{CH}_2)_8$, $\text{CH}_3(\text{CH}_2)_{12}$
	dark green	83-85	A115	R = C_6H_5
$[(\pi\text{-C}_5\text{H}_5)_2\text{Ti}]_2(\text{OCO})_2\text{R}$		> 240d	A115	{ R = $-\text{CH}_2\text{CH}_2-$ - $\text{CH}=\text{CH}$ - cis & trans
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OCsR})$	dark green	range 40-100	A116	{ R = H, CH_3 , C_2H_5 , $\text{CH}_3(\text{CH}_2)_{16}$.
	teal blue	88-89	A116	R = C_6H_5

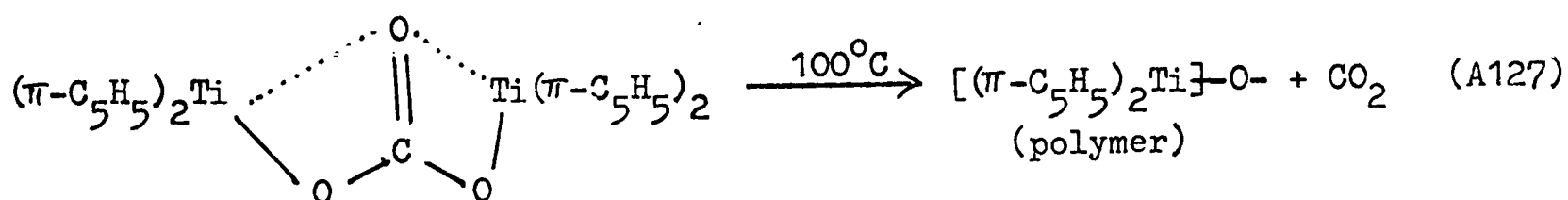
Table 3 - continued

Compound	Colour	Melting or decomp. point	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{PR}_2)_2$	deep violet	d203-205	A118	R = C_2H_5
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{dipy})$	deep violet	d158-160	A118	R = n C_4H_9
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{OCOCF}_3)_2$	blue-black	116-117	A119, A120	hygroscopic
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{OR})(\text{Cl})$		70d	A121	R = C_2H_5
			A34	R = i C_3H_7
$(\pi\text{-C}_5\text{H}_5)_2\text{ZrXOZrOC}_2\text{H}_5(\pi\text{-C}_5\text{H}_5)_2$		147-156	A34	X = Cl
		184-192		X = Br
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{OC}_6\text{H}_5)_2$	colourless	118-120d	A122	
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{PR}_2)_2$	brown-red	280-282	A118	R = C_2H_5
	brown-red	238-240	A118	R = n C_4H_9
$[(\pi\text{-C}_5\text{H}_5)_2\text{Zr}]_2\text{C}(\text{CH}_2\text{PC}_6\text{H}_5)_4$	yellow	270	A123	a spiran
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{S}_2\text{C}_2\text{H}_2)$	yellow-orange	183-186	A109	
$(\pi\text{-C}_5\text{H}_5)_2\text{Zr}(\text{N}(\text{CH}_3)_2)_2$	oil	b.p. 120/0.1mm	A144	
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{C}_2\text{H}_5\text{CO}_2)$	dark brown	d ~ 225	A124	
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{C}_2\text{C}_6\text{H}_4)$	dark red	d ~ 160	A3	

Table 3 - continued

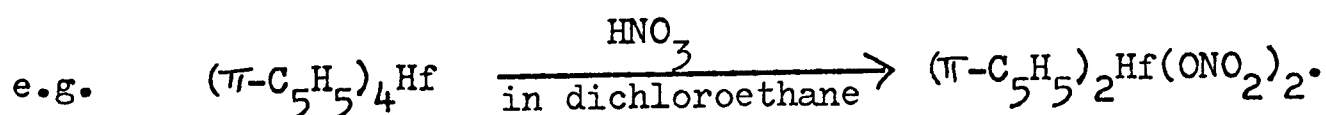
Compound	Colour	Melting or decomp. point	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SR})_2$	brown-red	d in range 170-185	A124	R = CH_3 , C_2H_5
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SCH}_2)_2$	yellow-brown	d205	A3	R = C_6H_5
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SCH}_2)_2$	dark red	d ~ 170	A124	
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SCH}_2)_2(\text{CN})_2$	red-orange	d ~ 180	A3	
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$	purple	229	A3	X-ray structure A125
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NH}_2\text{C}_2\text{H}_4\text{S})\text{X}$	red		A126	X = Cl, Br, I
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCHRCO}_2)$	brown	d > 200	A124	R = H, CH_3
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_6\text{H}_4)$	red-brown	d160	A3	
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SR})_2$	golden-red	d	A124, A3	R = CH_3 , C_2H_5 , C_6H_5
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{R})$	brown-red	d	A124	R = $-(\text{CH}_2)_2^-$, $-(\text{CH}_2)_3^-$
$(\pi\text{-C}_5\text{H}_5)_2\text{WS}_2\text{C}_2(\text{CN})_2$	orange	d220	A3	
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$	orange	d230	A3	
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2\text{CH}_2\text{NH}_2)\text{Cl}$	red		A126	

The Ti(III) complexes, $[(\pi\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{SO}_4$ and $[(\pi\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{CO}_3$ are paramagnetic but, whereas there is no spin-spin interaction between the two Ti atoms in the former bridged dimer such an interaction occurs in the latter complex. The carbonato complex also decomposes:



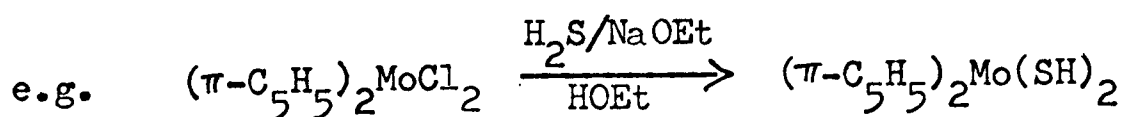
Other oxyanions were found to give polymers with Ti(III).

The action of a mixture of $\text{H}_2\text{SO}_4/\text{CH}_3\text{COOH}$ on $(\pi\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$ gives the bis-bisulphate but electrophilic attack of one $\pi\text{-C}_5\text{H}_5$ ring also takes place and the product is $[(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{SO}_3\text{H})\text{Zr}(\text{OSO}_3\text{H})_2] \cdot \text{A} \cdot \text{C}_2\text{O}$ (A135). Nitrate derivatives of Zr and Hf have been made using nitric acid dissolved in organic solvents (A20, A37).



Mono and disilanoates of bis- π -cyclopentadienyl titanium (IV) have been made using the appropriate NaOSiR_3 derivative (or $(\text{C}_2\text{H}_5)_3\text{N}/\text{HOSi}(\text{C}_6\text{H}_5)_3$) (A128, A129). Related polymers have been made from $(\text{CH}_3)_2\text{Si}(\text{OH})_2/\text{amine}$.

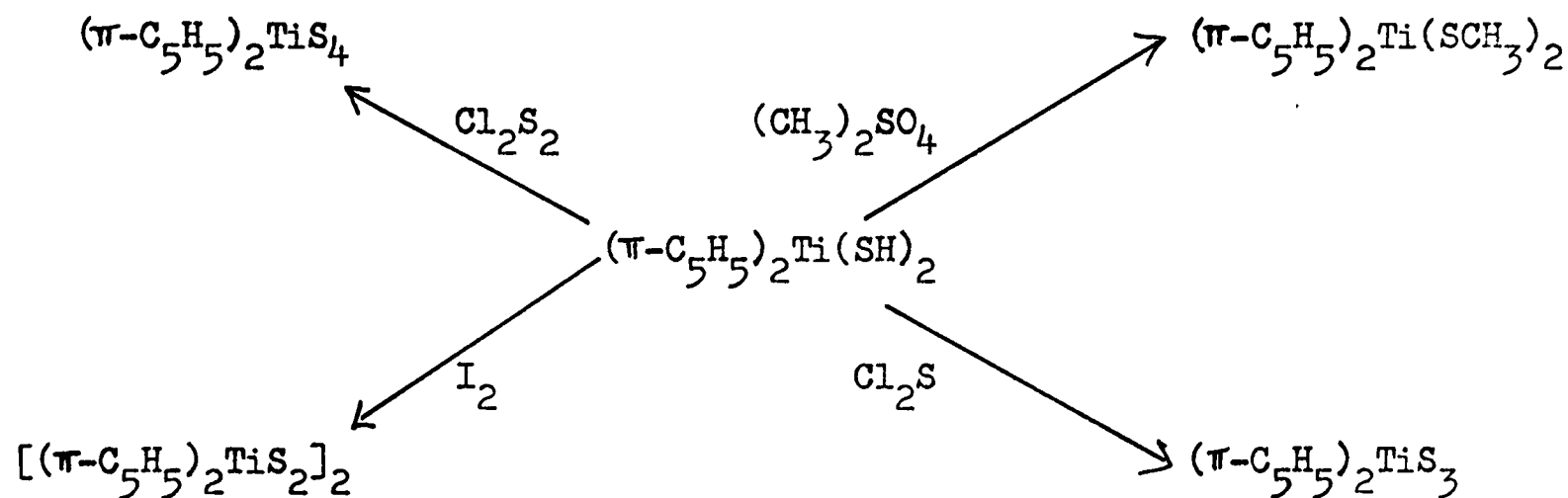
Sulphur derivatives of Ti, Nb, Mo and W have been made. The sulphohydryl complexes $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{SH})_2$ ($\text{M} = \text{Ti, Mo, W}$) have been prepared from hydrogen sulphide,



The titanium complex has also been prepared from titanocene (A95). Several

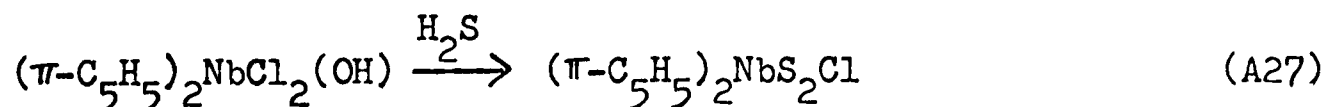
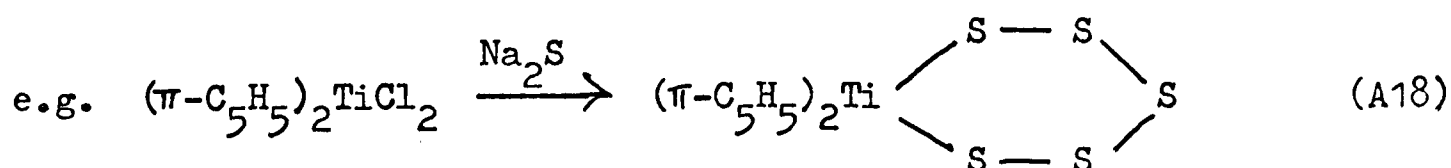
reactions have been carried out with the titanium complex; (A95, A130)

e.g.

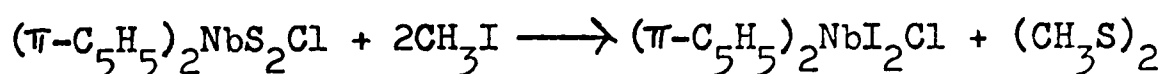


However similar reactions did not appear to occur with the Mo and W complexes. It was noted (A3) that the proton resonance of the thiol proton in the 'H.M.R. of the Mo and W complexes appeared at high field (12.36 and 11.46 γ respectively) whereas that of the Ti compound appeared at 6.56 γ . This difference could be related to the difference in reactivity.

Several compounds containing sulphur rings have been made



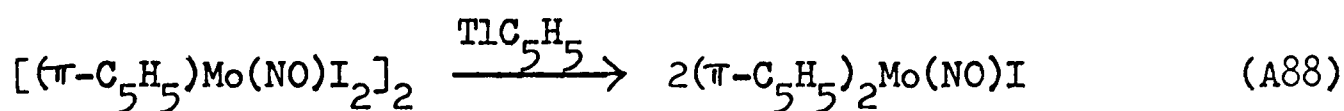
(also see above). Polymers of Ti and Nb have also been obtained. An interesting reaction of the Nb species shown above is:



A byproduct formed in the latter reaction is $(\pi\text{-C}_5\text{H}_5)_2\text{NbOCl}$.

An interesting molecule is $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ which has been used to prepare several other π -cyclopentadienyl derivatives (see previously). It is very air sensitive and is formed by the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ with CO (110 atmos.) in the presence of $\text{C}_5\text{H}_5\text{Na}$ (A131). It can also be formed from $(\pi\text{-C}_5\text{H}_5)_3\text{Ti}$ with CO (150 atmos.) (A74). No zirconium analogue could be made.

A bis- π -cyclopentadienyl molybdenum nitrosyl complex has been formed:



On the basis of the 18-electron rule and the ν NO infra-red frequency of the nitrosyl ligand it has been argued that one cyclopentadienyl group acts as an allyl ligand. However if this is so the $^1\text{H.M.R.}$ spectrum requires rapid exchange processes to occur.

Compounds of bis- π -cyclopentadienyl Ti and Zr systems with group III B and IV B elements have also been prepared, as shown in table.

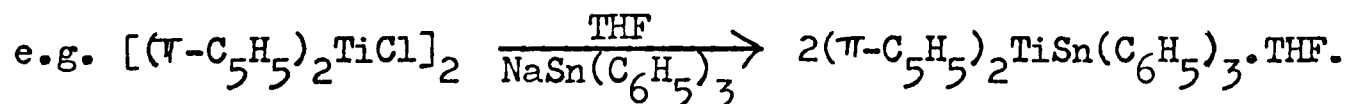


Table 4

BIS- π -CYCLOPENTADIENYL COMPLEXES OF TRANSITION METALS WITH MISCELLANEOUS LIGANDS

Compound	Colour	Melting or decomp. point	Reference	Comments
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{ClO}_4)_2$	orange		A100	explosive
$[(\pi\text{-C}_5\text{H}_5)_2\text{TiNO}_3]_2\text{O}$			A18	
$(\pi\text{-C}_5\text{H}_5)_2\text{TiBF}_4$	light blue		A12	
$[(\pi\text{-C}_5\text{H}_5)_2\text{Ti}]_2(\text{SO}_4)$			A127	polymers from other oxy anions
$[(\pi\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{CO}_3$		d > 100	A127	
$(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}(\text{OSiR}_2\text{R}')$	orange		A128, A129	R = R' = CH_3
			A94	R = R' = C_6H_5
			A128, A129	R = C_6H_5 , R' = CH_3
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OSi}(\text{C}_6\text{H}_5)_3)_2$	bright yellow	208-210	A130, A95	Similar polymeric species known
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{SH})_2$	black-brown	d150-160		
$(\pi\text{-C}_5\text{H}_5)_2\text{TiS}_x$	brown-red	d	A95, A18	x = 3, 4, 5
$[(\pi\text{-C}_5\text{H}_5)_2\text{TiS}_2]_2$	red-brown	d195-200	A95	
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$	red-brown	d > 90	A131	
$(\pi\text{-C}_5\text{H}_5)_2\text{TiX}(\text{BY}_2)$	violet-black	300d	A132	X = Cl, Y = C_6H_5 ; X = Br, Y = Br; X = Cl, Y = Cl.
$[(\pi\text{-C}_5\text{H}_5)_2\text{TiAl}(\text{C}_2\text{H}_5)_2]_2$			A39	Structure A133 Ti-Al and Ti-Ti bonds.

Table 4 - continued

Compound	Colour	Melting or decomp. point	Reference	Comments
$(\pi-C_5H_5)_2Ti(Sn(C_6H_5)_3)_2$	green	80d	A112	M = Sn, Ge (also impure Zr analogues) M = Sn, Ge
$(\pi-C_5H_5)_2Ti(M(C_6H_5)_3)Cl$	dark green		A112	
$(\pi-C_5H_5)_2Ti(M(C_6H_5)_3) \cdot THF$	emerald green		A112	
$(\pi-C_5H_5)(\pi-C_5H_4SO_3H)Zr(OSO_3H)_2 \cdot Ac_2O$	brown		A134, A135	X = Cl, Br, I, SCN (and polymers)
$(\pi-C_5H_5)_2ZrCl(ONO_2)$			A20	
$(\pi-C_5H_5)_2ZrClSi(C_6H_5)_3$	orange	175-178	A136	
$(\pi-C_5H_5)_2Hf(ONO_2)_2$			A37	
$(\pi-C_5H_5)_2HfCl(ONO_2)$		185.5-186	A37	
$(\pi-C_5H_5)_2NbS_2X$		225-230d	A27	
$[(\pi-C_5H_5)_2NbS_4]_n$	brown		A27	
$(\pi-C_5H_5)_2Mo(NO)I$	green-black	157-159	A88	
$(\pi-C_5H_5)_2Mo(SH)_2$	deep red	d150	A3	
$(\pi-C_5H_5)_2W(SH)_2$	sandy brown	d135	A3	

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Chapter II

BIS- π -CYCLOPENTADIENYL PSEUDOHALIDE DERIVATIVES OF MOLYBDENUM AND TUNGSTEN

The dihalide species, $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2$, ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) and the related cations, $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$, ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}$), as mentioned in chapter I, were first characterised by Cooper (A2). The corresponding cations and neutral complexes are interconvertible by reduction or oxidation respectively and the cations gave electron spin resonance, (E.S.R.), signals in which ligand superhyperfine splittings were observed, except in the spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$. It was thus decided to try to prepare similar complexes with related ligands.

A. Bis- π -cyclopentadienyl diazides of molybdenum and tungsten

Several attempted preparations of azide complexes of the bis- π -cyclopentadienyl tungsten system were made in the earlier stages of this work. Thus, $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ and NaN_3 refluxed in alkaline aqueous ethanol were noted to react but only a pink coloured, water soluble product was obtained which showed no absorption frequencies in its infra-red spectrum assignable to the $(\pi\text{-C}_5\text{H}_5)$ ligand. Neither NaN_3 and $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ in acetone nor AgN_3 and $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ in dimethyl sulphoxide reacted.

When $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ was reacted with an excess of LiN_3 in a mixture of acetone and a little ethanol a blue coloured solution was obtained from which, by chromatography and recrystallisation, mauve crystals which became brown in colour on crushing were formed. Analysis* gave a stoichiometry

* All analytical figures are reported in chapter VII.

corresponding to the formula $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{N}_3)_2$. The crystals decomposed explosively when heated in a flame and decomposed slowly at room temperature. The compound is fairly soluble in the polar organic solvents dichloromethane and acetone, giving blue solutions but barely soluble in ethanol and insoluble in water and ether.

The analogous tungsten compound, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{N}_3)_2$, was made from LiN_3 and $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ in an acetone-alcohol mixture in a similar way. Purple, needle shaped crystals were obtained which decomposed violently on heating. This compound was less thermally stable than the molybdenum compound and, after leaving for a month at room temperature, little of the pure compound could be regained by chromatography. It is also unstable to abrasion, since on one occasion removal of a sample from a flask with a spatula caused a violent explosion. The tungsten compound is fairly soluble in dichloromethane and acetone, but negligibly soluble in water and insoluble in ether.

The infra-red spectra* of both molybdenum and tungsten complexes show bands characteristic of the $(\pi\text{-C}_5\text{H}_5)$ ligand - principal bands are $\sim 3100\text{cm}^{-1}$ C-H stretch, $\sim 1430\text{cm}^{-1}$ antisymmetric C-C stretch, $\sim 1100\text{cm}^{-1}$ antisymmetric ring breathing or C-H $\perp$ deformation, 1000cm^{-1} C-H $\parallel$ deformation, $\sim 840\text{cm}^{-1}$ C-H $\perp$ deformation or C-C vibration (B1, B2). Both spectra show a strong rather broad band assignable to N_3 at 2076cm^{-1} (Mo) and 2050cm^{-1} (W).

The proton magnetic resonance spectra** (^1HMR) show a single peak in

* All infra-red spectra reported in Chapter VII.

** See Table 7 for all ^1HMR spectra for Chapter II.

the region expected for a $(\pi\text{-C}_5\text{H}_5)$ ligand (B3) and this is consistent with the postulated structure. In view of the instability of the complexes, mass spectra were not recorded, also, the complexes were not soluble enough for a solution molecular weight determination but are probably monomeric as are the other similar complexes.

Addition of a few drops of concentrated nitric acid to a suspension of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{N}_3)_2$ in water and shaking gave a deep turquoise solution. An excess of NH_4PF_6 in saturated aqueous solution added to the oxidised solution gave a deep blue-purple coloured precipitate. This precipitate was washed, dried and could be recrystallised from liquid sulphur dioxide - dichloromethane mixtures. A sample treated in this way showed bands assignable to νN_3 (2065 s, 2042 sh, cm^{-1}), $(\pi\text{-C}_5\text{H}_5) - (\text{e.g.}) \nu\text{C-H}$ 3120m, cm^{-1}) and PF_6^- ($\nu\text{P-F}$ 890-810 s(br), cm^{-1}), but analysis showed very low N content. The oxidised product gave an E.S.R. signal in acetone (see chapter VI) but this fairly rapidly decreased in intensity while the solution turned from blue to colourless. The oxidised product decomposed more rapidly in dimethyl sulphoxide solution. Action of excess concentrated nitric acid on a suspension of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{N}_3)_2$ in water gave a yellow-orange solution which gave no precipitate with NH_4PF_6 .

Similar oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{N}_3)_2$ by nitric acid in water gave a deep brownish-blue coloured solution from which NH_4PF_6 precipitated a blue solid which was washed with water and dried. The infra-red spectrum showed bands assignable to νN_3 ($\sim$ 2085 s, 2052 sh, cm^{-1}), $\pi\text{-C}_5\text{H}_5$ (e.g.) $\nu\text{C-H}$ 3124m, cm^{-1}) and PF_6^- ($\nu\text{P-F}$ 890-810 s (br), cm^{-1}). This solid decomposes rapidly in nitromethane and dimethylsulphoxide solutions but less rapidly

in acetone. The purple-red solution in acetone gave an E.S.R. spectrum (see chapter VI).

B. Cyano derivatives of bis- π -cyclopentadienyl molybdenum and tungsten

Several unsuccessful attempts to form a dicyano complex of bis- π -cyclopentadienyl molybdenum or tungsten were made. However in one reaction $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ was refluxed with excess KCN in water to give a deep red solution which, after evaporation to dryness, extraction of the residue with liquid sulphur dioxide and then, further recrystallisation from liquid sulphur dioxide-dichloromethane mixtures yielded a yellow crystalline solid. The infra-red spectrum of this solid was consistent with the presence of $(\pi\text{-C}_5\text{H}_5)$ and CN ligands ($\nu\text{CN } 2110 \text{ s, cm}^{-1}$) but also showed a band at $1623 \text{ w-m, cm}^{-1}$. This latter band could be caused by an O-H group. The analytical results were low for a species $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CN})_2$ but could be explained if 1-2 molecules of water were present. (Compare the discussion in the following section.)

Bis- π -cyclopentadienyl-ethoxy-cyano-tungsten

When NaCN is refluxed in a suspension of acetone with $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ no reaction occurs but addition of ethanol to the acetone caused the compounds to react. An orange crystalline solid was obtained, after purification by chromatography and recrystallisation, which melts with decomposition ($196\text{-}197^\circ\text{C}$). It is fairly soluble in dichloromethane and acetone giving orange-red coloured solutions. It is also soluble in water to give yellow solutions. However, its solubility in water is markedly increased if acidified and the colour of the solution becomes deeper orange. Large cations

can be precipitated from these aqueous solutions (see later). It was also found that, when partitioned between water and dichloromethane, the compound remained in the aqueous layer unless this was made basic and that subsequent acidification of the aqueous layer re-extracted the compound from dichloromethane. Thus the compound exhibits acid-base behaviour. The compound also dissolves in liquid sulphur dioxide but could be recovered from this only as an oil and, as shown by the 'H.M.R. in this solvent, the compound probably reacts with sulphur dioxide.

The infra-red spectrum of the orange prismatic crystals was unusual in that large broad bands were found above 3100cm^{-1} which must be caused by O-H or N-H stretching modes and also a band at 1679cm^{-1} which is probably a related bending mode. Otherwise the spectrum is in accord with a formula $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}$ and contains one sharp νCN band (2116cm^{-1}) and characteristic $(\pi\text{-C}_5\text{H}_5)$ bands, although the latter seem to be split but this could be a solid state effect or due to slight inequivalence of the two cyclopentadienyl rings.

The mass spectrum* shows a parent peak, $m/e = 385$, assignable to the ion, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}^+$, and other peaks at $m/e = 356$, $m/e = 340$, $m/e = 314$, $m/e = 291$, $m/e = 275$, $m/e = 265$, $m/e = 249$ may be assigned to the ions $(\text{C}_5\text{H}_5)_2\text{WOCN}^+$, $(\text{C}_5\text{H}_5)_2\text{WCN}^+$, $(\text{C}_5\text{H}_5)_2\text{W}^+$, $\text{C}_5\text{H}_5\text{WOCN}^+$, $\text{C}_5\text{H}_5\text{WCN}^+$, $\text{C}_5\text{H}_5\text{WO}^+$ and $\text{C}_5\text{H}_5\text{W}^+$ respectively.

The conductivity** in nitromethane was very low as expected for a

* See Table 8 for all mass spectra for chapter II.

** All conductivities reported in chapter VII.

non electrolyte.

The 'H.M.R. spectrum in deuterochloroform showed three peaks assignable to $(\pi-C_5H_5)$ protons and the CH_2 and CH_3 protons of an ethyl group in intensity ratios 10:2:3 as expected for $(\pi-C_5H_5)_2W(OC_2H_5)CN$ and no other ^1H resonances were found. Thus it remains to explain the bands in the infra-red spectrum above $3100cm^{-1}$ that consistently appeared.

It was also found that analytical results varied - C $\sim$ 39-40%. The figure required for $C_{13}H_{15}ONW$ is C = 40.5% and for $C_{13}H_{15}ONW.H_2O$, C = 38.7%. All this evidence suggested the presence of up to one molecule of water of crystallisation. To prove this several experiments were performed.

1) The compound was dissolved in water and then recovered by removal of the solvent under vacuum. No change in the infra-red spectrum of the compound was noted.

2) The compound was dissolved in D_2O and then the solvent was removed under vacuum at room temperature. The infra-red spectrum of the product in a KBr disc was recorded and it was found that the bands above $3100cm^{-1}$ and at $1679cm^{-1}$ were markedly decreased in intensity and new bands appeared at 2553 m (br), 2470 m (br), 2410 m (br) and at $1225 m cm^{-1}$.

$\nu X-H cm^{-1}$	3459	3340	3275	1679
$\nu X-D cm^{-1}$	2553	2470	2410	1225
$\frac{\nu X-H}{\nu X-D}$	1.35	1.35	1.36	1.37

The ratios $\frac{\nu X-H}{\nu X-D}$ as shown in the table have approximately the value predicted using the simple relationship, $\nu = \frac{1}{2C} \sqrt{\frac{K}{\mu}}$, assuming the same force constants.

This experiment proves that these bands are X-H frequencies and that

the hydrogens or the complete system, X-H, can be readily replaced in water.

3) Drying the compound on a vacuum line at 100°C for 3 hours and then observing the infra-red spectrum in a KBr disc gave a spectrum with no noticeable bands that could be assigned to X-H. However, the rest of the spectrum was altered slightly being simplified by a reduction in the number of peaks (see chapter VII). To prove no substantial change had taken place this dried compound was dissolved again in water and recovered by evaporation of the solvent. The solid now obtained had the same spectrum as in experiment 1).

A sample that was well dried gave the correct analytical results for $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}$ and was monomeric in chloroform.

Thus the compound $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}$ readily takes up water of crystallization which cannot be easily removed by drying under vacuum (10^{-2} mm Hg) at room temperature.

The 'H.M.R. in liquid sulphur dioxide was also run several times and, although bands due to absorption by $(\pi\text{-C}_5\text{H}_5)$ and C_2H_5 protons were present, other bands also occurred. Another set of two bands (a triplet and a quartet) assignable to another ethyl peak and another singlet in the region of absorption by $(\pi\text{-C}_5\text{H}_5)$ appeared in varying intensities relative to the other bands. These results can be explained as a result of sulphur dioxide decomposing the complex. It was found that the compound was recovered as an oil from liquid sulphur dioxide and it could not be obtained crystalline. The infra-red spectrum of this recovered material was different to that of the starting product.

Preparation of $[(\pi-C_5H_5)_2W(OC_2H_5)(CN)H]PF_6$

The action of NH_4PF_6 solution on a solution of $(\pi-C_5H_5)_2W(OC_2H_5)CN$ in dilute sulphuric acid gave a yellow crystalline precipitate, which after recrystallisation from liquid sulphur dioxide gave a yellow micro-crystalline solid (d. 260-265°C). This had the stoichiometry corresponding to $[(\pi-C_5H_5)_2W(OC_2H_5)(CN)H]PF_6$ and a conductivity (Δ) corresponding to a 1:1 electrolyte (B4). It was soluble in liquid sulphur dioxide and slightly soluble in acetone and water.

The infra-red spectrum showed typical $(\pi-C_5H_5)$ frequencies and PF_6^- frequencies (900-800 vs, 557 cm^{-1}) but also showed broad intense peaks centred around ~ 2480 and ~ 1750 cm^{-1} and a sharp ν CN, (2133 cm^{-1}). The broad peaks must be assigned to a strongly hydrogen bonded X-H system. Similar broad peaks are found in some complex metal cyano acids - e.g. $H_4Fe(CN)_6$ (B5) in which the protons are believed to be unsymmetrically hydrogen bonded to nitrogen atoms. The increase in the ν CN frequency compared to the neutral complex (18 cm^{-1}) is also paralleled by the protonation of complex cyano anions such as $Fe(CN)_6^{4-}$, $Pt(CN)_4^{2-}$, $Rh(CN)_6^{3-}$, which show an increase of ~ 60 cm^{-1} (B5). Whether the proton is principally attached to the nitrogen (as in $H_4Fe(CN)_6$, $(\pi-C_5H_5)Mn(CO)_2CNH$ (B6) or $(OC)_5WCNH$ (B7)) or to the oxygen atom of the ethoxy ligand to give an ethanol adduct (as postulated for $W_2Cl_4(OEt)_4 \cdot 2EtOH$ (B8)) is unknown, but it is most probably N-bonded and strongly hydrogen bonded to the oxygen atom.

This cationic complex when dissolved in acetone gave no E.S.R. signal. However if $(\pi-C_5H_5)_2W(OC_2H_5)CN$ was dissolved in dilute nitric acid, precipitated by NH_4PF_6 from the solution and the precipitate separated and washed as

quickly as possible and dried, solutions of this precipitate gave a single E.S.R signal of g value comparable to that obtained by electrolytic oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}$ in 1,2-dimethoxyethane (see chapter VI). This suggests that, as well as a protonated cation, a cation, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}^+$, formed by oxidation may exist. Such a system would be analogous to the system $\text{W}(\text{CN})_8^{4-} \xrightleftharpoons[+e]{-e} \text{W}(\text{CN})_8^{3-}$.

Bis- π -cyclopentadienyl-methoxy-cyano-tungsten

Refluxing $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with NaCN in a mixture of acetone and methanol gave a similar orange crystalline compound (m.p. 217-218°C) to that obtained from acetone-ethanol mixtures. This has the stoichiometry required for $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCH}_3)\text{CN}$ and was also soluble in dichloromethane, acetone, ethanol and water as was the corresponding ethoxy derivative.

The mass spectrum showed a parent ion peak $M/e = 371$, corresponding to $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCH}_3)\text{CN}^+$. Other prominent peaks were $M/e = 356$, $M/e = 340$, $M/e = 329$, $M/e = 314$, $M/e = 265$, $M/e = 249$, assignable to fragmentation ions $(\text{C}_5\text{H}_5)_2\text{WOCN}^+$, $(\text{C}_5\text{H}_5)_2\text{WCN}^+$, $(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{WO}^+$, $(\text{C}_5\text{H}_5)_2\text{W}^+$, $\text{C}_5\text{H}_5\text{WO}^+$, $\text{C}_5\text{H}_5\text{W}^+$.

The 'H.M.R. spectrum in CDCl_3 showed two sharp singlet bands of intensity ratios 10:3 which may be ascribed to $(\pi\text{-C}_5\text{H}_5)$ and CH_3 protons respectively. It was proposed to run the 'H.M.R. spectrum in liquid sulphur dioxide as the compound is very soluble in this solvent. However the infra-red spectrum of a sample, recovered from a liquid sulphur dioxide solution and subsequently recrystallised from dichloromethane-ether mixtures, was different to the infra-red spectrum of pure $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCH}_3)\text{CN}$ and included broad bands in the 950-1200 cm^{-1} region which could be assigned to sulphur dioxide (cf. $\text{W}(\text{CO})_2(\text{bipy})\text{SO}_2$ (B9)). This might have been due to strongly held sulphur

dioxide of crystallisation or to the formation of an SO_2 complex.

The infra-red spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCH}_3)\text{CN}$, unlike that of the ethoxy compound, showed no large bands that could be attributed to O-H frequencies. The analytical results also showed no large discrepancy from the expected values for an unhydrated complex. Thus it must be concluded that the compound does not include water in its lattice as readily as the ethoxy derivative. This may be due in part to the larger size of the ethoxy compound.

Solutions of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCH}_3)\text{CN}$ in water gave a yellow precipitate with silicotungstic acid showing the presence of a large cation. The compound is more soluble in dilute acids and NH_4PF_6 precipitated an orange crystalline solid from a dilute sulphuric acid solution. This solid was fairly soluble in water and slightly soluble in polar organic solvents such as methanol and acetone. It probably has the constitution $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCH}_3)(\text{CN})\text{H}]\text{PF}_6$.

C. Bis- π -cyclopentadienyl thiocyanato derivatives of molybdenum and tungsten

Bis- π -cyclopentadienyl-dithiocyanato-molybdenum

Refluxing $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ with an excess of KSCN in water and purifying the resulting product gave a purple crystalline solid ($d \sim 260^\circ\text{C}$), the stoichiometry of which corresponded to the formula $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CNS})_2$. The compound is insoluble in organic solvents and water but soluble in dimethyl sulphoxide and liquid sulphur dioxide from which it could be recrystallised.

The 'H.M.R. in liquid sulphur dioxide showed one singlet band, as expected, assignable to the $(\pi\text{-C}_5\text{H}_5)$ protons. The mass spectrum showed a parent ion peak of $M/e = 344$ corresponding to $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CSN})_2^+$ (based on most abundant isotope ^{98}Mo). Other prominent peaks occurred at $M/e = 312$,

$M/e = 286$, $M/e = 254$, $M/e = 228$ corresponding to the ions $C_{10}H_{10}Mo(CNS)NC^+$, $C_{10}H_{10}Mo(CNS)^+$, $C_{10}H_{10}MoNC^+$ and $C_{10}H_{10}Mo^+$. However there must have been a very small amount of the compound $(\pi-C_5H_5)_2MoCl(CNS)$ present in this sample as other small peaks could be assigned to this and its fragmentation (characteristic doubling of peaks caused by ^{35}Cl and ^{37}Cl).

The upper region infra-red spectrum had bands corresponding to $(\pi-C_5H_5)$ frequencies and a very strong band at 2105 cm^{-1} assignable essentially to νCN and no band in the region $690-720\text{ cm}^{-1}$ but several bands in the region $800-900\text{ cm}^{-1}$ where both $(\pi-C_5H_5)$ and νCS of $MNCS$ systems have absorption frequencies.

All the above evidence is in favour of the formula $(\pi-C_5H_5)_2Mo(CNS)_2$ and suggests that the thiocyanate groups are N-bonded rather than S-bonded. However further evidence for the latter fact will be presented at the end of this section.

The compound, when suspended in water and a few drops of concentrated nitric acid added, did not give any noticeable reaction. A large excess of nitric acid caused the compound to dissolve to give a deep orange coloured solution and gas was evolved, but no precipitate could be obtained from this solution with NH_4PF_6 . On the other hand electrolytic oxidation (see chapter VI) in dimethyl sulphoxide gave an unstable paramagnetic species with a single ESR spectrum.

Bis- π -cyclopentadienyl-dithiocyanato-tungsten complexes

The reaction of $(\pi-C_5H_5)WCl_2$ with $KCNS$ in water gave a deep red solid which was separated and found to be a mixture of two products 'A' and 'B'.

'A' was soluble in acetone and was extracted from 'B' by digesting the

mixture with acetone and, then, was purified by chromatography and recrystallisation to give a pink microcrystalline solid (d ~ 310°C). Analytical results gave a stoichiometry corresponding to a complex $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CNS})_2$. The solid was fairly soluble in acetone and chloroform and insoluble in less polar organic solvents. It was also soluble in dimethylsulphoxide and liquid sulphur dioxide, and an 'H.M.R. spectrum in the latter solvent showed one proton resonance at $\tau = 4.32$ which is assignable to $(\pi\text{-C}_5\text{H}_5)$ protons.

The mass spectrum showed a parent peak of $M/e = 430$ caused by $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CSN})_2^+$ and other prominent peaks at $M/e = 398$, $M/e = 372$, $M/e = 314$, $M/e = 307$, assignable to $\text{C}_{10}\text{H}_{10}\text{W}(\text{CNS})\text{NC}^+$, $\text{C}_{10}\text{H}_{10}\text{WCNS}^+$, $\text{C}_{10}\text{H}_{10}\text{W}^+$ and $\text{C}_5\text{H}_5\text{WCNS}^+$ respectively.

The upper region infra-red spectrum showed typical $(\pi\text{-C}_5\text{H}_5)$ frequencies and several strong bands in the νCN region ($\sim 2100\text{ cm}^{-1}$).

The action of concentrated nitric acid on an aqueous suspension of 'A' gave a blue solution which became brown and precipitated a white solid in the presence of excess nitric acid. By careful addition of nitric acid, oxidation was allowed to proceed only to the first stage and, after centrifuging to give a clear solution, a blue precipitate was formed with aqueous NH_4PF_6 solution. This precipitate was collected, dried and recrystallised twice from liquid sulphur dioxide-ether mixtures to give a small quantity of a purple crystalline solid. This was believed to be $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CSN})_2]\text{PF}_6$ but, if so, it was not obtained completely pure. [Found: C, 26.4; H, 1.8; N, 4.9% (C). $\text{C}_{12}\text{H}_{10}\text{S}_2\text{N}_2\text{F}_6\text{PW}$ requires: C, 25.1; H, 1.8; N, 4.9%.] This solid was soluble in acetone and gave an E.S.R. signal consisting of

one single band with small shoulders on either side (due to ^{183}W , $I = \frac{1}{2}$, 14% abundant) at $g = 1.96$. Electrolytic oxidation of 'A' in dimethyl sulphoxide solution (see chapter VI) initially gave one signal at $g = 1.966$ but continued electrolysis caused another signal to grow at the high field side of the original, $g = 1.963$.

Product 'B' was insoluble in organic solvents but soluble in liquid sulphur dioxide and dimethyl sulphoxide. It was obtained as a purple micro-crystalline solid (d 220-250°C) from liquid sulphur dioxide-dichloromethane mixtures. Analysis showed that it had the same stoichiometry as product 'A' and thus could also have the formula $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CNS})_2$.

'H.M.R. investigation in liquid sulphur dioxide revealed one proton resonance at $\tau = 4.22$ assignable to the protons of $(\pi\text{-C}_5\text{H}_5)$. The mass spectrum, again, showed the parent peak $M/e = 430$ assignable to $\text{C}_{10}\text{H}_{10}\text{W}(\text{CSN})_2^+$ and a similar fragmentation pattern to that of 'A'. The upper region infra-red spectrum showed typical $(\pi\text{-C}_5\text{H}_5)$ frequencies and νCN frequencies of a thiocyanato group at 2119 and 2107 cm^{-1} as expected for the predicted formula.

The action of nitric acid on an aqueous suspension of 'B' gave a blue solution but, also, much insoluble material probably formed by further oxidation. Adding NH_4PF_6 solution to clear blue solution gave a very small quantity of purple coloured precipitate. An E.S.R. investigation of this in acetone gave one main signal $g = 1.94$ but also a smaller one at $g = 1.96$. Electrolytic oxidation of 'B' in dimethyl sulphoxide gave one signal, $g = 1.946$ (see chapter VI). The signal at $g = 1.96$ is, therefore, probably due to the same paramagnetic species formed by oxidation of complex 'A'.

The nature of the thiocyanate bonding in the two complexes, 'A' and 'B' will be discussed at the end of this section.

Bis- π -cyclopentadienyl-thiocyanato-tungsten chloride

The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ in a suspension of a solution of KCNS in acetone gave a mauve compound which, after chromatography and recrystallisation, gave prismatic micro-crystals ($d \sim 260^\circ\text{C}$). These were soluble in dichloromethane and acetone. Stoichiometry, found by analysis, was consistent with the formula $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}(\text{CNS})$.

The 'H.M.R. spectrum in acetone showed only one band corresponding to $(\pi\text{-C}_5\text{H}_5)$ protons. The mass spectrum of this compound showed a peak of $M/e = 407$, assignable to $(\pi\text{-C}_5\text{H}_5)_2\text{WClCSN}^+$ with characteristic W and Cl isotopic pattern but also a small peak of $M/e = 430$ which must have been due to $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CSN})_2^+$. This latter ion may have resulted from rearrangement of the monochloride at the temperature of admission to the spectrometer (220°C) or be due to impurity. The former explanation is probably more likely since peaks around $M/e = 384$ which must be assigned to $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$ also occur and any $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ impurity would have been separated in the purification procedure adopted for $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}(\text{CNS})$. Other fragments in the spectrum were: $M/e = 372$, $M/e = 349$, $M/e = 342$, $M/e = 319$, $M/e = 314$ and $M/e = 284$. assignable to $\text{C}_{10}\text{H}_{10}\text{WCSN}^+$, $\text{C}_{10}\text{H}_{10}\text{WCl}^+$, $\text{C}_5\text{H}_5\text{WClSCN}^+$, $\text{C}_5\text{H}_5\text{WCl}_2^+$, $\text{C}_{10}\text{H}_{10}\text{W}^+$ and $\text{C}_5\text{H}_5\text{WCl}^+$ respectively. The infra-red spectrum showed a strong band at 2120 cm^{-1} assignable to $\nu\text{ CN}$ of the thiocyanate ligand and typical $(\pi\text{-C}_5\text{H}_5)$ frequencies. No absorption was found in the region $690\text{-}720\text{ cm}^{-1}$.

The compound was found to be quite stable but a sample that had been

left in a flask (under nitrogen) for several weeks was then found to be less soluble in acetone than before, and to have 3 'H.M.R. bands in the region expected for $(\pi\text{-C}_5\text{H}_5)$ absorption at $\tilde{\nu} = 4.38$, $\tilde{\nu} = 4.31$, $\tilde{\nu} = 4.25$. This again could be accounted for by ligand exchange taking place, slowly, at room temperature in the solid state. A similar solid state reaction involving thiocyanate ligands is the isomerisation of N- and S-bonded thiocyanate in $(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CNS}$, (B10).

Bis- π -cyclopentadienyl-thiocyanato tungsten chloride cation

The action of nitric acid on $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}(\text{CNS})$ in water gave a deep magenta coloured solution of the cation $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}(\text{CSN})^+$ which could be isolated as the hexafluoro phosphate and recrystallised from liquid sulphur dioxide to give purple needle shaped crystals (d 150-200°C) of stoichiometry corresponding to $[(\pi\text{-C}_5\text{H}_5)_2\text{WCl}(\text{CNS})]\text{PF}_6$. It also had the conductivity in nitromethane expected for a 1:1 electrolyte. This compound was soluble in sulphur dioxide and fairly soluble in acetone. The upper region infra-red spectrum showed typical $(\pi\text{-C}_5\text{H}_5)$ bands and a strong ν CN of the thiocyanate group at 2044 cm^{-1} . No absorption was found in the region $690\text{-}720\text{ cm}^{-1}$.

The cation was paramagnetic and it showed a single ESR signal in acetone solution $g = 1.949$.

Reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ with KSCN in acetone

When $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ was reacted with KSCN in acetone solution in a similar manner to the reaction with $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ a pale purple solid was obtained. This was chromatographed using dichloromethane-acetone mixtures giving a purple band which formed a purple solid on evaporation to dryness. However it was found on attempted recrystallisation that the product would

not all redissolve in dichloromethane or acetone and that some insoluble green solid was left behind. Addition of ether to the dichloromethane-acetone solution gave a microcrystalline purple solid which gave analytical results [Found: a) C, 42.2; H, 3.3; N, 5.5% (C); b) C, 40.8; H, 2.8; S, 14.3; Cl, 7.9% (B)]. These results differ appreciably in carbon content and are not consistent with any pure compound. $[C_{10}H_{10}MoClSCN]$ requires: C, 41.3; H, 3.2; N, 4.4; S, 10.0; Cl, 11.1%.] As the product was both high in S and N, and low in Cl, the analyses suggest that the purple solid was a mixture of the complexes $(\pi-C_5H_5)_2MoCl(CNS)$ and $(\pi-C_5H_5)_2Mo(CNS)_2$. In agreement, the infra-red spectrum showed typical $(\pi-C_5H_5)$ and (SCN) frequencies.

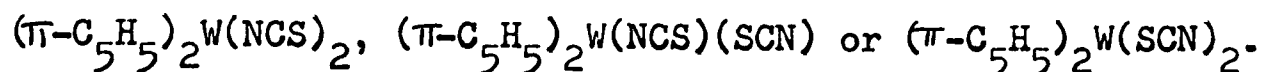
The formation of the mixture could be explained by disproportionation of the compound $(\pi-C_5H_5)_2MoCl(CNS)$, which may be the relatively pure product obtained after chromatography, into $(\pi-C_5H_5)_2Mo(CNS)_2$ and $(\pi-C_5H_5)_2MoCl_2$. The latter compound is virtually insoluble in organic solvents and this could explain the anomalous solubility properties noted above.

Bonding in the thiocyanate complexes

It is of interest to find out whether the thiocyanate ligands are S- or N- bonded to the metal in the above species, especially in the case of the two compounds 'A' and 'B' of formula $(\pi-C_5H_5)_2W(CNS)_2$ which probably differ only in this respect. All the evidence indicates that the complexes are monomeric. Thus, the mass spectral results show no peaks above the parent ion peak expected for the monomer; the infra-red spectra show $\vee$ CN frequencies in the region expected for terminal SCN groups and at lower frequencies than expected for bridging SCN groups which usually occur at

2150-2180 cm^{-1} (B11); and, the close analogy which exists to the monomeric dihydride, dibromide, disulphhydryl and organic ligand complexes on which solution molecular weights or X-ray structural analyses have been done.

Therefore 'A' and 'B' must each have one of the following formulae:



It could have been hoped that N-bonded thiocyanate ligands would have given nitrogen superhyperfine splittings in the E.S.R. spectra of their oxidised cations (cf. $(\pi\text{-C}_5\text{H}_5)_2\text{MBr}_2^+$). However, the fact that none was observed is not inconsistent with N-bonding since no splittings were observed for the postulated $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{N}_3)_2^+$ species. The halide cation $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$ does not show superhyperfine splitting and it is likely that a_{N} values would be smaller than a_{Cl} (N has a lower magnetic moment than Cl) and so would be lost in the broadness of the E.S.R. signal.

The mass spectra are also not very helpful. It must be realised that at the temperature of introduction to the spectrometer ($>200^\circ\text{C}$) considerable rearrangement at the ligand site could occur. Thus the species 'A' and 'B' show virtually identical fragmentation patterns. However it must be noted that in all thiocyanate spectra loss of sulphur occurs readily and species with CN groups are observed. If these latter species are formed from the primary complex the ready loss of S atoms could be taken to indicate N-bonding.

The usual methods of determining whether N- or S-bonding occurs (other than by X-ray structural analysis) are i) infra-red spectroscopy and ii) visible and ultra-violet spectroscopy.

i) Three regions of the infra-red spectrum have been used to determine N- or S-bonding.

a) It has been noted (B12) that CN stretching frequencies follow the

order $M-N=C=S \ll M-S-C=N < M \dots \bar{S}-C=N^+-M$ but exceptions to this order are known - e.g. $M(NH_3)_5(CNS)^{2+}$ ($M=Rh, Ir$) (B13) - and no figures are quoted. The values obtained for the bis- π -cyclopentadienyl compounds seem to be roughly comparable and since the accuracy is of the order $\pm 6 \text{ cm}^{-1}$ no deductions can be made in this region. However it must be noted that the most complex spectrum in this region ($\sim 2100 \text{ cm}^{-1}$) is possessed by $(\pi-C_5H_5)_2W(CSN)_2$, 'A'. There is also a marked lowering of ν CN for $(\pi-C_5H_5)_2WCl(CNS)$ when oxidised to $[(\pi-C_5H_5)_2WCl(CNS)]^+PF_6^-$ (2120 to 2044 cm^{-1}).

b) The C-S stretching vibration has been taken by other workers to indicate N- or S-bonding. It is found that N-bonded thiocyanates, $M-N=C=S$, exhibit absorption frequencies in the range $780-860 \text{ cm}^{-1}$ whereas S-bonded thiocyanates, $M-S-C\equiv N$, absorb in the range $690-720 \text{ cm}^{-1}$ (B14). These bands, however, are often weak and may be obscured by overtones or other ligand vibrations.

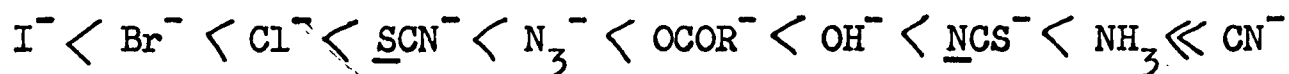
In bis- π -cyclopentadienyl complexes, only the latter region is clear of $(\pi-C_5H_5)$ frequencies and can be clearly observed. The only compound to show an absorption in the $690-720 \text{ cm}^{-1}$ region is compound 'A', $(\pi-C_5H_5)_2^-W(CNS)_2^*$ and this would indicate the presence of at least one S-bonded thiocyanate. The other compounds are probably N-bonded.

c) The SCN bending mode has also been used to assign N- or S-bonding. The respective frequencies for N- and S-bonded thiocyanates are $450-490 \text{ cm}^{-1}$ and $410-440 \text{ cm}^{-1}$ (with, possibly, other smaller peaks in a wider range) (B15). The low frequency infra-red spectra are shown in table 5 and compared with

* See table 5.

some related dihalides (A2). The absence of any $410-440\text{ cm}^{-1}$ band in $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CNS})_2$ is in accord with N-bonding. The spectra of the two tungsten species $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CNS})_2$ are rather inconclusive but the peak at 423 cm^{-1} in specimen 'B' is very weak and may be an overtone or combination band whereas specimen 'A' shows a stronger peak at 435 cm^{-1} . All compounds show peaks in the $450-490\text{ cm}^{-1}$ region and this would be consistent with M-N=C=S groups.

ii) It has been observed (B16) that d-d transitions in the ultra-violet and visible spectra of complexes of the same metal in the same oxidation state in the same steric environment shift regularly to higher energies in the following series, the spectro-chemical series:



Thus N-bonded and S-bonded thiocyanates should absorb at different frequencies.

The visible and near ultra-violet spectra of several bis- π -cyclopentadienyl compounds are recorded in table 6. The spectra generally show 2 bands, of molecular extinction coefficient (ϵ) between 10^2 and 10^3 , above $300\text{ m}\mu$. At higher energies charge transfer bands are observed of much greater intensity (cf. (A3)). It is to be noted that the second band of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CNS})_2$, product 'A', appears to have disappeared into this region.

Since ϵ values for the 2 bands are low it can be postulated, as it has been for the dihalides (B17), that the bands correspond primarily to d - d transitions with a small amount of charge transfer character. This seems especially true for the lowest energy band for which $\epsilon \sim 1-3 \times 10^2$.

No regular order is discernible in the λ_{max} values of the higher energy

Table 5

LOW FREQUENCY INFRA-RED SPECTRA OF BIS- π -CYCLOPENTADIENYL-DITHIOCYANATO AND DIHALOGENO-MOLYBDENUM AND TUNGSTEN COMPLEXES* WITH TENTATIVE ASSIGNMENTS

$(\pi-C_5H_5)_2W(CNS)_2$ 'A'	$(\pi-C_5H_5)_2W(CNS)_2$ 'B'	$(\pi-C_5H_5)_2WBr_2$ 'B'	$(\pi-C_5H_5)_2Mo(CNS)_2$	$(\pi-C_5H_5)_2MoBr_2$ 'g'	
993 m	990 m	990 w	994 m	990 w	a
964 w	960 w		953 w		
949 w	943 w				
896 w-m	885 w	873 m	886 sh	880 sh	b
840 s	840 s	833 m-s	838 s	829 s	
814 w	818 sh	808 m	826 sh	815 sh	c
700 w					
589 w	595 w	592 m	593 w	649 m	
	523 w			592 m	
463 w	458 w		459 vw		d
435 w	423 vw				
387 m	392 m	391 m		405 sh	e
366 m	369 m	357 m	396 m	389 s	e
	348 w	338 m	323 w	346 vw	e
275 sh			292 m	321 vw	e
				286 vw	f
255 m	269 m		257 m		f
	244 w-m				
221 w				222vw	f

* All thiocyanato compounds were run in CsI discs. All halogeno compounds were run in nujol mulls. $(\pi-C_5H_5)_2W(CNS)_2$ 'B' was also run in a nujol mull and the same spectrum with bands within $\pm 3\text{ cm}^{-1}$ obtained but with poorer resolution.

a C-H deformation of cyclopentadienyl ring

b π -cyclopentadienyl vibration

c C-S stretching vibration

d NCS bending vibration

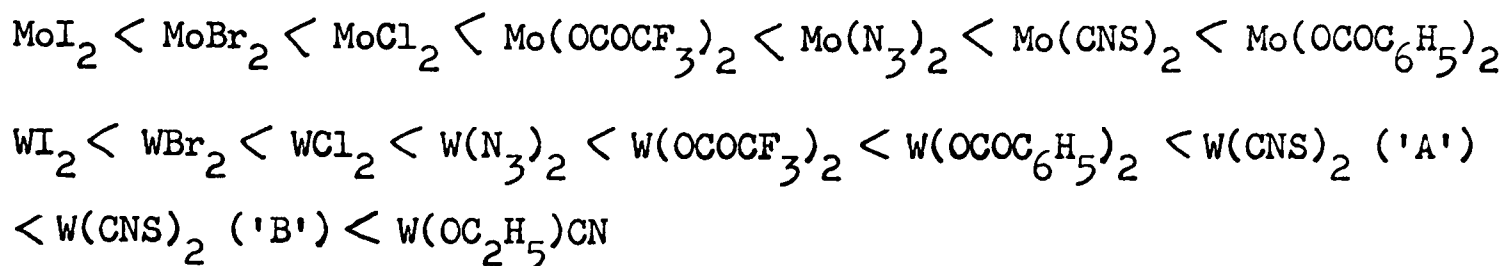
e metal-cyclopentadienyl ring vibrations

f metal-thiocyanate ligand vibrations

g the spectra of $(\pi-C_5H_5)_2WBr_2$ and

$(\pi-C_5H_5)_2MoBr_2$ were recorded by Cooper (A2)

band. However, the lower energy band gives the following energy sequences (the $(\pi-C_5H_5)$ ligands are omitted):



The two series follow approximately the order of the spectrochemical series of the known ligands. The only significant anomaly is the position of $(\pi-C_5H_5)_2Mo(OCOC_6H_5)_2$ compared to $(\pi-C_5H_5)_2Mo(OCOCF_3)_2$ and the similar tungsten compounds. This could arise from the steric effect of the large (C_6H_5) groups in the Mo complex since Mo is slightly smaller than tungsten.

The above series both indicate that the thiocyanate ligands are N-bonded. However, in the isomers $(\pi-C_5H_5)_2W(CNS)_2$, 'A' absorbs at lower energy than 'B'. Thus if the difference between 'A' and 'B' is only in the thiocyanate bonding, as postulated, 'A' must have an S-bonded thiocyanate ligand.

On the basis of all the above evidence it is suggested that all the thiocyanate ligands are N-bonded except $(\pi-C_5H_5)_2W(CNS)_2$, 'A', for which the structure $(\pi-C_5H_5)_2W(SCN)(NCS)$ is postulated. The 'H.M.R. spectra of the species 'A' and 'B' are also in accord with this suggestion. The $(\pi-C_5H_5)$ resonance of 'A' occurs at higher τ value. Thus the ring is less shielded in 'B' and this might be expected with the presence of two nitrogen bound ligands since N is more electronegative than S. Further evidence to corroborate the proposed structures based on E.S.R. results is to be found in chapter VI.

Table 6

VISIBLE AND NEAR ULTRA-VIOLET SPECTRA OF SOME BIS- π -CYCLOPENTADIENYL COMPOUNDS OF MOLYBDENUM AND TUNGSTEN

Compound	Solvent	$\lambda_{\max}^{(\text{m}\mu)}$	ϵ	$\lambda_{\max}^{(\text{m}\mu)}$	ϵ
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}$	$(\text{CH}_3)_2\text{SO}$	332 sh	340	423 sh	210
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CNS})_2^{\text{a}}$	$(\text{CH}_3)_2\text{SO}$	344	440	474	200
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CNS})_2^{\text{b}}$	$(\text{CH}_3)_2\text{SO}$	(<300)	(>2x10 ³)	490	140
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCOC}_6\text{H}_5)_2$	$(\text{CH}_3)_2\text{SO}$	324	880	513	140
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCOCF}_3)_2$	$(\text{CH}_3)_2\text{SO}$	340	350	527	100
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{N}_3)_2$	$(\text{CH}_3)_2\text{SO}$	372	410	533	210
$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^{\text{c}}$	CHCl_3	366	250	560	90
$(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2^{\text{c}}$	CHCl_3	380	150	610	110
$(\pi\text{-C}_5\text{H}_5)_2\text{WI}_2^{\text{c}}$	CHCl_3	334	5000	645	300
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OCOC}_6\text{H}_5)_2$	$(\text{CH}_3)_2\text{SO}$	424	170	536	170
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CNS})_2$	$(\text{CH}_3)_2\text{SO}$	405	250	538	
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{N}_3)_2$	$(\text{CH}_3)_2\text{SO}$	435		601	250
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OCOCF}_3)_2$	$(\text{CH}_3)_2\text{SO}$	414	180	607	130
$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^{\text{c}}$	CHCl_3	441	150	655	90
$(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2^{\text{c}}$	CHCl_3	426	300	680	230
$(\pi\text{-C}_5\text{H}_5)_2\text{MoI}_2^{\text{c}}$	CHCl_3	368	5000	702	204

a - Compound 'B' (see text)

b - Compound 'A' (see text)

c - Recorded by Cooper (A2)

D. Derivatives formed from cyanates

Several attempts were made to prepare bis- π -cyclopentadienyl cyanate complexes.

The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ with NaOCN

When $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ was refluxed in an aqueous solution of NaOCN a red solution resulted and, from this, deep red-brown crystals (m.p. 210-212 d) were obtained. These crystals were soluble in water and liquid sulphur dioxide and sparingly soluble in alcohol. The analytical results showed a stoichiometry consistent with the formula $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CH}_2\text{O}_2\text{N})_2$. However if not dried thoroughly before analysis, lower figures for C and N % were obtained and it must be concluded that the compound is hygroscopic. The mass spectrum showed a parent ion peak $M/e = 348$ assignable to $\text{C}_{10}\text{H}_{10}\text{MoC}_2\text{H}_4\text{O}_4\text{N}_2^+$ (based on ^{98}Mo) and other prominent peaks $M/e = 288$, $M/e = 244$, $M/e = 228$ and $M/e = 179$ assignable to $\text{C}_{10}\text{H}_{10}\text{MoCO}_2\text{H}_2\text{N}^+$, $\text{C}_{10}\text{H}_{10}\text{MoO}^+$ (or, less likely, $\text{C}_{10}\text{H}_{10}\text{MoNH}_2^+$), $\text{C}_{10}\text{H}_{10}\text{Mo}^+$ and $\text{C}_5\text{H}_5\text{MoO}^+$ (or less likely, $\text{C}_5\text{H}_5\text{MoNH}_2^+$). Also present were peaks due to non-metallic fragments at $M/e = 60$ and $M/e = 44$ assignable to CO_2NH_2^+ and CO_2^+ (or CONH_2^+) and also large H_2O^+ , OH^+ and NH_2^+ peaks.

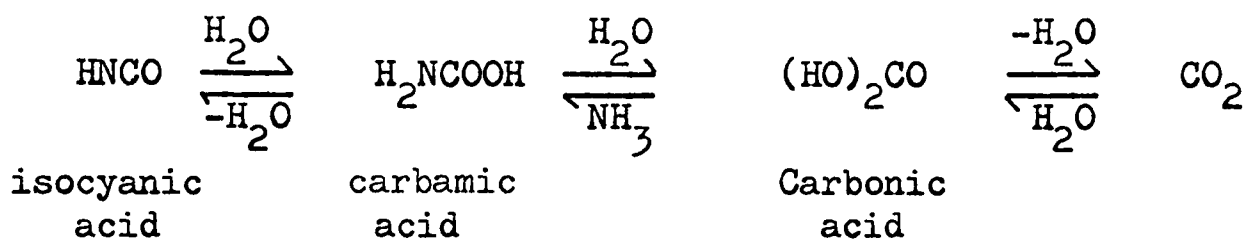
The conductivity of an approximately 10^{-3} M solution in water was low but would be correct for a weak electrolyte (N.B. the compound was not soluble in nitromethane and so the conductivity cannot be directly compared with the conductivities of other compounds).

The $^1\text{H.M.R.}$ spectrum in liquid sulphur dioxide showed one sharp singlet band, assignable to $(\pi\text{-C}_5\text{H}_5)$ protons, of relative intensity 10 and a broad band of relative intensity ~ 4 (N.B. broadness made integration difficult).

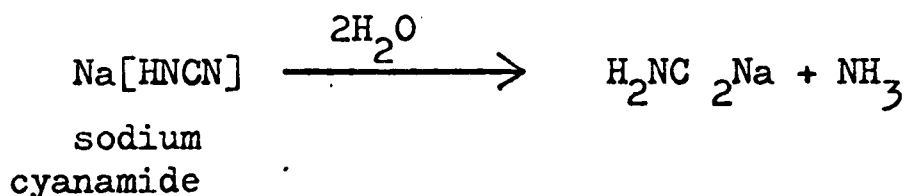
The infra-red spectrum showed typical bands of the $(\pi-C_5H_5)$ moiety and also strong absorptions at 3436 cm^{-1} , $\sim 3318\text{ cm}^{-1}$, $\sim 3200\text{ cm}^{-1}$, 1620 cm^{-1} , 1593 cm^{-1} and 1277 cm^{-1} . No absorption was noted in the region expected for $\backslash\text{NCO}$ - i.e. ca. 2200 cm^{-1} .

Thus it was inferred that the cyanate ion had been transformed in the reaction to give another species as ligand.

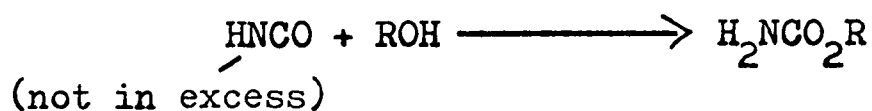
It is known that cyanates hydrolyse easily. The postulated scheme of hydrolysis for isocyanic acid is (B18):



Carbamic acid is a postulated intermediate but cannot be isolated itself or as a substituted acid, R-NHCOOH . However, salts of carbamic acid can be obtained by indirect means, e.g.:



Also esters of carbamic acid are obtainable, e.g. by the reaction:



Since carbamates are the first species formed on hydrolysis of cyanates, the molybdenum complex is postulated to have the structure $(\pi-C_5H_5)_2\text{Mo}(\text{OCONH}_2)_2$ which would fit the above experimental data.

The structures $(\pi-C_5H_5)_2\text{Mo}(\text{NHCOOH})_2$ or $(\pi-C_5H_5)_2\text{Mo}(\text{NHCOOH})(\text{OCONH}_2)$ are also possible. The presence of only one additional proton resonance to that

of (π -C₅H₅) in the 'H.M.R. spectrum would argue against these latter structures but exchange could occur between NH and OH protons and give rise to a single broad band as observed. Mass spectral peaks at $M/e = 244$, 179 and 153 probably arise from ions with Mo=O links which would favour the postulated structure. However, these could also be assigned to Mo-NH₂ linkages although one would then probably expect to see Mo=NH and Mo $\equiv$ N containing species.

The infra-red spectrum is difficult to interpret since the influence of the Mo atom is not known. However the strong bands at 1620 and 1593 cm⁻¹ are rather low for a free COOH group and are nearer the region expected for RCO₂⁻ salts (B19). When the compound was dissolved in D₂O and, then after approximately 30 minutes, the solution evaporated to dryness, the infra-red spectrum of the resulting solid showed changes from the original spectrum. The bands in the region above 3100 cm⁻¹ were reduced in intensity, but not completely, and new bands occurred at 2576, 2403 and 2361 cm⁻¹ (m-s). These had $\frac{\nu_{X-H}}{\nu_{X-D}}$ ratios with the respective ν_{X-H} bands of 1.38, 1.38 and 1.35. Other differences in the spectrum were slight, but the strong band at 1277 cm⁻¹ appeared broader in the deuterated sample and a definite shoulder appeared at ~ 1242 cm⁻¹. Assuming an $\frac{\nu_{X-H}}{\nu_{X-D}}$ ratio of ~ 1.37 , this could have arisen from exchange with an X-H group absorbing at ~ 1700 cm⁻¹. Careful inspection of the band at 1670 cm⁻¹ revealed a diminished relative intensity in the deuterated sample. This band, therefore, must be an X-H deformation - probably of an NH₂ group (B19). The compound was soluble in water and addition of silicotungstic acid to a concentrated solution gave a copious precipitate, indicating the presence of a large cation probably formed by

protonation of an -NH_2 group. Saturated NH_4PF_6 solution caused only the separation of a small amount of solid which was not enough to characterise and hexafluorophosphoric acid decomposed the compound. No change in colour of the compound occurred on basification of the aqueous solution, as might have been expected if M-NHCOOH formed a salt. Also it was noted that the compound did not liberate carbon dioxide from sodium bicarbonate in solution.

All this evidence, and comparing the compound to the compounds $(\pi\text{-C}_5\text{H}_5)_2\text{M(OCOR)}_2$ ($\text{M}=\text{Mo}, \text{W}$; $\text{R}=\text{CF}_3, \text{C}_6\text{H}_5$; - see chapter IV), makes the structure $(\pi\text{-C}_5\text{H}_5)_2\text{Mo(OCONH}_2)_2$ the most likely and argues fairly strongly against Mo-NHCOOH groups being present.

Reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with NaOCN

The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with NaOCN in water gave rise to two products.

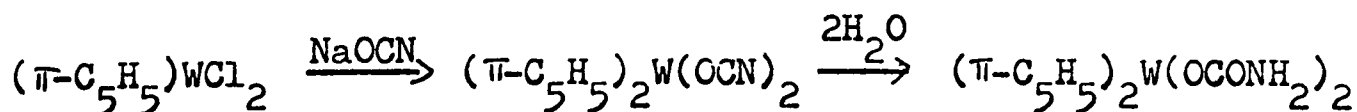
a) One product was a red-brown crystalline solid (m.p. $197\text{-}198^\circ\text{C d.}$) soluble in water, liquid sulphur dioxide and slightly in alcohol. The infra-red spectrum was similar to that of the molybdenum complex described above and the NH frequencies could be reduced in intensity by exchange in D_2O . The largest ion fragment in the mass spectrum was $M/e = 330$ and other peaks occurred at $M/e = 314$, $M/e = 304$ and $M/e = 249$ which could be assigned, respectively to $\text{C}_{10}\text{H}_{10}\text{WO}^+$, $\text{C}_{10}\text{H}_{10}\text{W}^+$, $\text{C}_8\text{H}_8\text{WO}^+$ and $\text{C}_5\text{H}_5\text{W}^+$. The $^1\text{H.M.R}$ spectrum in liquid sulphur dioxide showed a single peak attributable to $(\pi\text{-C}_5\text{H}_5)$ of relative intensity 10 and a very broad band (probably of relative intensity ~ 4). The analytical results gave C and N% low for $(\pi\text{-C}_5\text{H}_5)_2\text{W(OCONH}_2)_2$ but consistent for such a complex containing one molecule of water of crystallisation. It has been noted that $(\pi\text{-C}_5\text{H}_5)_2\text{Mo(OCONH}_2)_2$

is hygroscopic and thus the formula $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCONH}_2)_2 \cdot \text{H}_2\text{O}$ is postulated.

b) Another compound was formed in the reaction. This compound was water insoluble and could only be obtained in any reasonable quantity if the reaction proceeded for just a few minutes at refluxing temperature. It was observed as a dark red solid but further reaction resulted in its dissolution and, thus, it may be inferred that it is an intermediate in the formation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCONH}_2)_2$. Recrystallisation from liquid sulphur dioxide in which it was soluble gave deep red microcrystals (d 215-220°C). The mass spectrum of this compound showed a large parent ion peak $M/e = 398$ corresponding to $\text{C}_{10}\text{H}_{10}\text{W}(\text{OCN})_2^+$ and other peaks, $M/e = 356$, $M/e = 333$, $M/e = 305$ and $M/e = 278$ assignable to $\text{C}_{10}\text{H}_{10}\text{WOCN}^+$, $\text{C}_5\text{H}_5\text{W}(\text{OCN})_2^+$, $\text{C}_5\text{H}_5\text{WO}_2\text{C}_2^+$ and $\text{C}_3\text{H}_2\text{WO}_2\text{C}_2^+$ (?) respectively.

The infra-red spectrum showed typical $(\pi\text{-C}_5\text{H}_5)$ frequencies and a strong band at 2260 cm^{-1} assignable to an NCO stretching vibration. No bands assignable to CO_2 or NH frequencies were observed but a weak very broad band in the region $3000\text{-}3600$ and a small band at $\sim 1630\text{ cm}^{-1}$ were present which could be caused by hydrogen bonded H_2O . Analytical results gave a stoichiometry which could be explained by the formula $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCN})_2 \cdot \text{H}_2\text{O}$, suggesting that up to one molecule of crystallisation is present in the compound, the infra-red spectrum suggests that the water is hydrogen bonded to the cyanato ligands.

The formation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCN})_2$ first, leads to the propositions either that the compound $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCONH}_2)_2$ (and the molybdenum analogue) is formed by the sequence



or that the anion OCNH_2^- is more slowly formed in solution and subsequently displaces OCN ligands.

The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with NaOCN in an acetone-ethanol medium gave, after purification, a pink coloured microcrystalline solid which was probably a mixture of $(\pi\text{-C}_5\text{H}_5)_2\text{W(CNO)}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{WCl(CNO)}$ as shown by analysis and infra-red spectrum.

E. Other reactions of bis- π -cyclopentadienyl molybdenum and tungsten compounds

Several small scale reactions of the neutral or cationic bis- π -cyclopentadienyl dihalides with 40% hydrofluoric acid led to no readily isolable fluoro derivative.

The reaction of a mixture of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with silver monofluoride, AgF, in 1:2 molar ratio in reagent grade acetone at room temperature gave a deep blue solution after 10-15 minutes. A blue solid was separated but this could not be purified by chromatography and was difficult to crystallise as it readily decomposed giving insoluble material. It was, therefore, uncharacterised and may be an oxy Mo(VI) species formed by oxidation with Ag(I) rather than a fluoro derivative. However it gave no E.S.R. signal in solution.

The formation and the E.S.R. spectra of mixed halide derivatives are reported in chapters V and VI.

F. Discussion

The work described in this chapter indicates that the $(\pi\text{-C}_5\text{H}_5)_2\text{M}$, (M=Mo, W), system can act as an acceptor of several pseudo-halide ligands to give stable, neutral complexes analogous to the dihalides, $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2$,

although in some solvents side reactions occur and the major product is not the single dipseudo-halide.

However, cationic species analogous to $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$ (X=Cl, Br, M=Mo, W) do not seem to be so readily formed. The only well characterised cation reported is $(\pi\text{-C}_5\text{H}_5)_2\text{WCl(NCS)}^+$. The stability of this can be readily explained by the presence of the more electronegative Cl ligand. There is also good evidence for cation formation on oxidation of the species $(\pi\text{-C}_5\text{H}_5)_2\text{W(CNS)}_2$ 'A' and 'B' although the resulting products were not fully characterised. However the analogous molybdenum complex gave no indication of cation formation on chemical oxidation and this appears to show that tungsten species are more stable in higher oxidation states than related molybdenum species, as might be expected. The diazide complexes show evidence for cation formation but the paramagnetic species formed were rather unstable and again were not fully characterised.

The evidence presented which seems to indicate that M-N bonds predominate in thiocyanate complexes suggests that the $(\pi\text{-C}_5\text{H}_5)_2\text{M}$ systems act as hard acids. However this result appears to contradict the readiness of the systems to complex with thio ligands (A3). A similar anomaly occurs with $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}$ (A45, A44). Thus the complexes, in the formally 4 oxidation state, show both hard and soft character.

Table 7

PROTON MAGNETIC RESONANCE SPECTRA OF COMPOUNDS DESCRIBED IN CHAPTER II

Compound	Solvent	τ value ^a	Intensity ^b	Fine Structure	Assignment
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{N}_3)_2$	$(\text{CH}_3)_2\text{CO}$	4.35		singlet	$\pi\text{-C}_5\text{H}_5$
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{N}_3)_2$	CDCl_3	4.44		singlet	$\pi\text{-C}_5\text{H}_5$
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}$	CDCl_3	4.58	10	singlet	$\pi\text{-C}_5\text{H}_5$
		6.62	2	quartet	CH_2
		9.21	3	triplet	CH_3
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCH}_3)\text{CN}$	CDCl_3	4.58	10	singlet	$\pi\text{-C}_5\text{H}_5$
		6.68	3	singlet	CH_3
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NCS})_2$	SO_2	4.10		singlet	$\pi\text{-C}_5\text{H}_5$
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CNS})_2$ 'A'	SO_2	4.32		singlet	$\pi\text{-C}_5\text{H}_5$
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CNS})_2$ 'B'	SO_2	4.22		singlet	$\pi\text{-C}_5\text{H}_5$
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})\text{Cl}$	$(\text{CH}_3)_2\text{CO}$	4.39		singlet	$\pi\text{-C}_5\text{H}_5$
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OCONH}_2)_2$	SO_2	4.29	10	singlet	$\pi\text{-C}_5\text{H}_5$
		~ 5.4	~ 4	broad	NH_2
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCONH}_2)_2$	SO_2	4.25		singlet	$\pi\text{-C}_5\text{H}_5$
		~ 5.5		very broad	$\text{NH}_2(?)$

a - relative to T.M.S. as internal standard

b - relative to $(\pi\text{-C}_5\text{H}_5)$ band = 10

Table 8

MASS SPECTRA OF COMPOUNDS DESCRIBED IN CHAPTER II

$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}^a$			$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCH}_3)\text{CN}^a$		
M/e	rel.int. ^b	assignment ^e	M/e	rel.int. ^b	assignment ^e
385	26	$\text{C}_{10}\text{H}_{10}\text{WOC}_2\text{H}_5\text{CN}^+$	420	3	$\text{W}_2(\text{CN})_2^+ ?$
356	100	$\text{C}_{10}\text{H}_{10}\text{WOCN}^+$	418	3	$\text{W}_2\text{CCN}^+ ?$
340	18	$\text{C}_{10}\text{H}_{10}\text{WCN}^+$	371	38	$\text{C}_{10}\text{H}_{10}\text{WOCH}_3\text{CN}^+$
329	15	$\text{C}_{10}\text{H}_x\text{WO}^+ ?$	356	100	$\text{C}_{10}\text{H}_{10}\text{WOCN}^+$
328	15		340	25	$\text{C}_{10}\text{H}_{10}\text{WCN}^+$
327	17		329	13	$\text{C}_{10}\text{H}_x\text{WO}^+ ?$
314	10	$\text{C}_{10}\text{H}_{10}\text{W}^+$	327	13	
301	24	$\text{C}_7\text{H}_7\text{WCN}^+ ?$	314	28	$\text{C}_{10}\text{H}_{10}\text{W}^+$
291	9	$\text{C}_5\text{H}_5\text{WOCN}^+$	301	20	$\text{C}_7\text{H}_7\text{WCN}^+ ?$
289	13	?	287	17	$\text{C}_6\text{H}_5\text{WCN}^+ ?$
287	10	?	277	22	$\text{C}_5\text{H}_5\text{WOC}^+$
285	10	?	265	33	$\text{C}_5\text{H}_5\text{WO}^+$
275	7	$\text{C}_5\text{H}_5\text{WCN}^+$	263	35	$\text{C}_5\text{H}_5\text{WN}^+ ?$
265	43	$\text{C}_5\text{H}_5\text{WO}^+$	249	16	$\text{C}_5\text{H}_5\text{W}^+$
249	7	$\text{C}_5\text{H}_5\text{W}^+$	238	11	$\text{CWOCN}^+ ?$
238	11	$\text{CWOCN}^+ ?$	222	8	$\text{CWCN}^+ ?$
222	3	$\text{CWCN}^+ ?$	210	3	WCN^+
170	10	$\text{C}_{10}\text{H}_{10}\text{WO}^{++}$	200	2	WO^+
156.5	7	$\text{C}_{10}\text{H}_9\text{W}^{++}$	184	1	W^+
65	11	C_5H_5^+	170.5	6	$\text{C}_{10}\text{H}_{10}\text{WOH}^{++}$
39	14	C_3H_3^+	157	11	$\text{C}_{10}\text{H}_{10}\text{W}^{++}$
			65	13	C_5H_5^+

Table 8 - continued

$(\pi\text{-C}_5\text{H}_5)_2\text{W(NCS)Cl}^c$			$(\pi\text{-C}_5\text{H}_5)_2\text{Mo(OCONH}_2)_2^d$		
M/e	rel.int. ^b	assignment ^e	M/e	rel.int. ^b	assignment ^e
430	2	$\text{C}_{10}\text{H}_{10}\text{W(NCS)}_2^+$	348	9	$\text{C}_{10}\text{H}_{10}\text{Mo(OCONH}_2)_2^+$
407	27	$\text{C}_{10}\text{H}_{10}\text{W(NCS)Cl}^+$	289	9	$\text{C}_{10}\text{H}_{10}\text{MoH(OCONH}_2)^+$
384	29	$\text{C}_{10}\text{H}_{10}\text{WCl}_2^+$	288	10	$\text{C}_{10}\text{H}_{10}\text{Mo(OCONH}_2)^+$
375	5	$\text{C}_{10}\text{H}_{10}\text{WNCCl}^+$	263	14	$\text{C}_8\text{H}_8\text{MoH(OCONH}_2)^+$
372	5	$\text{C}_{10}\text{H}_{10}\text{WNCS}^+$	244	100	$\text{C}_{10}\text{H}_{10}\text{MoO}^+$
349	100	$\text{C}_{10}\text{H}_{10}\text{WCl}^+$	228	99	$\text{C}_{10}\text{H}_{10}\text{Mo}^+$
342	7	$\text{C}_5\text{H}_5\text{WNCSCl}^+$	214	30	$\text{C}_9\text{H}_8\text{Mo}^+ ?$
319	35	$\text{C}_5\text{H}_5\text{WCl}_2^+$	179	39	$\text{C}_5\text{H}_5\text{MoO}^+$
314	12	$\text{C}_{10}\text{H}_{10}\text{W}^+$	153	15	$\text{C}_3\text{H}_3\text{MoO}^+$
293	17	$\text{C}_3\text{H}_2\text{WCl}_2^+ ?$	66	68	C_5H_6^+
284	12	$\text{C}_5\text{H}_5\text{WCl}^+$	65	29	C_5H_5^+
269	4		64	53	$\text{C}_5\text{H}_4^+ ?$
256	12		60	$>10^3$	OCONH_2^+
245	3	$\text{WClCN}^+ ?$	44	v.strong	CO_2^+
220	2	$\text{HWCl}^+ ?$	(strong peaks below 30)		
203.5	2	$\text{C}_{10}\text{H}_{10}\text{WNCSCl}^{++}$			
174.5	13	$\text{C}_{10}\text{H}_{10}\text{WCl}^{++}$			
(many small peaks in region 55-74 and below 45.)					

Table 8 - continued

$(\pi\text{-C}_{55})_2\text{W(OCN)}_2^a$			$(\pi\text{-C}_{55})_2\text{W(OCN)}_2$ - continued		
M/e	rel.int. ^b	assignment ^e	M/e	rel.int. ^b	assignment ^e
398	100	$\text{C}_{10}\text{H}_{10}\text{W(OCN)}_2^+$	129	2	double ion (?)
356	24	$\text{C}_{10}\text{H}_{10}\text{WOCN}^+$	66	25	C_5H_6^+
333	32	$\text{C}_5\text{H}_5\text{W(OCN)}_2^+$	65	22	C_5H_5^+
330 (?)	10	$\text{C}_{10}\text{H}_{10}\text{WO}^+$	44	30	CO_2^+
314	10	$\text{C}_{10}\text{H}_{10}\text{W}^+$	43	30	HNCO^+
305	96	$\text{C}_5\text{H}_5\text{W(OC)}_2^+$	39	23	C_3H_3^+
301	11	$\text{C}_5\text{H}_5\text{W(NC)}_2^+$			
288	7	$\text{C}_8\text{H}_8\text{W}^+$			
278	36	$\text{C}_3\text{H}_2\text{W(OC)}_2^+ ?$			
275 (?)	10	$\text{C}_5\text{H}_5\text{WCN}^+$			
265	11	$\text{C}_5\text{H}_5\text{WO}^+$			
250	17	$\text{C}_5\text{H}_5\text{WH}^+$			
235	9	$\text{C}_3\text{H}_3\text{WC}^+ ?$			
223	12	$\text{C}_3\text{H}_3\text{W}^+$			
222	12	$\text{C}_3\text{H}_2\text{W}^+$			
199	7	$\text{C}_{10}\text{H}_{10}\text{W(OCN)}_2^{++}$			
178	4	$\text{C}_{10}\text{H}_{10}\text{WOCN}^{++}$			
164	2	$\text{C}_{10}\text{H}_8\text{WO}^{++} ?$			
157	3	$\text{C}_{10}\text{H}_{10}\text{W}^{++}$			
150	4	$\text{C}_5\text{H}_4\text{W(NC)}_2^{++} ?$			
149	5	double ion (?)			

Table 8 - continued

$(\pi-C_5H_5)_2Mo(NCS)_2^d$			$(\pi-C_5H_5)_2W(CNS)_2^a, 'A'$		
M/e	rel.int. ^b	assignment ^e	M/e	rel.int. ^b	assignment ^e
344	3	$C_{10}H_{10}Mo(NCS)_2^+$	430	71	$C_{10}H_{10}W(CNS)_2^+$
312	4	$C_{10}H_{10}MoN_2C_2S^+$	398	4	$C_{10}H_{10}WN_2C_2S^+$
286	22	$C_{10}H_{10}MoNCS^+$	372	100	$C_{10}H_{10}WNCS^+$
254	31	$C_{10}H_{10}MoNC^+$	365	5	$C_5H_5W(NCS)_2^+$
242	5	$C_{10}H_{10}MoN^+$	345 (?)	34	$C_{10}H_xWS^+ ?$
228	100	$C_{10}H_{10}Mo^+$	344 (?)	26	
162	12	$C_5H_4Mo^+ ?$	340	20	$C_{10}H_{10}WNC^+$
136	14	$C_3H_2Mo^+ ?$	314	42	$C_{10}H_{10}W^+$
114	7	$C_{10}H_{10}Mo^{++}$	307	17	$C_5H_5WNCS^+$
98	12	Mo^+	281	18	$C_5H_5WS^+$
76	21	CS_2^+	279 (?)	20	?
65	34	$C_5H_5^+$	254 (?)	7	$C_3H_2WS^+ ?$
59	70	$HNCS^+$	186	18	$C_{10}H_{10}WNCS^{++}$
44	22	CS^+	172.5(?)	4	$C_{10}H_xWS^{++} ?$
39	62	$C_3H_3^+$	172	6	

(several peaks at lower M/e values.
Also peaks observed at
 $M/e = 321, 263, 198$ assignable
to chloro-molybdenum species.)

(many peaks due to organic fragments
in lower region)

Table 8 - continued

$(\pi\text{-C}_{55}\text{H}_{52})\text{W}(\text{NCS})_2^a$, 'B'			$(\pi\text{-C}_{55}\text{H}_{52})\text{W}(\text{NCS})_2$, 'B' - cont.		
M/e	rel.int. ^b	assignment ^e	M/e	rel.int. ^b	assignment ^e
430	64	$\text{C}_{10}\text{H}_{10}\text{W}(\text{CNS})_2^+$	215	5	$\text{C}_{10}\text{H}_{10}\text{W}(\text{CNS})_2^{++}$
398	7	$\text{C}_{10}\text{H}_{10}\text{WN}_2\text{C}_2\text{S}^+$	186	25	$\text{C}_{10}\text{H}_{10}\text{WNCS}^{++}$
372	100	$\text{C}_{10}\text{H}_{10}\text{WNCS}^+$	172.5	5	$\text{C}_{10}\text{H}_x\text{WS}^{++} ?$
345 (?)	37	$\text{C}_{10}\text{H}_x\text{WS}^+ ?$	172	5	
344 (?)	28		157	6	$\text{C}_{10}\text{H}_{10}\text{W}^{++}$
340	26	$\text{C}_{10}\text{H}_{10}\text{WNC}^+$	65	15	C_5H_5^+
318 (?)	10	$\text{C}_8\text{H}_6\text{WS}^+ ?$	64	65	$\text{S}_2^+ ?$
314	25	$\text{C}_{10}\text{H}_{10}\text{W}^+$	59	37	HNCS^+
307	16	$\text{C}_5\text{H}_5\text{WNCS}^+$	48	29	$\text{H}_2\text{NS}^+ ?$
281	17	$\text{C}_5\text{H}_5\text{WS}^+$	44	34	CS^+
279 (?)	17	?	39	25	C_3H_3^+
254 (?)	7	$\text{C}_3\text{H}_2\text{WS}^+ ?$	(many small peaks in region $M/e = 55-100$ and < 40)		

a - All M/e values for W species based on isotope ^{184}W .

b - Relative intensity, based on largest M/e (for metal containing species) = 100.

c - All M/e values for Cl species based on isotope ^{35}Cl .

d - All M/e values for Mo species based on isotope ^{98}Mo .

e - Tentative assignment - most chemically probable fragment to fit M/e value (cf. B20).

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Chapter III

π -CYCLOPENTADIENYL COMPOUNDS OF MOLYBDENUM AND TUNGSTEN WITH PENTAFLUOROPHENYL OR PHENYL LIGANDS

The similarity between the electronegativity of the pentafluorophenyl radical and that of chlorine or bromine (C1) led to the suggestion that pentafluorophenyl compounds of molybdenum and tungsten (similar to the known titanium complexes (A90)) could probably be made which, like the complexes $(\pi\text{-C}_5\text{H}_5)\text{MX}_2$, (X = Cl, Br), would oxidise to give paramagnetic cations. The preparation of several pentafluorophenyl complexes is reported in this chapter.

The existence of these pentafluorophenyl complexes prompted the study of probable, related phenyl derivatives and some rather unstable phenyl complexes of molybdenum and tungsten are also described.

A. Pentafluorophenyl derivatives of bis π -cyclopentadienyl molybdenum and tungsten

a) The reaction of $\text{C}_6\text{F}_5\text{Li}$ with $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ in 2:1 molar proportions in ether gave rise to one major product (product 'A' in Chapter VII) which, although difficult to purify, could be obtained as yellow, air unstable microcrystals (m.p. $105\text{-}106^\circ\text{C}$, d). This solid was very soluble in ether, benzene, chloroform (in which it was not decomposed after several hours) and methanol, fairly soluble in petrol and insoluble in water. The elemental analysis of the complex indicated a stoichiometry corresponding to the formula $\text{C}_{22}\text{H}_{10}\text{F}_{10}\text{Mo}$ and a molecular weight in chloroform solution showed the compound to be monomeric (found 571, required 560).

The infra red spectrum of the complex showed bands that could be assigned to (π -C₅H₅), (e.g. 3146 sh, 3132 cm⁻¹), and other bands that may arise from the C₆F₅ group (e.g. 1629, 1531, 1497, 1058, 1047, 978 and 958 cm⁻¹ (C1, C2, A90)). Also, a weak band occurred at 1926 cm⁻¹ which could be due to $\backslash$ Mo-H.

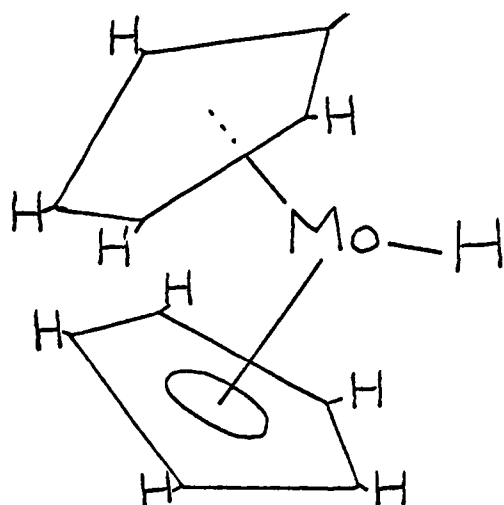
NMR* spectroscopy of the compound threw most light upon its structure. The ¹H.M.R. spectrum at room temperature (25°C) is shown in Figure 1. There is one sharp peak at τ = 5.23 of relative intensity 5 which may be assigned to a π -C₅H₅ group. However around this sharp peak are 4 broad bands of which the two overlapping bands at τ = 4.5 and 4.6 have total relative intensity of 2 and the single bands at τ = 5.05 and 5.41 (which under high resolution seemed to have some fine structure) each have relative intensity values of 1. In addition to these bands a doublet (J = 7.4 c/s) of relative intensity 1 was observed at τ = 16.99. The spectrum was run at 100 Mc/s and 60 Mc/s and no change occurred in the doublet splitting of the high field band and hence the splitting must be due to a coupling process and not to two protons of different chemical shifts. At 60 Mc/s the two bands at τ = 4.5 and 4.6 merged into a broader singlet showing these to be 2 separate proton resonances. It is almost certain that the high field resonance is due to a hydrogen attached to the molybdenum.

Varying the temperature changes the ¹H.M.R. spectrum. Two spectra (in the π -C₅H₅ absorption region), at low temperatures, are shown in Figures 2 and 3. The broad overlapping bands occurring at τ = 4.5 and 4.6 at room

* See table 9 for all ¹H.M.R. spectra of compounds described in chapter III.

temperature become more resolved and the band at $\tau = 5.05$ coalesces with the $\pi\text{-C}_5\text{H}_5$ band on cooling. It was also noticed that on warming to $50\text{-}60^\circ\text{C}$ the two bands at $\tau = 4.5$ and 4.6 (at 25°C) merged into one broader band. This temperature dependence of the spectrum suggests that an intramolecular motion, with an energy barrier that is significant at the temperatures used, is present in the molecule.

The doublet splitting of the hydride resonance must be due, either to interaction with another single hydrogen atom or with a single fluorine atom. No other proton resonances at high fields were observed. Therefore, probably no other metal hydride protons are present and relative intensity measurements will account for 10 hydrogen atoms as suggested by analysis and mass spectrum (see below). It is, therefore, likely that the doublet splitting is due to a unique fluorine atom and the other 9 hydrogen atoms are attached to carbon atoms of cyclopentadienyl rings. A fragment of the molecule being:



The ^{19}F .M.R. spectrum of the compound in CHCl_3 was recorded at both 100 Mc/s and 56.4 Mc/s.

At 100 Mc/s the spectrum obtained is shown in Figures 4(a)-(e). The two triplet bands at 89.65 and 91.02 ppm (above $\text{C}_6\text{H}_5\text{CF}_3$) may be assigned

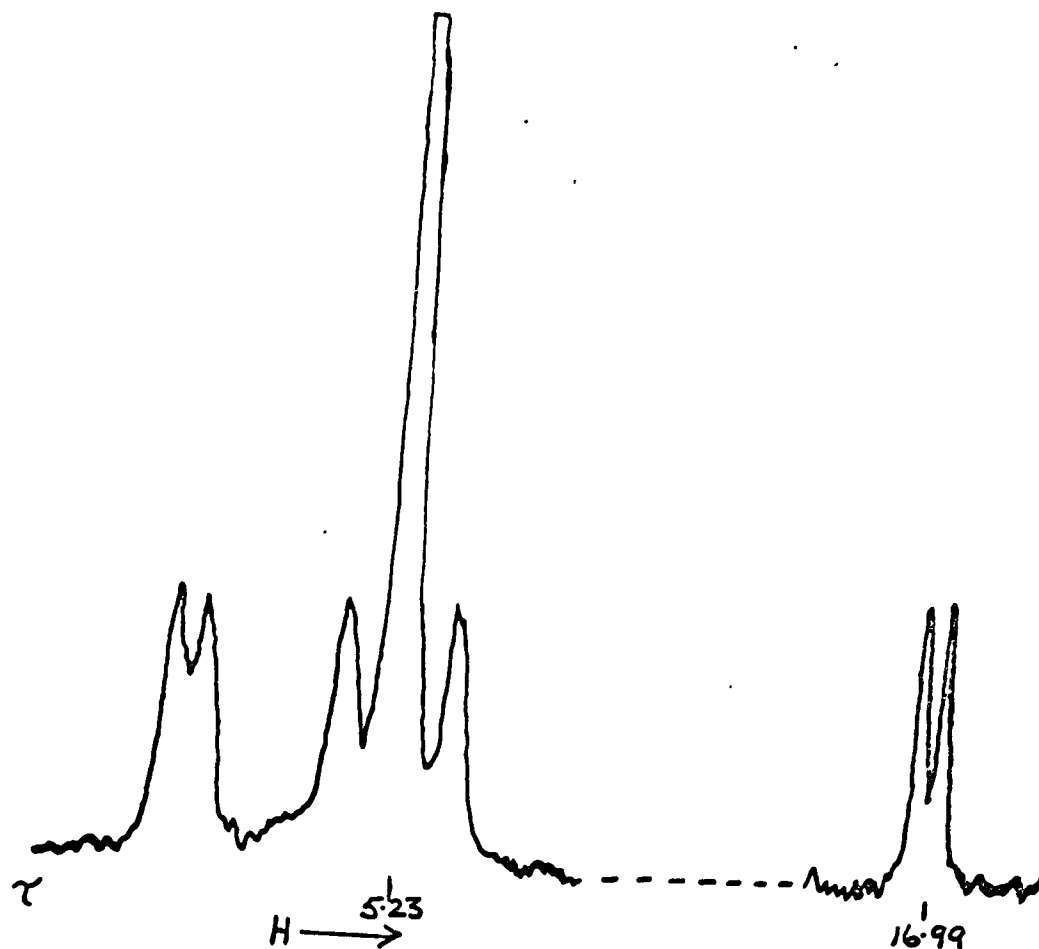


Figure 1. Proton magnetic resonance spectrum of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_6\text{F}_5)$ in CDCl_3 at 25°C .

Figure 2
 $\sim 0^\circ - -10^\circ\text{C}$

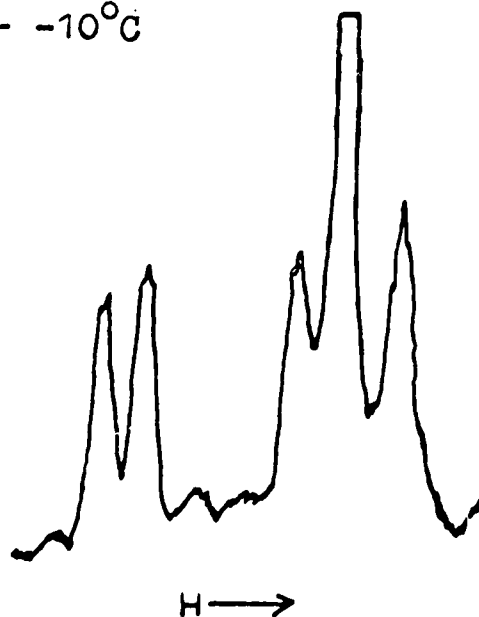
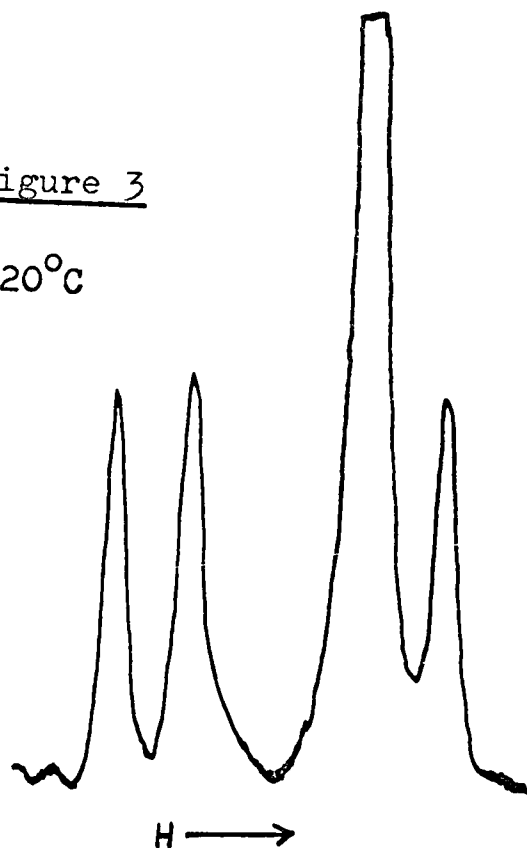
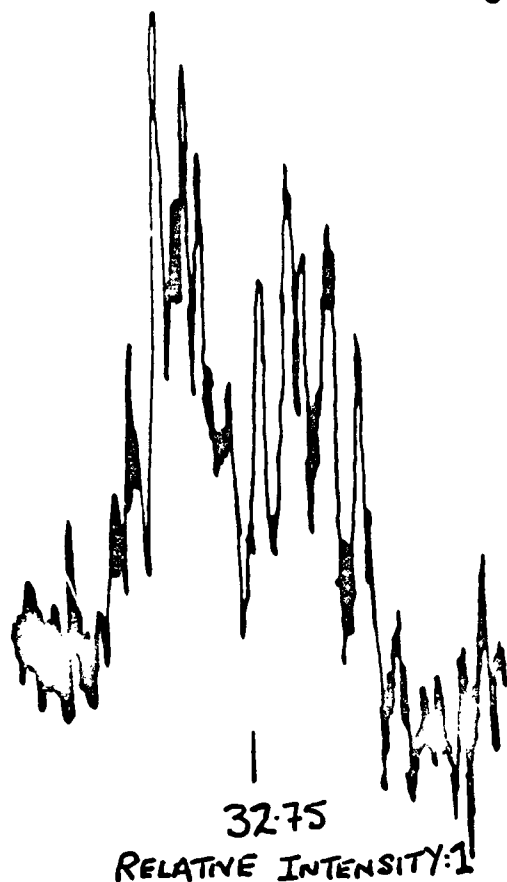


Figure 3
 $< -20^\circ\text{C}$



Proton magnetic resonance spectra of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_6\text{F}_5)$ in CDCl_3 at low temperatures.

(a)



(b)

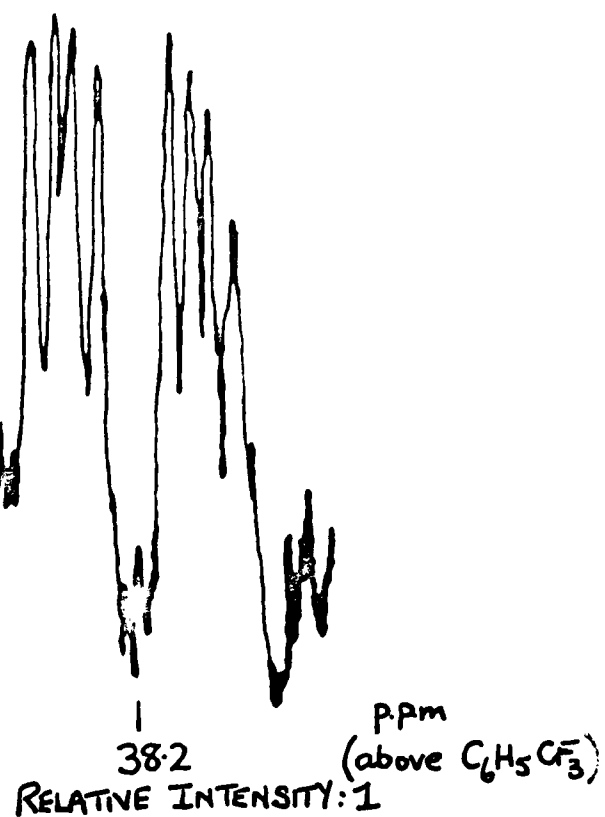


Figure 4

Fluorine magnetic
resonance spectrum of
 $(\pi-C_5H_5)(\pi-C_5H_4C_6F_5)MoH(C_6F_5)$
in $CDCl_3$ at 100 Mc/s.,
at room temperature.

(c)

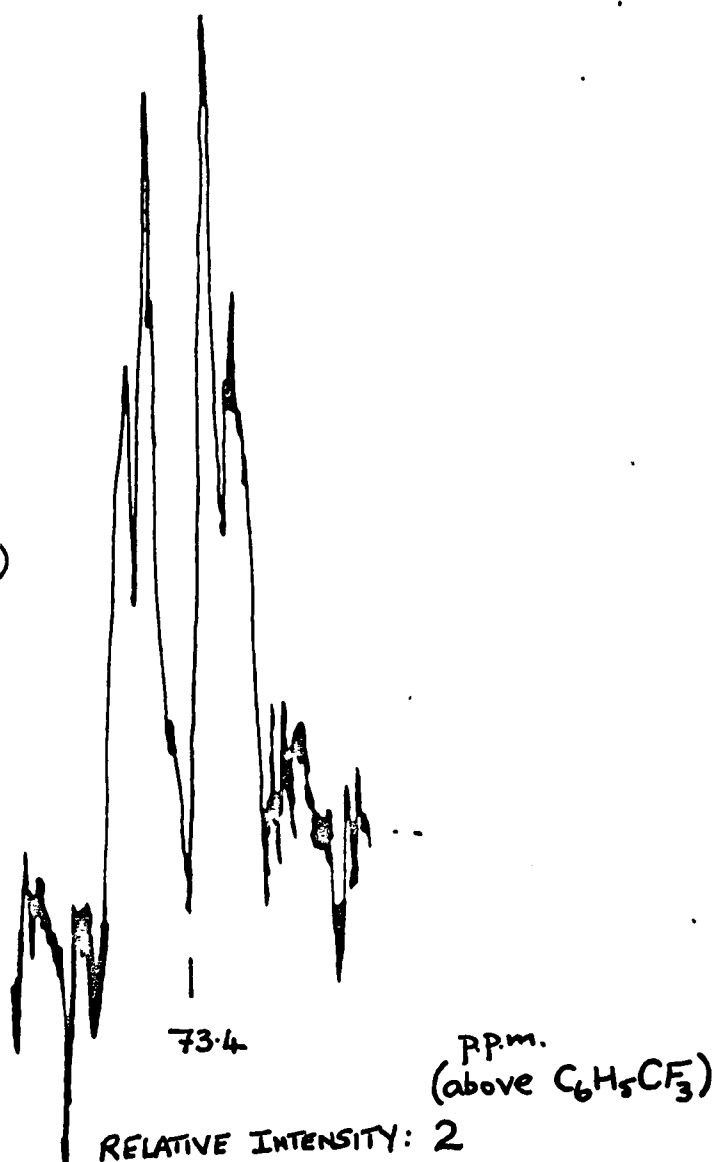
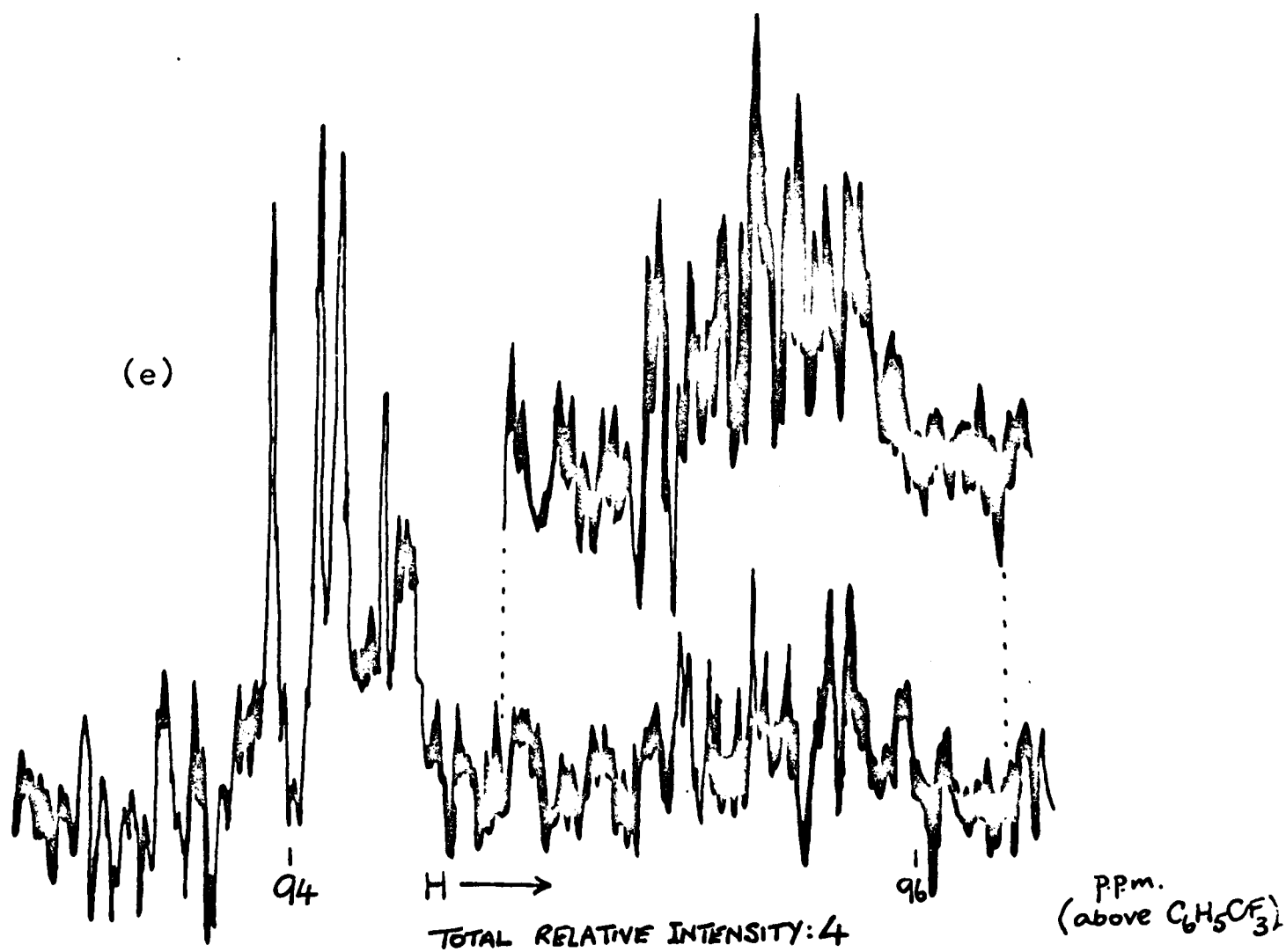
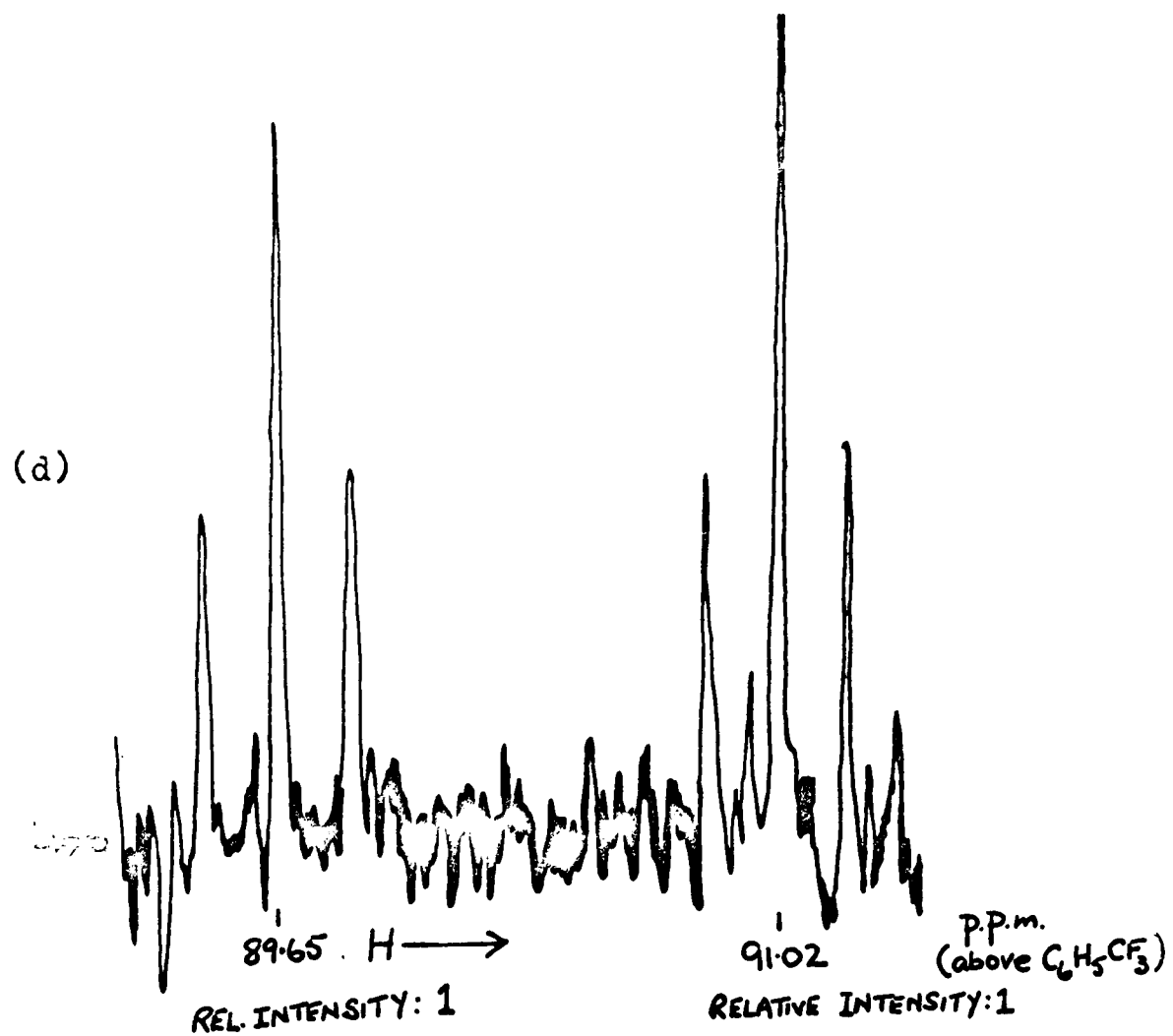


Figure 4 - continued



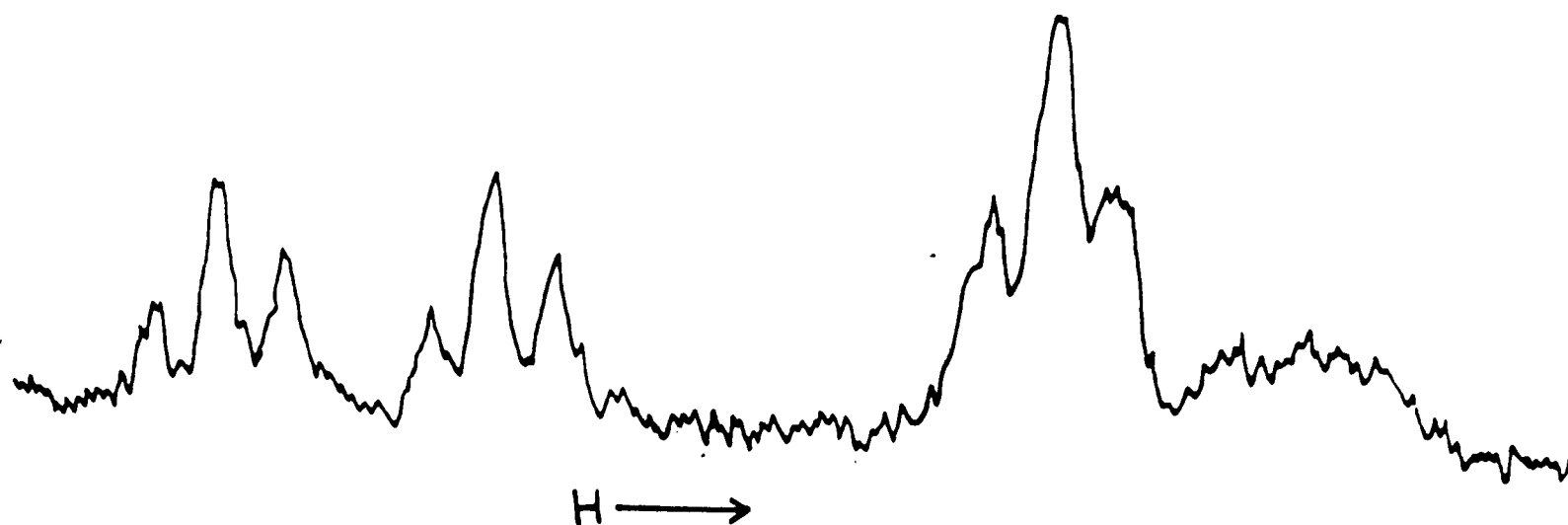
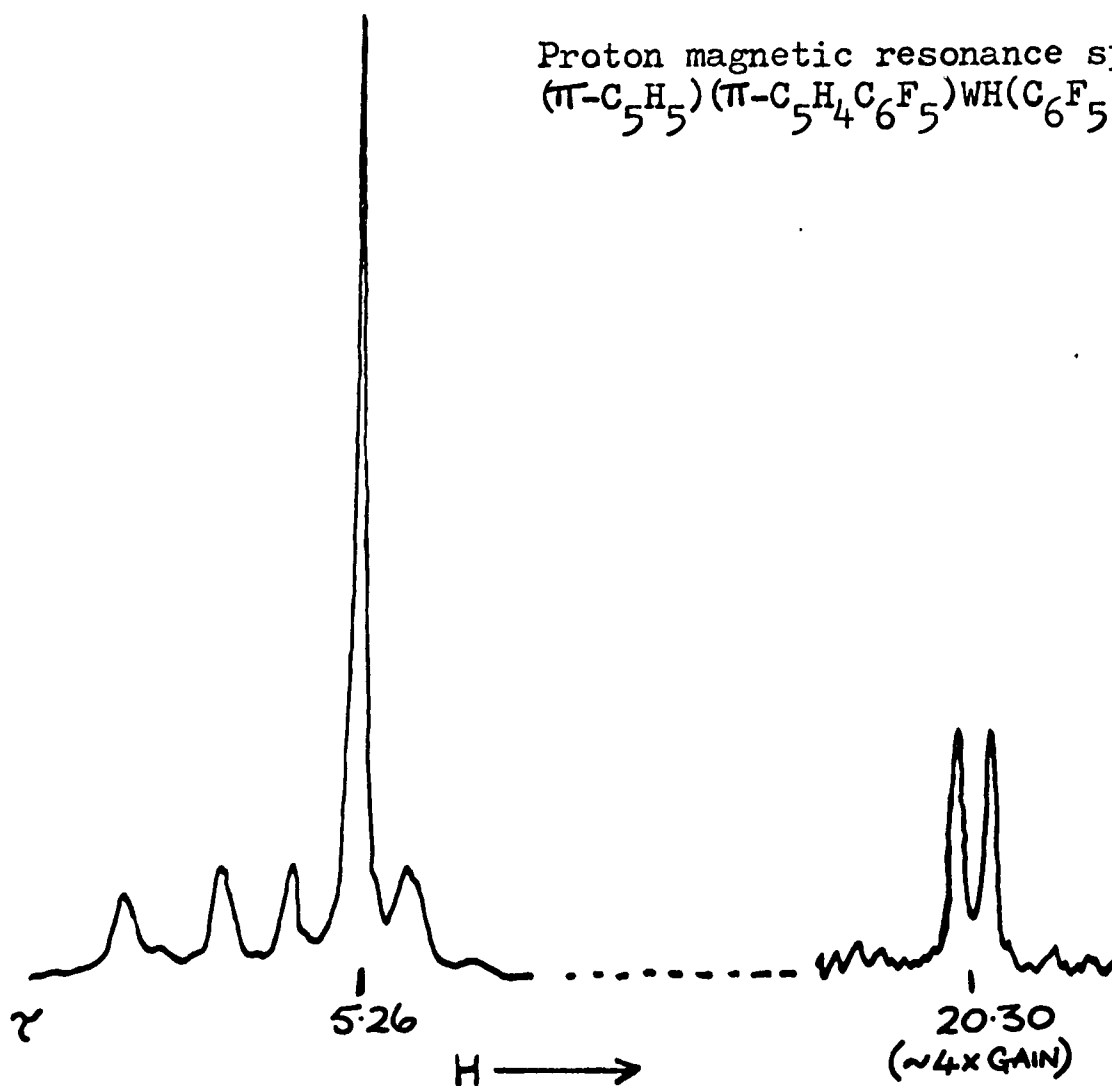


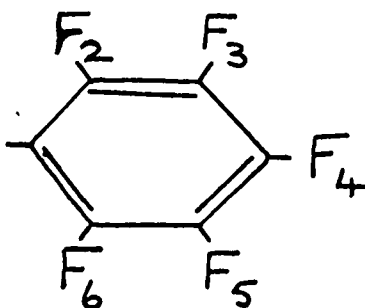
Figure 5. High field bands of fluorine magnetic resonance spectrum of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_6\text{F}_5)$ at 56.4 Mc/s., at room temperature.

Figure 6.

Proton magnetic resonance spectrum of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WH}(\text{C}_6\text{F}_5)$ at 35°C.



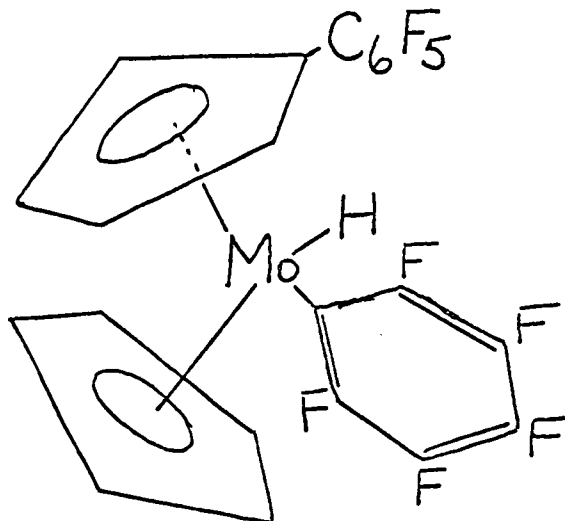
to para fluorine atoms in two different pentafluorophenyl rings (with $J_{34} = 21.1$ and 20.0 c/s respectively and $J_{24} \sim 0$).



The complex band at higher fields (94-96 ppm) must be assigned to meta-fluorine atoms (compare known pentafluorophenyl compounds - meta- and para-fluorine resonances usually occur at comparable chemical shifts and the meta usually occur at higher fields whereas ortho-fluorine resonances occur at much lower fields ($\sim 20-40$ ppm). (C1, C3, C4.)). The band at 73.4 ppm seems to be showing second order effects but is at the position expected for an ortho-fluorine resonance of a normal organic pentafluorophenyl compound. The two bands at 32.75 and 38.2 ppm are at rather low fields but it is known that low field ortho-fluorine shifts occur when pentafluorophenyl groups are bonded to transition metals (C1) and it is likely that these bands are due to ortho-fluorine atoms of $\text{Mo-C}_6\text{F}_5$. No other fluorine resonances were observed when the spectrometer was swept from very low to very high fields so that metal bonded fluorine atoms are probably absent (metal fluorides have fluorine resonances at low fields (e.g. C5)). The relative intensities of the peaks could not be measured accurately at 100 Mc/s and the compound was also run at 56.4 Mc/s at which intensity measurements were possible. The spectrum at 56.4 Mc/s was essentially the same as that at 100 Mc/s and although the resolution was not so good splittings appeared to be approximately the same. The intensities are given

under figures 4 and 5.

The ^{19}F .M.R. and ^1H .M.R. data can be explained by a structure:



One of the triplets at 89.65 or 91.08 ppm is due to the para-fluorine of the $\text{C}_5\text{H}_4\text{C}_6\text{F}_5$ group and the ortho-fluorine resonance occurs at 73.4 ppm. The larger peaks at the lower field side of the complex band must be assigned to the meta-fluorines of this group and this band should be split by $J_{34} = 20.0$ (or 21.1) c/s and J_{23} and J_{25} but it is impossible to ascertain these values by inspection.

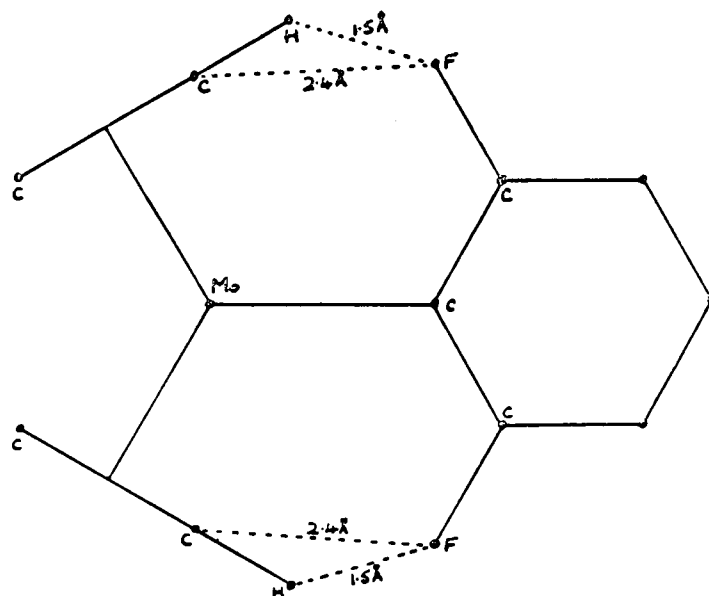
The pentafluorophenyl ring attached to the molybdenum atom has a para-fluorine resonance at 91.08 (or 89.65) ppm, but it appears that the meta- and ortho-fluorine atoms are individually inequivalent. The complex band between 94-95 ppm contains 2 broad multiplet signals of total relative intensity 2. The separation of these signals in cycles/sec. increases on going from 56.4 to 100 Mc/s suggesting that they are due to two separate resonances and may be assigned to 2 inequivalent meta-fluorine atoms. The 2 low field peaks, each of relative intensity 1, may be assigned to 2 non-equivalent ortho-fluorine atoms. The band at 38.2 ppm can be reproduced by 3 coupling constants, $J_{23} \sim 34$ c/s, $J_{25} \sim 10$ c/s, $J_{26} \sim 6$ c/s. The band at 32.75 ppm is more complex and this suggests additional coupling. The com-

plexity could be explained if the fluorine atom (F_6) couples with 3 other fluorine atoms and also the hydrogen attached to the metal. If $J_{26} \sim 6$ c/s (as above), $J_{36} \sim 10$ c/s, $J_{56} \sim 34$ c/s and $J_{6H} \sim 7.4$ (see $^1H.M.R.$) a resonance pattern similar to that observed can be reproduced. However the spectrum is too noisy to obtain any reliable J values. The H-F coupling will be discussed presently.

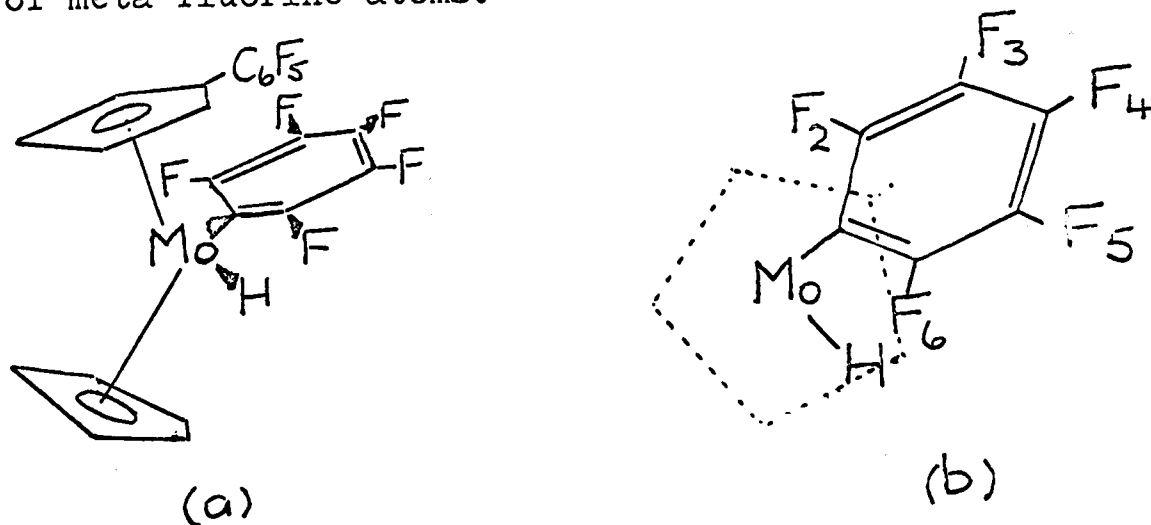
The explanation for the non equivalence of the fluorine atoms in the metal bound ring seems to be basically steric (compare polypentafluorophenyl compounds of group IV B (C4, C6)). If a theoretical model of the compound is built using estimated bond lengths and van der Waals radii it is found that free rotation about the Mo-C bond is restricted by the presence of two $\pi-C_5H_5$ rings (this will be even more true since one of the rings is substituted with C_6F_5).

The Mo-C bond distances in $(\pi-C_5H_5)Mo(CO)_3C_2H_5$ and $(\pi-C_5H_5)Mo(CO)_3C_3F_7$ for sp^3 hybridised carbon are 2.4 and 2.28 Å respectively (C7, C8). The Mo-C distance in $(\pi-C_5H_5)Mo(CO)(COHC(COOEt)NNH)$ in which there is sp^2 hybridised carbon but probably some double bond character is 2.1 Å (C9). The Mo-C bonds in $[(\pi-C_5H_5)Mo(CO)_3]_2$ are 1.96 Å (C10). The molybdenum- $\pi-C_5H_5$ ring distance is 2.0 Å in the related compounds $(\pi-C_5H_5)_2Mo(S_2C_6H_3CH_3)$ (A125, C11), $(\pi-C_5H_5)_2Mo(SC_2H_4NH_2)I$ (C12) and $(\pi-C_5H_5)_2MoH_2$ (A140), and the ring-metal-ring angle in these compounds is not less than 131° and even at this angle (C12) interaction between hydrogen atoms of cyclopentadienyl rings causes the rings to be staggered in the solid state. Also, electron diffraction studies on $(\pi-C_5H_5)_2TiCl_2$ have given a ring-metal-ring angle of 121° (A10).

Thus, with Mo-C distance estimated at $2.2 \text{ \AA}$ and a ring-metal-ring-angle of 120° , C-C and C-F distances of 1.40 and $1.33 \text{ \AA}$ (as measured for $\text{C}_6\text{H}_5\text{F}$ (C13)), Mo- C_5H_5 ring distance of 2.0 (as above), and C-C and C-H distances of cyclopentadienyl rings of 1.4 and $1.1 \text{ \AA}$ (C11, C12, A10), the following projection diagram with the C_6F_5 ring perpendicular to the C_5H_5 rings can be obtained.



The ortho-F-C (of cyclopentadienyl ring) distance is then $2.4 \text{ \AA}$ and the ortho-F-H (of cyclopentadienyl ring) distance is $1.5 \text{ \AA}$. But these values are considerably smaller than the sum of the respective van der Waals radii ($\text{F} = 1.35 \text{ \AA}$, $\text{H} = 1.2 \text{ \AA}$, and, although not strictly comparable, $\text{CH}_2 = 2.0 \text{ \AA}$ (C14)). This indicates that the C_6F_5 bonded to the metal is constrained to the structure shown below which causes inequivalences of ortho and of meta fluorine atoms.



The interaction of one fluorine atom with the metal hydrogen atom with $J_{FH} \approx 7.4$ c/s can be explained on this model (see diagram (b) in which the relevant fragment of the molecule lies in the plane of the paper, although the C_6F_5 group may vibrate about this mean position). The Mo-ortho-F distance predicted by the model is $3.3 \text{ \AA}$ and this relatively short distance may force a "through space" interaction of the F_6 atom and the metal hydrogen (a similar "through space" F-F coupling has been postulated for $o-C_6H_4FCCl_2F$ in which steric hindrance was also observed (C15)). This interaction may be a weak type of hydrogen bonding, since F is noted for this type of bonding, and this may further constrain the C_6F_5 ring in the structure shown. However the F-H interaction could possibly, but less likely, be explained by normal coupling if the J values of F_2 and F_6 are markedly different. F_2 and F_6 are roughly cis and trans, respectively, to the metal hydrogen and it is known for olefins that cis and trans coupling constants are different and that the trans coupling is larger than the cis. Therefore if one J_{FH} is very small and another is 7.4 c/s the spectrum can be explained and in this case the splitting could even be due to F_2 , in which case the assignment of bands in the ^{19}FMR spectrum to F_2 and F_6 must be reversed.

The temperature dependence of the $^1H.M.R.$ can be easily explained as being due to restricted rotation of the $(\pi-C_5H_4C_6F_5)$ group about the metal, π -bond caused by the presence of the bulky C_6F_5 group. Free rotation, however, appears to occur with the $(\pi-C_5H_5)$ group since a rather sharp $^1H.M.R.$ resonance signal is observed.

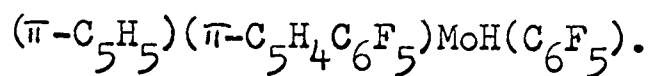
The structure proposed above is substantiated by mass spectral studies

and the reaction with CCl_4 mentioned later.

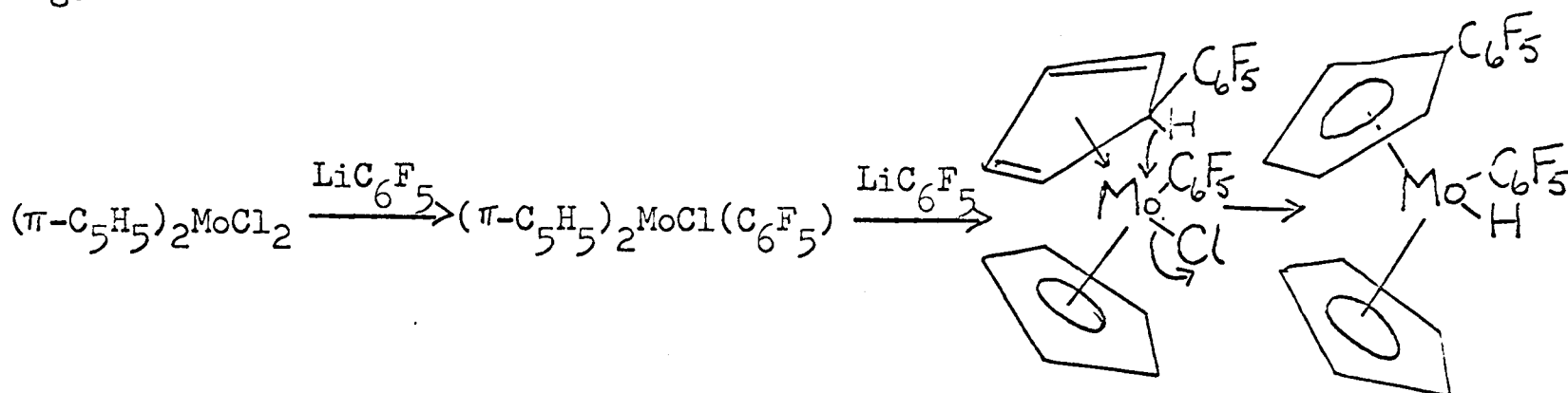
The mass spectrum* of the compound gave a peak at $m/e = 562$ assignable to the parent ion $\text{C}_{22}\text{H}_{10}\text{F}_{10}\text{Mo}^+$ (based on ^{98}Mo). Also a very small peak was noted at $m/e = 578$, probably formed by decomposition. The major fragmentation ions were $m/e = 542$, $m/e = 496$, $m/e = 395$, $m/e = 375$, peaks in the region $m/e = 330-327$, $m/e = 304$, $m/e = 232$, $m/e = 231$ and $m/e = 168$ which can be assigned to $\text{C}_{22}\text{H}_9\text{F}_9\text{Mo}^+$ (loss of HF), $(\text{C}_5\text{H}_4\text{C}_6\text{F}_5)\text{Mo}(\text{C}_6\text{F}_5)^+$, $(\text{C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_5\text{H}_5)^+$, $\text{C}_{16}\text{H}_9\text{F}_4\text{Mo}^+$, $\text{C}_5\text{H}_x\text{C}_6\text{F}_5\text{Mo}^+$, $\text{C}_3\text{H}_3\text{MoC}_6\text{F}_5^+$, $\text{C}_6\text{F}_5\text{C}_5\text{H}_5^+$, $\text{C}_6\text{F}_5\text{C}_5\text{H}_4^+$ and $\text{C}_6\text{F}_5\text{H}^+$. These fragments can be readily accounted for by decomposition of the structure shown above. Another mass spectrum determined at a different temperature gave a parent ion peak, P, but also a large peak at $m/e = P-1$ which shows that one H atom can be readily lost - probably the metal attached hydrogen (cf. $(\pi\text{-C}_5\text{H}_5)_2\text{ReH}$ (B20)). The fragmentation pattern of this second spectrum was essentially the same as the above but large peaks also occurred at $m/e = 394$ and 374 again probably arising from hydride loss from peaks $m/e = 395$ and 375 mentioned above.

It remains to suggest why this compound is the major product of the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ and LiC_6F_5 . One possible reason for this to occur is that initial attack of the $\text{C}_6\text{F}_5\text{Li}$ on $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ gives the mono-chloro species but that this molecule is sterically hindered to nucleophilic attack at the Mo-Cl bond. Thus the remaining $\text{C}_6\text{F}_5\text{Li}$ attacks the ring to give an initially unstable 17 electron cyclopentadiene complex which undergoes hydride transfer and Cl^- elimination to give the product

* See table 10 for all mass spectra of compounds described in Chapter III.



e.g.



However, it is known that $(\pi\text{-C}_5\text{H}_5)_2\text{WH}_2$ undergoes ring lithiation with $\text{C}_4\text{H}_9\text{Li}$ to give $(\pi\text{-C}_5\text{H}_4\text{Li})_2\text{WH}_2$ and such a process may also occur with LiC_6F_5 and $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ initially.

Although it was possible to obtain small crystals of the compound it was found impossible to grow large enough crystals for X-ray study. The difficulty of crystallisation and the tendency of the compound to occlude organic solvents, becoming oily, may be associated with its unsymmetrical structure.

Another product of the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ and LiC_6F_5 was obtained in small yields as a yellow-brown solid ('B' in Chapter VII). This compound showed higher F% and lower C% than the above compound and could be impure tri-pentafluorophenyl substituted complex.

The reaction of $\text{C}_6\text{F}_5\text{MgBr}$ with $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ gave only starting material. Reactions of the bis- π -cyclopentadienyl dihydride complexes with C_6F_6 or SiF_4 gave no fluoro products (see Chapter VII).

b) The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with LiC_6F_5 gave orange microcrystals (d . 128-130°C) as the major product. This compound had the stoichiometry required for $\text{C}_{22}\text{H}_{10}\text{F}_{10}\text{W}$ and was monomeric in benzene. It was soluble in petrol, and very soluble in ether, benzene and chloroform. On the basis of physical studies mentioned below it was shown to be $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WH}(\text{C}_6\text{F}_5)$, an analogue of the molybdenum complex.

The infra-red spectrum was similar to that of the molybdenum analogue and showed $\pi\text{-C}_5\text{H}_5$ and CF vibrations. No significant hydride band was noted around 1800 cm^{-1} .

The $^1\text{H.M.R.}$ spectrum in CDCl_3 at room temperature was similar to that of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_6\text{F}_5)$ and is shown in figure 6. The sharp band at $\tau = 5.26$ of relative intensity 5 is assignable to one $(\pi\text{-C}_5\text{H}_5)$ ring and the 4 broader peaks at $\tau = 4.49, 4.80, 5.65$ and 5.43 each of intensity 1 are assignable to the four H atoms in the $\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5$ group. The hydride resonance of relative intensity 1 comes at $\tau = 20.3$ and is a doublet ($J \sim 11.5$ c/s) split by the ortho-fluorine atom as proposed for the molybdenum compound. Unfortunately we were unable to run the spectrum at variable temperatures.

The $^{19}\text{F.M.R.}$ spectrum was not run at 100 Mc/s but an attempt was made to run the compound at 56.4 Mc/s. The spectrum was observed on the cathode ray oscilloscope and appeared similar to that of the analogous molybdenum compound although the high field triplet bands seemed to be overlapping with the complex meta-fluorine resonance band. However it was found impossible to record this well, due to decomposition, and the spectrum was not calibrated.

The mass-spectrum showed several peaks above the parent ion peak. This

may have been due to impurity present in the sample sent for mass spectrometry (since, as noted in the experimental section, other products also formed in the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with LiC_6F_5 and the major product $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WH}(\text{C}_6\text{F}_5)$ had to be carefully purified by chromatography) or, more probably, may be due to pentafluorophenyl ring and fluorine atom migration at the temperature of introduction to the mass spectrometer ($>$ decomp. temp.). The main peaks above the parent ion were $m/e = 814$, $m/e = 796$, $m/e = 776$, $m/e = 704$, $m/e = 686$ and $m/e = 668$ (see table for possible assignments). The parent ion peak was observed at $m/e = 648$ $((\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WH}(\text{C}_6\text{F}_5)^+)$ but a larger peak occurred at $m/e = 647$ and the two tungsten isotope patterns overlapped. This shows that hydrogen loss, probably the metal attached hydrogen atom, occurs readily. The fragmentation pattern is shown in table 10 and includes ions expected from decomposition of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WH}(\text{C}_6\text{F}_5)$ although some rearrangement seems to have taken place to produce other ions.

Reactions of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MH}(\text{C}_6\text{F}_5)$

Both complexes $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MHC}_6\text{F}_5$ ($\text{M} = \text{Mo}, \text{W}$), reacted with carbon tetrachloride over several hours at room temperature to give complexes $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MCl}(\text{C}_6\text{F}_5)$ ($\text{M} = \text{Mo}, \text{W}$). Both products had the stoichiometry required by the given formula. The molybdenum complex (green microcrystals, m.p. 150-152 d.) and the tungsten complex (yellow-brown microcrystals) were soluble in liquid sulphur dioxide, negligibly soluble in dichloromethane and insoluble in ether.

The infra-red spectra of both molybdenum and tungsten complexes were similar and both showed $\pi\text{-C}_5\text{H}_5$ type vibrations and strong CF vibrations of

a pentafluorophenyl ring.

The $^1\text{H.M.R.}$ spectrum of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoCl}(\text{C}_6\text{F}_5)$ was recorded in liquid sulphur dioxide at 35°C . A rather sharp band at $\tau = 4.44$ is assignable to the $(\pi\text{-C}_5\text{H}_5)$ and broad bands around this (cf. the spectrum in figure 1) in the region $3.9 - 4.7$, but not well resolved, are assignable to the $(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)$ group which has restricted rotation as postulated in $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_6\text{F}_5)$. The relative intensities of the sharp peak to the broad bands were difficult to measure but are approximately in the ratio 5 : 4.

The mass spectrum of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoCl}(\text{C}_6\text{F}_5)$ was also recorded and a parent ion peak was observed but a few peaks of $m/e > 596$, of very small relative intensity, were observed and fluoroaromatic ion peaks were the most intense (see table 10). The data obtained is consistent with the postulated structure.

This reaction of the compounds $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{M}(\text{C}_6\text{F}_5)\text{H}$ with carbon tetrachloride supports the proposed structures of the hydrides and also shows that under these conditions (probably free radical halogen attack) the metal-hydrogen bond is more readily cleaved than the metal-perfluoro-carbon bond.

Oxidation of both molybdenum and tungsten monochloro-complexes with nitric acid gave cations which could be isolated as hexafluorophosphate salts. The molybdenum complex, $[(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoCl}(\text{C}_6\text{F}_5)]\text{PF}_6$, (purple microcrystals) and the analogous tungsten complex (red microcrystals) were soluble in liquid sulphur dioxide and fairly soluble in acetone and dichloromethane but insoluble in ether. Both complexes were shown to have approxi-

mately the required carbon and hydrogen analyses (although the molybdenum complex was a little impure) and the infra-red spectra showed the presence of frequencies assignable to $\pi\text{-C}_5\text{H}_5$ and C_6F_5 groups. The two complexes were paramagnetic and, in acetone or 1,2-dimethoxyethane solution, gave strong, well resolved E.S.R. signals that showed quartet (1:1:1:1) splitting of the main band (and also splitting of the $^{95}\text{Mo}/^{97}\text{Mo}$ or ^{183}W satellite bands). This splitting clearly indicates the presence of one Cl atom ($I = 3/2$) in the complex and supports the postulated formula. See chapter VI for details of the E.S.R. spectra.

When the compound $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{W}(\text{C}_6\text{F}_5)\text{H}$ was dissolved in bromoform and left for a long period at room temperature a small amount of greenish solid was formed. This solid was oxidised by nitric acid to give a cation which gave a salt with NH_4PF_6 solution. The hexafluorophosphate salt (red-brown in colour) gave an E.S.R. signal with a four line splitting when dissolved in dimethyl sulphoxide or 1,2-dimethoxyethane solution. The splitting of the E.S.R. signal was larger than observed in the monochloro species mentioned above and is probably caused by a Br atom (see chapter VI). It is very likely that the complex salt had the formula $[(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WBr}(\text{C}_6\text{F}_5)]\text{PF}_6$.

The compound $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_6\text{F}_5)$ did not react readily with CHBr_3 at room temperature. When a solution of the compound in CHBr_3 was refluxed for approximately 45 minutes a dark green product was formed which gave a cation on oxidation that had an E.S.R. spectrum similar to the spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2^+$ with very similar parameters (i.e., $g = 2.053$, $A_{\text{Br}} = 15.5 \pm 0.5$ gauss) and this indicates that cleavage of the molybdenum-

pentafluorophenyl bond had occurred. Analysis of the neutral dark green compound showed the presence of fluorine and bromine but also indicated decomposition of the other pentafluorophenyl group [Found C, 30.5; H, 2.1; Br, 36.95; F, 8.5% (B)] probably forming a mixture of π -fluorocyclopentadienyl compounds of the type $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_x\text{F}_{5-x})\text{MoBr}_2$. These are probably formed by rearrangement at the boiling point of bromoform (149.5°C).

B. Phenyl derivatives of bis- π -cyclopentadienyl molybdenum and tungsten

a) The reaction of lithium phenyl with $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$, in approximately 2:1 molar proportions, in ether gave rise to two products in varying yields.

The major product ('A') in most reactions, was obtained as a red-brown microcrystalline solid ($d \sim 73^\circ\text{C}$) which was very air unstable and soluble in organic solvents such as benzene, ether and less soluble in petrol. It was decomposed by chloroform to give dark coloured precipitates.

The total analysis of the compound, 'A', gave a stoichiometry corresponding to $\text{C}_{22}\text{H}_{\sim 20}\text{Mo}$ indicating the presence of two cyclopentadienyl and two phenyl groups. The infra-red spectrum also showed typical $\pi\text{-C}_5\text{H}_5$ vibrations (e.g. 3097 and 833 cm^{-1}) and also aromatic frequencies (e.g., 1559 , 735 and 702 cm^{-1}).

The mass spectrum of the compound gave highest peaks at $m/e = 372\text{--}383$ which seemed to be due to several overlapping molybdenum isotope patterns. The main peaks discernible were $m/e = 380$ and 378 (based on ^{98}Mo) and assignable to the ions $\text{C}_{22}\text{H}_{18}\text{Mo}^+$ and $\text{C}_{22}\text{H}_{16}\text{Mo}^+$. The peak at $m/e = 382$ which would be expected from an ion $\text{C}_{22}\text{H}_{20}\text{Mo}^+$ was very small and is probably part of the isotopic pattern of the ion $\text{C}_{22}\text{H}_{18}\text{Mo}^+$ (^{100}Mo). The only other well defined Mo species occurred at $m/e = 304$, assignable to $(\text{C}_5\text{H}_4\text{C}_6\text{H}_5)\text{MoC}_5\text{H}_5^+$.

Organic fragments also occurred (see table 10).

The $^1\text{H.M.R.}$ spectrum of complex 'A' was run in various solvents. In CDCl_3 rapid decomposition occurred and no satisfactory spectrum was obtained. In CS_2 the compound decomposed while the spectrum was recorded but complex bands assignable to phenyl protons at $\tau \sim 2.7$ and 3.3 and several bands, at $\tau = 4.98, 5.20, 5.25, 5.45$ and 5.53 , which may be due to cyclopentadienyl protons were observed. However the spectrum changed while recording and good relative intensity measurements could not be made although the total aromatic proton resonance was more intense than that in the region $\tau \sim 5$. Again, in $(\text{CH}_3)_2\text{CO}$ solid formed while the spectrum was recorded but aromatic resonances at $\tau \sim 2.8$ (broad) and 3.27 (complex) and a sharp peak at $\tau = 5.10$, with other small resonances near it, were observed. A solution in $(\text{C}_2\text{H}_5)_2\text{O}$ was found to be too dilute for a good spectrum. Spectra were run in C_6D_6 in which the compound did not decompose. Aromatic resonances occurred at $\tau = 2.5$ and 2.93 and a sharp singlet band occurred at $\tau = 5.65$ but other smaller bands were observed in the latter region at $\tau = 4.93, 5.19, 5.33, 5.58$ and 5.8 . The relative intensity of aromatic bands to the bands at $\tau \sim 5-6$ were difficult to measure, owing to the presence of an undeuterated benzene resonance in the aromatic region, but this was approximately 10:6-7. The spectrum was scanned to $\tau = 40$ and no hydride resonance was observed and, unless this was very broad, this should have been observed, if present, with the concentration of solution used.

Another product, 'B', was obtained from the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ and LiC_6H_5 as a yellow solid. This solid was soluble in benzene and fairly soluble in ether. A total analysis also was consistent with the stoicheio-

metry corresponding to $C_{22}H_{20}Mo$. The infra-red spectrum showed bands which could be assigned to $\pi-C_5H_5$ groups (e.g. 3160 cm^{-1}) and aromatic frequencies (e.g., $1599, 753, 691\text{ cm}^{-1}$), but also a rather strong band at 1815 cm^{-1} . This latter band is at the position expected for ν Mo-H (A1) and this might indicate the presence of a metal hydride ligand.

The ^1H .M.R. spectrum of 'B' was run in CS_2 solution and showed complex aromatic hydrogen resonances at $\tau = 2.88$ and 3.04 . Single hydrogen resonances of approximately equal intensity occurred at $\tau = 4.89, 5.01, 5.34$ and 5.52 and a larger singlet resonance occurred at $\tau = 5.81$. These bands around $\tau \sim 5$ are probably cyclopentadienyl hydrogen resonances and suggest that a substituted ring, e.g. $C_5H_4C_6H_5$, is present. No high field scan was made as the solution was rather dilute.

The nature of the products 'A' and 'B' is not clear. Product 'A', from the infra-red and ^1H .M.R. data is probably not a hydride and thus, since it is diamagnetic, it must have a formula $(C_5H_5)_2Mo(C_6H_5)_2$ or be a substituted molybdocene derivative such as $(\pi-C_5H_5)(\pi-C_5H_3(C_6H_5)_2)Mo$, unless rearrangement of the aromatic fragments has taken place. It will be discussed further at the end of this section. The data for product 'B' is not so extensive but the infra-red spectrum suggests the presence of a hydride and it is possible that the complex is $(\pi-C_5H_5)(\pi-C_5H_4C_6H_5)MoH(C_6H_5)$ analogous to the pentafluorophenyl complex.

b) The reaction of $(\pi-C_5H_5)_2WCl_2$ with LiC_6H_5 gave a yellow microcrystalline solid ($d \sim 60^\circ C$) which is very air unstable. Total analysis gave the stoichiometry $C_{22}H_{20}W$. The infra-red spectrum showed the presence of frequencies assignable to $\pi-C_5H_5$ and phenyl groups and no ν W-H band was observed.

The mass spectrum of the complex showed a peak at $m/e = 466$ (^{184}W) which would be expected for an ion $\text{C}_{22}\text{H}_{18}\text{W}^+$. If any other tungsten ions, at higher m/e values (i.e. 467, 468) were present, they must be present in very small amounts and their peaks are lost in the isotope pattern of $\text{C}_{22}\text{H}_{18}\text{W}^+$. Other metal fragments and organic fragments are listed in table 10.

The $^1\text{H.M.R.}$ spectrum in C_6D_6 showed aromatic hydrogen resonances around $\tau \sim 3.0$ and a complex resonance band in the region $\tau = 4.7-6.1$, with prominent peaks at $\tau = 5.76, 5.92$ and 6.00 . This complex band was shown to be temperature dependent and varied on raising the temperature to 60°C and the original spectrum was regained on cooling back to room temperature. No hydride resonances could be found at high fields. The relative intensity of aromatic hydrogen resonances was difficult to measure precisely, since some undeuterated benzene was present, but was approximately 10:7-8.

The above data shows that this complex is probably not a hydride. The appearance of the ion $\text{C}_{22}\text{H}_{18}\text{W}^+$ as the largest peak of any intensity in the mass spectrum can be compared to the similar case of product 'A' from the $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ and $\text{C}_6\text{H}_5\text{Li}$ reaction. The $^1\text{H.M.R.}$ spectrum of the tungsten compound is similar to that of the molybdenum compound, 'A', and the temperature dependence of the complex cyclopentadienyl hydrogen resonance suggests some hindered intramolecular motion.

Most of the data could be accounted for by the formula $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{C}_6\text{H}_5)_2$ if the complex $^1\text{H.M.R.}$ spectra arose from steric interaction of the C_6H_5 and C_5H_5 rings and a ready thermal phenyl migration to the $\pi\text{-C}_5\text{H}_5$ rings occurred to produce substituted metallocene ions in the ion source of the

mass spectrometer. Another possibility is that one C_5H_5 ring is σ -bonded (there appears to be one sharp $\pi-C_5H_5$ hydrogen resonance in the $^1H.M.R.$ spectra) and the formula of the complexes is $(\pi-C_5H_5)M(\sigma-C_5H_5)(C_6H_5)_2$ similar to the reported compound $(\pi-C_5H_5)Mo(\sigma-C_5H_5)_3$ (A87). However both the proposed formulae are not consistent with the $^1H.M.R.$ integrations since, regardless of how approximate the intensity ratios may be, they are not 1:1 and the intensity of the proposed cyclopentadienyl hydrogen resonance is low. This inconsistency could be due to decomposition of the complexes giving soluble aromatic fragments and insoluble cyclopentadienyl-metal fragments but this explanation is doubtful as the spectra in C_6D_6 were run on freshly recrystallised material and no decomposition to form solid was noted in the $^1H.M.R.$ sample.

Another possible explanation for low intensities of the cyclopentadienyl hydrogen resonances and for the complex nature of the resonances is the formation of the complexes $(\pi-C_5H_5)(\pi-C_5H_5(C_6H_5)_2)M$ or $(\pi-C_5H_4C_6H_5)_2M$ or a mixture of the two. This would also explain the mass spectra since parent ions of this composition were seen. The reduction to the formally $M(II)$ oxidation state could be achieved easily by C_6H_5Li . The complex $(\pi-C_5(C_6H_5)_5)_2Mo$ has been reported (A5) but this was a paramagnetic red-brown solid, practically insoluble in organic solvents.

Table 9

¹H.M.R. SPECTRA OF COMPOUNDS DESCRIBED IN CHAPTER III AT ROOM TEMPERATURE (25°C)

Compound	Solvent	τ value ^a	Intensity ^b	Fine Structure	Assignment
$(\pi-C_5H_5)(\pi-C_5H_4C_6F_5)MoH(C_6F_5)$	CDCl ₃	4.50	1	broad	$\pi-C_5H_4C_6F_5$ group
		4.60	1	broad	$\pi-C_5H_4C_6F_5$ group
		5.05	1	broad	$\pi-C_5H_4C_6F_5$ group
		5.23	5	singlet	$\pi-C_5H_5$ group
		5.41	1	broad	$\pi-C_5H_4C_6F_5$ group
		16.99	1	doublet (J=7.4 c/s)	Mo-H
$(\pi-C_5H_5)(\pi-C_5H_4C_6F_5)WH(C_6F_5)$ (35°C)	CDCl ₃	4.49	1	broad	$\pi-C_5H_4C_6F_5$ group
		4.80	1	broad	$\pi-C_5H_4C_6F_5$ group
		5.05	1	broad	$\pi-C_5H_4C_6F_5$ group
		5.26	5	singlet	$\pi-C_5H_5$ group
		5.43	1	broad	$\pi-C_5H_4C_6F_5$ group
		20.30	1	doublet (J=11.5 c/s)	W-H
$(\pi-C_5H_5)(\pi-C_5H_4C_6F_5)MoCl(C_6F_5)$ (35°C)	SO ₂	3.9-4.8		broad	$\pi-C_5H_4C_6F_5$ group
		4.44		singlet	$\pi-C_5H_5$

Table 9 - continued

Compound	Solvent	τ value ^a	Intensity ^b	Fine Structure	Assignment
$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2/\text{C}_6\text{H}_5\text{Li}$ product 'A'	C_6D_6	2.50		complex	aromatic group
		2.93		complex	aromatic group
		4.93		singlet (br)	cyclopentadienyl group ?
		5.19		singlet (br)	cyclopentadienyl group ?
		5.33		singlet (br)	cyclopentadienyl group ?
		5.58		singlet	cyclopentadienyl group ?
		5.65		singlet	$\pi\text{-C}_5\text{H}_5$?
		5.81		singlet	cyclopentadienyl group ?
$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2/\text{LiC}_6\text{H}_5$ product 'B' (too dilute for good intensity measurements)	CS_2	2.88		complex	aromatic group
		3.04		complex	aromatic group
		4.89		singlet (br)	cyclopentadienyl group ?
		5.01		singlet (br)	cyclopentadienyl group ?
		5.34		singlet (br)	cyclopentadienyl group ?
		5.52		singlet (br)	cyclopentadienyl group ?
		5.81		singlet	$\pi\text{-C}_5\text{H}_5$?
$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2/\text{LiC}_6\text{H}_5$ product	C_6D_6	3.0	1	complex	aromatic group
		4.7-6.1	} 7-8	complex (br)	cyclopentadienyl group ?
		5.92		singlet	$\pi\text{-C}_5\text{H}_5$?

a - τ value relative to T.M.S. as internal standard.

b - Relative intensity of bands.

Table 10

MASS SPECTRA OF COMPOUNDS DESCRIBED IN CHAPTER III

$(C_5H_5)_2MoCl_2/LiC_6H_5$ product 'A'			$(C_5H_5)_2WCl_2/LiC_6H_5$ product		
m/e^a	rel.int. ^c	assignment ^d	m/e^b	rel.int. ^c	assignment ^d
380	2	$C_{22}H_{18}Mo^+$	466	15	$C_{22}H_{18}W^+$
378	3	$C_{22}H_{16}Mo^+$	390	74	$C_5H_4C_6H_5MoC_5H_5^+$
304	3	$C_5H_4C_6H_5MoC_5H_5^+$	362	6	$C_{14}H_{10}W^+$
219	7.5	$C_{17}H_{15}^+$	336	2	$C_{12}H_8W^+$
218	33	$C_{17}H_{14}^+$	314	13	$C_{10}H_{10}W^+$
217	8	$C_{17}H_{13}^+$	228	23	$C_{18}H_{12}^+$
215	6		218	100	$C_{17}H_{14}^+$
202	6	$C_{16}H_{10}^+$	202	19	$C_{16}H_{10}^+$
142	58	$C_5H_5C_6H_5^+$	195	8	$C_5H_4C_6H_5MoC_5H_5^{++}$
141	31	$C_5H_4C_6H_5^+$	142	34	$C_5H_5C_6H_5^+$
129	4	$C_5H_4C_5H_5^+$	141	22	$C_5H_4C_6H_5^+$
91	100	$C_7H_7^+$	115	21	
89	5		91	36	$C_7H_7^+$
78	68	$C_6H_6^+$	78	67	$C_6H_6^+$
77	14	$C_6H_5^+$	77	13	$C_6H_5^+$
51	11	$C_4H_3^+$	51	22	$C_4H_3^+$
			39	19	$C_3H_3^+$

Table 10 - continued

$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_6\text{F}_5)$			$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoCl}(\text{C}_6\text{F}_5)$		
m/e^a	rel.int. ^c	assignment ^d	m/e^a	rel.int. ^c	assignment ^d
578	0.1	?	628	0.75	$\text{C}_{28}\text{H}_7\text{F}_{15}^+$?
562	20	$(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_6\text{F}_5)$	510	< 0.1	?
542	7	$\text{C}_{22}\text{H}_9\text{F}_9\text{Mo}^+$	609	< 0.1	?
496	2	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{MoC}_6\text{F}_5^+$	608	< 0.1	?
476	0.2	$\text{C}_5\text{H}_3\text{C}_6\text{F}_4\text{MoC}_6\text{F}_5^+$	596	0.6	$[\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoCl}(\text{C}_6\text{F}_5)^+]$
458	0.1	$\text{C}_{17}\text{H}_4\text{F}_8\text{Mo}^+$	561	3	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{Mo}(\text{C}_5\text{H}_5)(\text{C}_6\text{F}_5)^+$
433	0.3	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{MoF}_2\text{H}(\text{C}_6\text{F}_5)^+$	541	1	$\text{C}_{22}\text{H}_8\text{F}_9\text{Mo}^+$
414	2	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{MoFH}(\text{C}_6\text{F}_5)^+$	429	0.6	$\text{C}_5\text{H}_5\text{C}_6\text{F}_5\text{MoCl}(\text{C}_5\text{H}_5)^+$
395	100	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{MoH}(\text{C}_5\text{H}_5)$	399	12	$\text{C}_{17}\text{H}_5\text{F}_{10}^+$
375	98	$\text{C}_{16}\text{H}_9\text{F}_4\text{Mo}^+$	398	57	$\text{C}_{17}\text{H}_4\text{F}_{10}^+$
330 (?)	8	$\text{C}_{5x}\text{C}_6\text{F}_5\text{Mo}^+$?	394	2	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{MoC}_5\text{H}_5^+$
329 (?)	12		379	5	$\text{C}_{17}\text{H}_4\text{F}_9^+$
327 (?)	13		374	3	$\text{C}_{16}\text{H}_8\text{F}_4\text{Mo}^+$
304	9	$\text{C}_3\text{H}_3\text{MoC}_6\text{F}_5^+$?	364	0.8	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{MoCl}^+$
232	42	$\text{C}_6\text{F}_5\text{C}_5\text{H}_5^+$	359	5	$\text{C}_{17}\text{H}_3\text{F}_8^+$
231	17	$\text{C}_6\text{F}_5\text{C}_5\text{H}_4^+$	304	1	$\text{C}_3\text{H}_3\text{MoC}_6\text{F}_5^+$?
213	15	?	232	100	$\text{C}_6\text{F}_5\text{C}_5\text{H}_5^+$
193	57	$\text{C}_8\text{F}_5\text{H}_2^+$?	231	24	$\text{C}_6\text{F}_5\text{C}_5\text{H}_4^+$
187	46	?	187	8	?
182	26	$\text{C}_5\text{H}_5\text{MoF}^+$	182	5.5	$\text{C}_5\text{H}_5\text{MoF}^+$
168	86	$\text{C}_6\text{F}_5\text{H}^+$	181	5	$\text{C}_5\text{H}_4\text{FMo}^+$
167	14	C_6F_5^+	168	5	$\text{C}_6\text{F}_5\text{H}^+$
149	32	?	99	3	?
		?	39	4	C_3H_3^+

Table 10 - continued

$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WH}(\text{C}_6\text{F}_5)$			$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WH}(\text{C}_6\text{F}_5) - \text{cont.}$		
m/e^b	rel.int. ^c	assignment ^d	m/e^b	rel.int. ^c	assignment ^d
814	4	$(\text{C}_5\text{H}_4\text{C}_6\text{F}_5)(\text{C}_5\text{H}_5)\text{W}(\text{C}_6\text{F}_5)_2^+$	480	100	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{WC}_5\text{H}_5^+$
796	3	?	460	30	$\text{C}_{16}\text{H}_8\text{F}_4\text{W}^+$
776	2	?	454	4	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{WF}_2\text{H}^+$
704	13	$\text{FW}(\text{C}_6\text{F}_5)_3^+ ?$	434	12	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{WF}^+$
686	11	$\text{HW}(\text{C}_6\text{F}_5)_3 ?$	428	4	?
668	8	?	416	60	$\text{C}_5\text{H}_5\text{WC}_6\text{F}_5^+$
648	55	$(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WH}(\text{C}_6\text{F}_5)^+$	366	12	
647	96	$(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4\text{C}_6\text{F}_5)\text{W}(\text{C}_6\text{F}_5)^+$	341	13	(organic) ?
629	26	$\text{C}_{22}\text{H}_{10}\text{F}_9\text{W}^+$	321	15	(organic) ?
611	37	$(\text{C}_5\text{H}_4\text{C}_6\text{F}_5)\text{W}(\text{C}_6\text{F}_5)(\text{C}_2\text{H}_5)^+ ?$	287	34	$\text{C}_5\text{H}_5\text{WF}_2^+$
591	4	$\text{C}_{22}\text{H}_{10}\text{F}_7\text{W}^+$	240	31	$\text{C}_5\text{H}_5\text{C}_6\text{F}_5\text{WC}_5\text{H}_5^{++}$
582	4	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5\text{WC}_6\text{F}_5^+$	231	19	$\text{C}_5\text{H}_4\text{C}_6\text{F}_5^+$
518	30	$\text{W}(\text{C}_6\text{F}_5)_2^+$	230	18	$\text{C}_{16}\text{H}_8\text{F}_4\text{W}^{++}$
498	6	?	168	40	$\text{C}_6\text{F}_5\text{H}^+$

a - Based on ^{98}Mo

b - Based on ^{184}W

c - Relative intensity of peak

d - Most probable ion.

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Chapter IV

BIS- π -CYCLOPENTADIENYL DERIVATIVES OF MOLYBDENUM AND TUNGSTEN WITH ORGANIC LIGANDS

It has already been shown in previous work (A3) that bis- π -cyclopentadienyl dihalides of molybdenum and tungsten will react with certain sulphur and oxygen binding organic ligands under basic conditions. With the exception of the 3,4-toluenedithiol compounds (which will be discussed in Chapter V) none of the compounds prepared could be readily oxidised to isolable, paramagnetic, cationic species. Thus, it was decided to try to prepare compounds with other ligands which, then, might give stable species in the higher oxidation state. This preparative work would also throw more light on the chemistry of the bis- π -cyclopentadienyl-metal system.

A. Complexes from o-aminothiophenol

When $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ was reacted with $\text{o-NH}_2\text{C}_6\text{H}_4\text{SH}$ in basic solution purple, needle-like crystals (m.p. 215°C d.) were obtained after purification. These were soluble in acetone, dichloromethane and ethanol but insoluble in ether. The stoichiometry, shown by elemental analysis, corresponded with the formula $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_6\text{H}_4\text{NH})$ where one deprotonated o-aminothiophenol group is acting as a bidentate ligand.

The mass spectrum* showed a parent ion peak $m/e = 351$ assignable to $(\text{C}_5\text{H}_5)_2\text{Mo}(\text{SC}_6\text{H}_4\text{NH})^+$ (based on ^{98}Mo) and other prominent peaks occurred at $m/e = 318$, $m/e = 286$, $m/e = 284$, $m/e = 252$, $m/e = 228$, $m/e = 195$, $m/e = 130$

* All mass spectra for this chapter are given in Table 12.

and $m/e = 98$, assignable, probably, to $C_{10}H_{10}MoNC_6H_4^+$, $C_5H_5MoNEC_6H_4S^+$, $C_5H_5MoNC_6H_3S^+$, $C_5H_5MoNC_6H_3^+$, $C_{10}H_{10}Mo^+$, $C_5H_5MoS^+$, MoS^+ and Mo^+ . The solution molecular weight in acetone showed the compound to be monomeric. However, this value was rather high (391 compared to 349 required) and it must be noted here that all solution molecular weights measured were found to be rather higher than expected (usually within 5%). This was probably due to the inaccuracy of the instrument at the concentrations used ($\sim 0.01 - 0.02M$) which were necessitated by low solubility. The instrument was not well calibrated in this region which was outside the recommended range of use.

The infra-red spectrum showed typical frequencies of $(\pi-C_5H_5)$ groups and a 1,2-disubstituted aromatic ring and also a single sharp band at 3327 cm^{-1} which can be assigned to the single ν NH frequency.

The $^1H.M.R.$ spectrum* in $CDCl_3$ showed a sharp singlet assignable to $(\pi-C_5H_5)$ protons, of relative intensity 10, and absorption at low τ value in the region expected for aromatic protons, of relative intensity approximately 4. No resonance was found that could be attributed to the NH proton and this must be explained by broadening probably arising from exchange.

The compound dissolved slightly in water and it was found that a small quantity of purple precipitate could be formed by the addition of aqueous NH_4PF_6 solution (silicotungstic acid precipitated large amounts). The infra-red spectrum of the hexafluorophosphate precipitate showed $(\pi-C_5H_5)$ frequencies, two sharp NH bands at 3282 and 3258 cm^{-1} and a very strong absorption due to PF_6^- at $\sim 840\text{ cm}^{-1}(\text{br})$. Recrystallisation of a small amount from

* All $^1H.M.R.$ spectra for this chapter are given in Table 11.

a liquid sulphur dioxide-ether mixture gave a purple, micro-crystalline compound for which elemental analysis [Found: C, 38.1; H, 4.1; N, 2.7%(C)] suggested that it was slightly impure $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_6\text{H}_4\text{NH}_2)]\text{PF}_6$, [Required: C, 38.8; H, 3.3; N, 2.8%], indicating that protonation of the ligand can occur. In acids a deep green solution was formed from which precipitates were obtained with silicotungstic acid.

The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with o-aminothiophenol also gave a compound analogous to the molybdenum complex, which analysis showed to have the stoichiometry consistent with the formula $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SC}_6\text{H}_4\text{NH})$. This compound was obtained as deep red needles (d $\sim 150^\circ\text{C}$). It was soluble in acetone and dichloromethane and was also slightly soluble in water and more soluble in acid from which NH_4PF_6 precipitated a solid.

The mass spectrum showed a parent ion peak, $m/e = 437$, assignable to $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NHC}_6\text{H}_4\text{S})^+$ and also other peaks $m/e = 404$, $m/e = 371$, $m/e = 331$, $m/e = 292$ and $m/e = 281$ assignable to $\text{C}_{10}\text{H}_{10}\text{WNC}_6\text{H}_4^+$, $\text{C}_5\text{H}_5\text{WNC}_6\text{H}_4\text{S}^+$; $\text{C}_3\text{H}_3\text{WSC}_6\text{H}_4^+$, WSC_6H_4^+ and $\text{C}_5\text{H}_5\text{WS}^+$ respectively.

The infra-red spectrum was similar to that of the molybdenum complex and showed a sharp ν NH band at 3336 cm^{-1} . The 'H.M.R. spectrum in CDCl_3 showed bands assignable to $(\pi\text{-C}_5\text{H}_5)$ and aromatic protons but no band assignable to an NH proton.

Other products were also obtained from the reaction between $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ and o-aminothiophenol. Red-brown crystals (d $\rightarrow 200^\circ\text{C}$), insoluble in organic solvents but fairly soluble in water and soluble in liquid sulphur dioxide were obtained under certain conditions (see Chapter VII). The 'H.M.R. spectrum in liquid sulphur dioxide showed a sharp band assignable to $(\pi\text{-C}_5\text{H}_5)$

protons, bands at $\tau \sim 2.5-3.2$ assignable to aromatic protons and a broad band at $\tau \sim 3.6$ which could be due to NH protons.

The infra-red spectrum showed frequencies which could be assigned to $(\pi-C_5H_5)$ and an aromatic ring and two strong broad bands at 3000 and 2907 cm^{-1} which must be NH frequencies. The stoichiometry (based on C, H, S and Cl) indicated that the compound could be $(\pi-C_5H_5)_2W(SC_6H_4NH_2)Cl$ (but rather low on C%), and the fact a solution of it in water gave a precipitate with NH_4PF_6 suggests the ionic structure $[(\pi-C_5H_5)_2W(SC_6H_4NH_2)]Cl$.

Another orange-red solid, soluble in organic solvents was also obtained from $(\pi-C_5H_5)_2WCl_2$ and o-aminothiophenol and the infra-red spectrum showed 2 rather broad bands at ~ 3400 and ~ 3300 cm^{-1} . The analytical results showed the presence of more than one ortho-aminothiophenol group per molecule and the compound could be rather impure $(\pi-C_5H_5)_2W(SC_6H_4NH_2)_2$.

B. Bis- π -cyclopentadienyl-o-aminophenolato-molybdenum

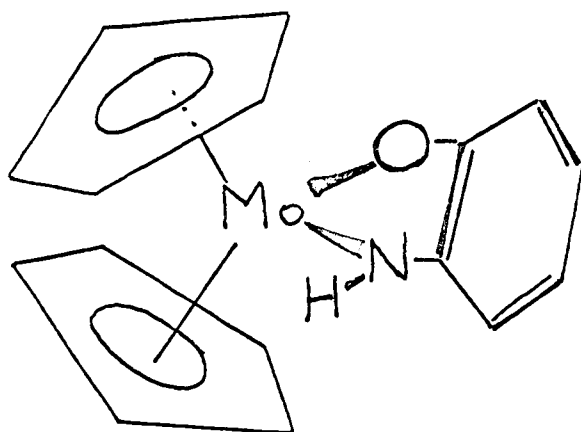
The reaction of $(\pi-C_5H_5)_2MoCl_2$ with o-aminophenol yielded purple needle-like crystals ($d \sim 195^\circ C$) which had the stoichiometry consistent with the formula $(\pi-C_5H_5)_2Mo(OC_6H_4NH)$. The compound was soluble in dichloromethane and acetone but insoluble in ether.

The mass spectrum showed a parent ion peak, $m/e = 335$, and other prominent peaks $m/e = 270$, $m/e = 269$, $m/e = 252$, $m/e = 228$, $m/e = 202$ and $m/e = 163$ assignable to $C_5H_5Mo(OC_6H_4NH)^+$, $C_5H_5Mo(OC_6H_4N)^+$, $C_5H_5MoNC_6H_3^+$, $C_{10}H_{10}Mo^+$, $C_8H_8Mo^+$ and $C_5H_5Mo^+$. The solution molecular weight in chloroform also showed the compound to be monomeric.

The 'H.M.R. spectrum in $CDCl_3$ showed a sharp $(\pi-C_5H_5)$ proton resonance

band and aromatic proton resonances, in relative intensities 10:4 as expected, and no NH proton resonance was observed. The infra-red spectrum also showed typical $(\pi-C_5H_5)$ and aromatic ring frequencies and a sharp ν NH peak at 3355 cm^{-1} .

All this evidence, and comparison with the analogous thio complexes, indicates a structure



The compound is less thermally stable than the thio complexes and leaving in a flask under nitrogen for several weeks led to extensive decomposition.

It appears that the tungsten complex with o-aminophenol is less stable than the molybdenum complex. A reaction in which a greenish coloured product was formed was noted to occur but purification of this by standard methods appeared to decompose this and only free o-aminophenol and an insoluble tungsten compound could be isolated.

C. The reaction between $(\pi-C_5H_5)_2WCl_2$ and nitrogen ligands

1) Several reactions between $(\pi-C_5H_5)_2WCl_2$ and o-phenylenediamine were attempted. In all cases the dichloride was noted to react but no large yield of a complex, such as $(\pi-C_5H_5)_2W(NHC_6H_4NH)$, was obtained. However on one occasion a small quantity of red-brown solid with a mass spectrum containing a parent ion peak $m/e = 420$ assignable to $(\pi-C_5H_5)_2W(NHC_6H_4NH)^+$ and fragmen-

tation ion peaks was obtained. The infra-red spectrum also showed bands assignable to $(\pi-C_5H_5)$ and NH groups.

2) The reaction of $(\pi-C_5H_5)_2MoCl_2$ with potassium pyrrolide yielded unreacted $(\pi-C_5H_5)_2MoCl_2$ on working up the mixture.

D. Bis- π -cyclopentadienyl-9,10-dioxophenanthrenetungsten

It has previously been shown that $(\pi-C_5H_5)_2MCl_2$ ($M = Mo, W$) react with catechol in basic media to give the complexes $(\pi-C_5H_5)_2M(O_2C_6H_4)$ (A5), and this complex was found not to oxidise readily to give a cation either by chemical or electrolytical means (see Chapter VI). Thus it was decided to make the complex from 9,10-phenanthrohydroquinone which might oxidise more readily in view of its extended ring system and the known, greater stability of its semiquinone radical.

The complex $(\pi-C_5H_5)_2W(O_2C_{14}H_8)$, the formula of which was supported by analysis, was made as dark red crystals (d. 175-180°C) soluble in dichloromethane, acetone and water. The mass spectrum showed a parent ion peak $m/e = 522$ and other prominent peaks at $m/e = 314$, $m/e = 288$, $m/e = 261$, $m/e = 239$, $m/e = 180$, $m/e = 156$, $m/e = 66$ and $m/e = 28$ assignable to the fragments, $C_{10}H_{10}W^+$, $C_8H_8W^+$, $C_{10}H_{10}WO_2C_{14}H_8^{++}$, $C_3H_3WO^+$, $C_{13}H_8O^+$, $C_{12}H_8^+$, $C_5H_6^+$ and CO^+ . The solution molecular weight was not determined but that of the similar compound $(\pi-C_5H_5)_2W(O_2C_6H_4)$ was determined (Found 431 (in $CHCl_3$); required 422) and this result and the similar properties of the phenanthrocompound, in conjunction with the mass spectral data, indicate the compound to be monomeric.

The $^1H.M.R.$ spectrum in $CDCl_3$ showed a sharp singlet assignable to

$(\pi\text{-C}_5\text{H}_5)$ protons, relative intensity 10, and complex bands between 2-3 μ assignable to aromatic protons of relative intensity 8. The infra-red spectrum showed typical $(\pi\text{-C}_5\text{H}_5)$ and aromatic frequencies.

No readily formed, stable cation could be obtained from the compound by oxidation. However electrolytic oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_{14}\text{H}_8)$ in 1,2-dimethoxyethane, unlike the compound $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_6\text{H}_4)$, did give an unstable paramagnetic species (see Chapter VI).

The reaction of the compounds $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_6\text{H}_4)$ and $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_{14}\text{H}_8)$ with iodine was interesting. Both compounds, when dissolved in dichloromethane, reacted smoothly with a solution of iodine in dichloromethane.

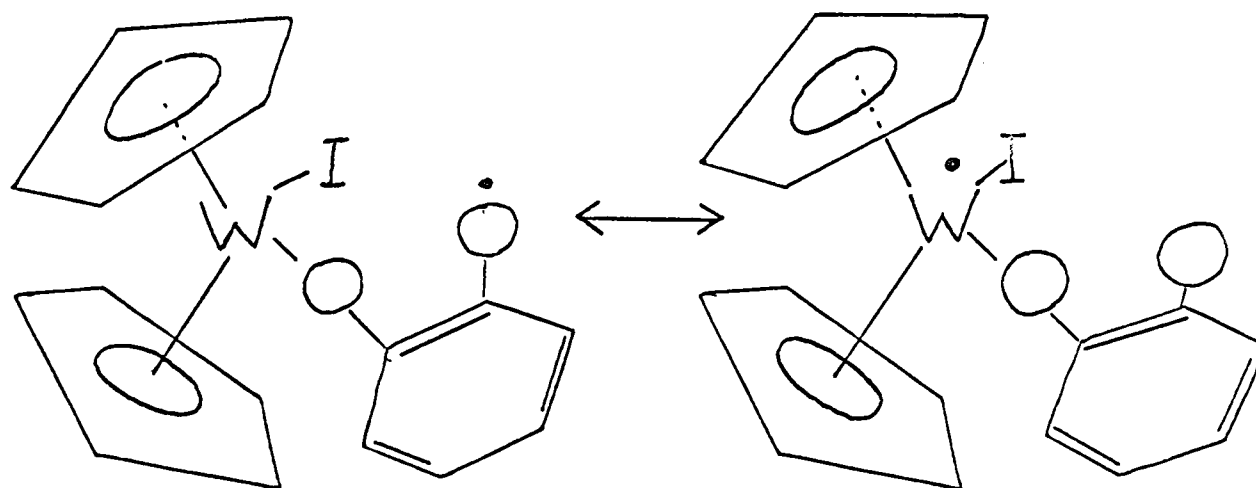
In the case of the compound $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_6\text{H}_4)$ addition of a slight excess of iodine resulted in the solution gradually ($\sim 3\text{-}5$ mins) changing from reddish-brown to green and the precipitation of a green solid. An E.S.R. signal was observed after the addition of iodine but this disappeared as the green solid formed. Trapping of the transient paramagnetic species by freezing the solution to a glass by liquid nitrogen gave a complex E.S.R. signal.

The infra-red spectrum of the freshly precipitated green solid differed from that of $(\pi\text{-C}_5\text{H}_5)_2\text{WI}_2$ but recrystallisation from liquid sulphur dioxide gave green crystals of $(\pi\text{-C}_5\text{H}_5)_2\text{WI}_2$ leaving a yellow coloured mother liquor.

In the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_{14}\text{H}_8)$ with iodine the colour change of the solution was not so marked as in the above reaction but dark green crystals were precipitated. The reaction mixture also gave a transient, broad E.S.R. signal at room temperature which gave a complex spectrum when frozen to a glass.

These observations suggest that iodine displaces the oxy ligands to give iodo species but does so via an oxidative mechanism. It is probable that quinones result from the aromatic ligands. The initial green precipitate could be a charge transfer complex between a quinone and $(\pi-C_5H_5)_2WI_2$ which is decomposed by recrystallisation from liquid SO_2 . The transient paramagnetic species may be due to semi-quinones attached to the $(\pi-C_5H_5)_2W$ system (the g value indicated that it was a metallic species and not an organic free radical).

e.g.



However, electrophilic attack of the activated aromatic rings with iodine probably also takes place and the mechanism is, probably, complex.

E. Bis- π -cyclopentadienyl molybdenum acetyl-acetonato derivatives

The reaction of a large excess of acetylacetone in water with $(\pi-C_5H_5)_2MoCl_2$ gave yellow needle shaped crystals (mp. 188-190 d.) which were soluble in water, ethanol, liquid sulphur dioxide and fairly soluble in dichloromethane.

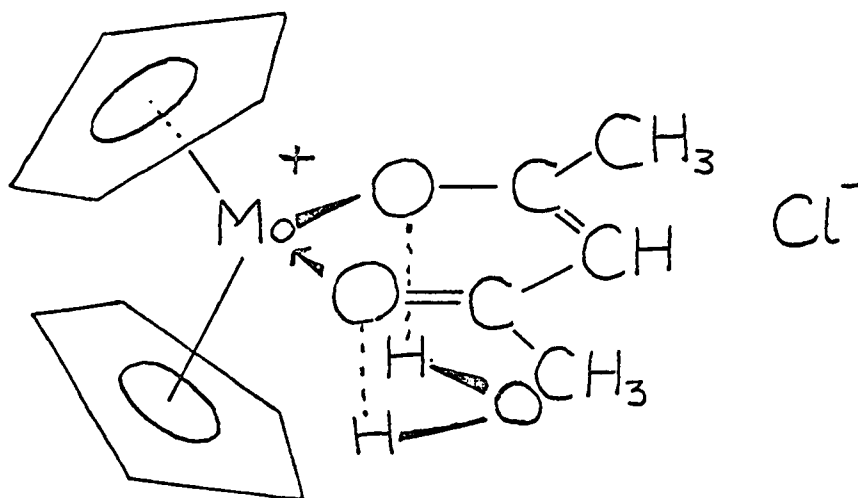
The 'H.M.R. spectrum in $CDCl_3$ showed singlet bands at 3.9, 8.1 and 4.3 τ of relative intensities 10:6:1 assignable to the protons of $(\pi-C_5H_5)$, 2 methyl groups and a deshielded proton of ethylenic type, respectively. No

other resonance was observed.

The infra-red spectrum of the complex showed typical (π -C₅H₅) frequencies, typical frequencies of an acetylacetonate ligand (in particular the bands 1579, 1560 and 1520 cm⁻¹ assignable to ν C=C and ν C=O) but also strong bands above 3100 cm⁻¹. These latter bands suggest the presence of an OH group, probably water, since the reaction was carried out in an aqueous medium.

Analytical results also gave a stoichiometry (based on C, H, Cl and O%) which corresponded to the formula $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{O}_2\text{C}_5\text{H}_7)\cdot\text{H}_2\text{O}]\text{Cl}$ in which one molecule of water is included in the lattice. This water is probably held by hydrogen bonding to the oxygen atoms of the acetylacetonate.

e.g.



It was also observed that the complex is rather hygroscopic and tended to pick up more water from the atmosphere. This tendency to be hygroscopic is common with the chlorides of large organometallic cations.

The mass spectrum did not give a parent ion peak that would be expected for the above formula. The largest m/e value observed was a small peak $m/e = 397$ which could possibly be assigned to $\text{C}_{10}\text{H}_{10}\text{MoO}_2\text{C}_5\text{H}_7\text{Cl}_2^+$ (based on ⁹⁸Mo) probably formed by solid state decomposition. Larger peaks were observed at $m/e = 263, 228, 198, 172, 100, 85, 72$, assignable to $\text{C}_{10}\text{H}_{10}\text{MoCl}^+$,

$C_{10}H_{10}Mo^+$, $C_5H_5MoCl^+$, $C_3H_3MoCl^+$, $C_5H_8O_2^+$, $C_4H_5O_2^+$ and $C_4H_8O^+$ which would be expected fragments in the decomposition of $(\pi-C_5H_5)_2Mo(O_2C_5H_7)Cl \cdot H_2O$.

A solution of $(\pi-C_5H_5)_2Mo(O_2C_5H_7)Cl$ in water gave precipitates when mixed with aqueous solutions of NH_4PF_6 or $NaBF_4$ giving compounds which were the corresponding salts $[(\pi-C_5H_5)_2Mo(O_2C_5H_7)]PF_6$ and $[(\pi-C_5H_5)_2Mo(O_2C_5H_7)]BF_4$. The former salt, however, was insoluble in all solvents tried and could not be purified by recrystallisation. The tetrafluoroborate gave deep red needle crystals (d. 255-256°C) from hot water but was also rather insoluble in common solvents at room temperature. Analysis of the tetrafluoroborate gave a stoichiometry that corresponded to the formula $[(\pi-C_5H_5)_2Mo(O_2C_5H_7)]BF_4$ showing that no water was present (contrast the related chloride).

The infra-red spectrum of the tetrafluoroborate also showed typical $(\pi-C_5H_5)$ and acetylacetonate bands but showed no bands assignable to νOH .

The conductivity of the complex in nitromethane was consistent with the value expected for a 1:1 electrolyte.

F. Bis- π -cyclopentadienyl carboxylato derivatives

Reaction of $(\pi-C_5H_5)_2MoCl_2$ with $NaOCOFCF_3$ gave a green microcrystalline product (d. 188-189°C) which had the stoichiometry required by the formula $(\pi-C_5H_5)_2Mo(OCOFCF_3)_2$. The compound was fairly soluble in acetone, slightly soluble in chloroform and insoluble in ether.

The 'H.M.R. spectrum in $(CD_3)_2CO$ showed one sharp singlet assignable to $(\pi-C_5H_5)$ protons and no other bands. The infra-red showed typical $(\pi-C_5H_5)$ frequencies, CO_2 group frequencies (the band at 1694 cm^{-1} is higher

than the corresponding bands of $(\pi-C_5H_5)_2Mo(OCOC_6H_5)_2$ or $(\pi-C_5H_5)_2Mo(OCONH_2)_2$ as would be expected for the higher electronegativity of the CF_3 group - the free acid vibration occurs at 1825 cm^{-1} compared to normal carboxylic acids at ca 1700 cm^{-1}) and strong ν CF absorptions at 1186 cm^{-1} and 1138 cm^{-1} .

The mass spectrum showed a large parent ion peak at $m/e = 454$ assignable to $C_{10}H_{10}Mo(OCOCF_3)_2^+$ but also two very small fragments at $m/e = 550$ and $m/e = 500$ which could be formed by association at the temperature of introduction to the mass spectrometers and are possibly assignable to $C_{10}H_{10}MoO_2CCF_2MoC_{10}H_{10}^+$ and $C_{10}H_{10}MoCO_2MoC_{10}H_{10}^+$ respectively. Other major peaks appear to be fragments of the parent compound (see Table 12).

The compound will oxidise electrolytically and an E.S.R. signal was seen by this method. With iodine in dichloromethane solution at room temperature a weak E.S.R. signal was seen which appeared to change with time. Nitric acid with $(\pi-C_5H_5)_2Mo(OCOCF_3)_2$ gave a red solution from which red precipitates were formed with silicotungstic acid.

The analogous tungsten compound $(\pi-C_5H_5)_2W(OCOCF_3)_2$ (purple, platelike crystals, $d \sim 206^\circ\text{C}$) was characterised by analysis and had 'H.M.R. and infra-red spectra similar to those of the molybdenum complex. This tungsten complex was soluble in dichloromethane and acetone. The compound decomposed slowly in air.

The mass spectrum showed a strong parent ion peak, $m/e = 540$ ($C_{10}H_{10}W(OCOCF_3)_2^+$) but also several small peaks above this which can be attributed to binuclear tungsten species with F or O bridges, i.e. $m/e = 657$, $m/e = 641$, $m/e = 609$ and $m/e = 590$ assignable to $C_{10}H_{10}W_2F_5O_4^+$, $C_{10}H_{10}W_2F_5O_3^+$, $C_{10}H_{10}W_2F_3O^+$ and $C_{10}H_{10}W_2F_4O^+$ respectively. It thus appears that the tri-

fluoroacetates in the solid state decompose thermally with fluorine migration to form dimeric species. Other peaks in the mass spectrum are shown in Table 12.

Electrolytic oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCOCF}_3)_2$ in 1,2-dimethoxyethane gave a small E.S.R. signal of an unstable species. A solution of the tri-fluoroacetato complex in dichloromethane with a solution of iodine gave a fairly stable, single E.S.R. signal but the nature of the paramagnetic species was not determined.

$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ react with $\text{NaOCOC}_6\text{H}_5$ to give the complexes $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{OCOC}_6\text{H}_5)_2$ ($\text{M} = \text{Mo}$, deep purple needles, $d \sim 170^\circ\text{C}$; $\text{M} = \text{W}$, purple needles, $d \sim 130^\circ\text{C}$) soluble in dichloromethane and acetone. These complexes were shown to have analyses consistent with the given formulae and the molybdenum species was shown to be monomeric in chloroform.

The 'H.M.R. spectra of molybdenum and tungsten complexes showed a sharp singlet, relative intensity 10, assignable to $(\pi\text{-C}_5\text{H}_5)$ protons and two bands in the region expected for aromatic protons of relative intensities 6 and 4 assignable to meta/para and ortho hydrogens of the phenyl groups, respectively.

The mass spectrum of the molybdenum compound was recorded and showed a parent ion peak $m/e = 470$ assignable to $\text{C}_{10}\text{H}_{10}\text{Mo}(\text{OCOC}_6\text{H}_5)_2^+$ and other major peaks occurred for fragments which might be expected in the decomposition of the complex.

The infra-red spectra of $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{OCOC}_6\text{H}_5)_2$ ($\text{M} = \text{Mo}, \text{W}$) showed typical $(\pi\text{-C}_5\text{H}_5)$, aromatic and carboxylate bands. It is to be noted that the carboxylate bands 1627 sh, 1614 cm^{-1} ($\text{M} = \text{Mo}$) or 1648, 1628 sh, 1607 sh

cm^{-1} ($M = W$) are well separated from the other carboxylate bands, 1344 cm^{-1} ($M = Mo$) or 1349 1324 cm^{-1} ($M = W$) indicating the monodentate nature of the benzoato ligands. Bidentate behaviour of benzoato ligands causes the two sets of bands to become closer in value (A115).

The tungsten compound seemed less stable than the molybdenum compound to decomposition in the air.

Electrolytic oxidation of both complexes in solution gave single E.S.R. signals due to unstable species. No readily formed cations could be made. The action of nitric acid on $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCOC}_6\text{H}_5)_2$ caused destructive oxidation to give a yellow solid (probably W(VI)). Other oxidants such as H_2O_2 , benzoyl peroxide and $\text{K}_3\text{Fe}(\text{CN})_6$ in water did not readily oxidise the compound, except destructively under vigorous conditions. Iodine in dichloromethane solution on a solution of the tungsten benzoato complex turned the solution a deep red colour; the colour then became paler and dark coloured solid was deposited. The solution gave an E.S.R. signal during the course of the reaction but no signal was obtained from the precipitate which was probably an iodo-tungsten complex.

Discussion

The chemistry detailed in this chapter shows that the system $(\pi\text{-C}_5\text{H}_5)_2\text{M}$ ($M = Mo, W$) will complex with a variety of organic ligands, mainly of the hard base type with N or O coordination.

The oxygen bonded species reported are stable complexes but no characterisable M(V) cations analogous to $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$ ($X = \text{Cl}, \text{Br}$) could be obtained by oxidation of the oxy-complexes by chemical means.

Complexes with nitrogen bonding organic ligands appear to be less stable. All attempts to make complexes with purely nitrogen bonding ligands failed. The complexes, $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{NHC}_6\text{H}_4\text{S})$, prepared from o-aminothiophenol were stable and definitely involved metal-nitrogen bonds. However in the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with o-aminothiophenol other complexes were formed and one of the postulated products $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SC}_6\text{H}_4\text{NH}_2)_2$ contained no nitrogen-metal bonds. The complex $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NHC}_6\text{H}_4\text{O})$ was less stable than the related thio-complex and the tungsten complex was not characterised since the product from the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with o-aminophenol decomposed readily. Again no oxidised products of these compounds were characterised but protonated species of the o-aminothiophenolato complexes were noted.

The results, compared with previous work, seem to indicate that organic thiols form more stable complexes (A3, A124) than related oxygen or nitrogen ligands with the bis- π -cyclopentadienyl systems of molybdenum and tungsten.

Table 11

PROTON MAGNETIC RESONANCE SPECTRA OF COMPOUNDS DESCRIBED IN CHAPTER IV

Compound	Solvent	τ value ^a	Intensity ^b	Fine Structure	Assign-ment
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NHC}_6\text{H}_4\text{S})$	CDCl_3	4.82 2.8 3.4;3.7	10 } ~ 4	singlet complex	$\pi\text{-C}_5\text{H}_5$ aromatic protons
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NHC}_6\text{H}_4\text{S})$	CDCl_3	4.82 2.7 3.5;3.7	10 } ~ 4	singlet complex	$\pi\text{-C}_5\text{H}_5$ aromatic protons
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SC}_6\text{H}_4\text{NH}_2)\text{Cl}$	SO_2	4.32 2.5-3.2 3.6	10 ~ 4	singlet complex broad	$\pi\text{-C}_5\text{H}_5$ aromatic protons NH?
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OC}_6\text{H}_4\text{NH})$	CDCl_3	4.69 3.5-3.7	10 ~ 4	singlet complex	$\pi\text{-C}_5\text{H}_5$ aromatic protons
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_{14}\text{H}_8)$	CDCl_3	4.47 2.65;2.10	10 ~ 8	singlet complex	$\pi\text{-C}_5\text{H}_5$ aromatic protons
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{O}_2\text{C}_5\text{H}_7)\text{Cl}$	CDCl_3	8.13 4.33 3.91	6 1 10	singlet singlet singlet	CH_3 (of acac.) CH (of acac.) $\pi\text{-C}_5\text{H}_5$
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OCOCF}_3)_2$	$(\text{CD}_3)_2\text{CO}$	3.97		singlet	$\pi\text{-C}_5\text{H}_5$
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCOCF}_3)_2$	$(\text{CH}_3)_2\text{CO}$	4.08		singlet	$\pi\text{-C}_5\text{H}_5$
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OCOC}_6\text{H}_5)_2$	$(\text{CD}_3)_2\text{CO}$	4.10 2.58 1.95	10 6 4	singlet complex complex	$\pi\text{-C}_5\text{H}_5$ m/p.-proton o-protons

Table 11 - continued

Compound	Solvent	τ value ^a	Intensity ^b	Fine Structure	Assign-ment
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCOC}_6\text{H}_5)_2$	CDCl_3	4.29	10	singlet	$\pi\text{-C}_5\text{H}_5$
		2.57	6	complex	m/p -protons
		1.99	4	complex	o-protons

a - relative to T.M.S. as internal standard

b - relative intensity ($\pi\text{-C}_5\text{H}_5$ peak $\equiv$ 10)

Table 12
MASS SPECTRA OF COMPOUNDS DESCRIBED IN CHAPTER IV

$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NHC}_6\text{H}_4\text{S})^a$			$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NHC}_6\text{H}_4\text{S})^b$		
m/e	rel.int. ^c	assignment ^d	m/e	rel.int. ^c	assignment ^d
351	100	$\text{C}_{10}\text{H}_{10}\text{MoNHC}_6\text{H}_4\text{S}^+$	437	100	$\text{C}_{10}\text{H}_{10}\text{WSC}_6\text{H}_4\text{NH}^+$
318	5	$\text{C}_{10}\text{H}_{10}\text{MoNC}_6\text{H}_4^+$	404	4	$\text{C}_{10}\text{H}_{10}\text{WNC}_6\text{H}_4^+$
286	70	$\text{C}_5\text{H}_5\text{MoNHC}_6\text{H}_4\text{S}^+$	371	51	$\text{C}_5\text{H}_5\text{WNC}_6\text{H}_4\text{S}^+$
284	80	$\text{C}_5\text{H}_5\text{MoNC}_6\text{H}_3\text{S}^+?$	345(?)	11	$\text{C}_5\text{H}_5\text{WSC}_5\text{H}_4^+?$
252	15	$\text{C}_5\text{H}_5\text{MoNC}_6\text{H}_3^+?$	343(?)	14	$\text{C}_5\text{H}_5\text{WC}_5\text{H}_2\text{S}^+?$
236(?)	7	?	331	3	$\text{C}_5\text{H}_5\text{WC}_4\text{H}_2\text{S}^+?$
228	16	$\text{C}_{10}\text{H}_{10}\text{Mo}^+$	317(?)	8	?
205(?)	6	$\text{MoSC}_6\text{H}_3^+$	292	5	WSC_6H_4^+
195	30	$\text{C}_5\text{H}_5\text{MoS}^+$	281	7	$\text{C}_5\text{H}_5\text{WS}^+$
175.5	18	$\text{C}_{10}\text{H}_{10}\text{MoNHC}_6\text{H}_4\text{S}^{++}$	218.5	17	$\text{C}_{10}\text{H}_{10}\text{WS}_6\text{H}_4\text{NH}^{++}$
167	5	C_3HMoS^+	203	2	(double ion) ?
130	5	MoS^+	88	6	$\text{C}_4\text{H}_8\text{S}^+?$
98	3	Mo^+	86	40	$\text{C}_4\text{H}_6\text{S}^+?$
86	19	$\text{C}_4\text{H}_6\text{S}^+?$	84	63	$\text{C}_4\text{H}_4\text{S}^+$
84	30	$\text{C}_4\text{H}_4\text{S}^+$	66	5	C_5H_6^+
66	7	C_5H_6^+	59	9	HNCS^+
65	7	C_5H_5^+	51	18	C_4H_3^+
59	5	HNCS^+	49	61	$\text{H}_2\text{NSH}^+?$
51	11	C_4H_3^+	39	7	C_3H_3^+
49	30	$\text{H}_2\text{NSH}^+?$			
44	15	CS^+			
39	14	C_3H_3^+			

Table 12 - continued

$(\pi-C_5H_5)_2Mo(NHC_6H_4O)^a$			$(\pi-C_5H_5)_2W(O_2C_{14}H_8)^b$		
m/e	rel.int. ^c	assignment ^d	m/e	rel.int. ^c	assignment ^d
335	60	$C_{10}H_{10}MoNHC_6H_4O^+$	522	100	$C_{10}H_{10}WO_2C_{14}H_8^+$
270(?)	3	$C_5H_5MoNHC_6H_4O^+$	455	4	$C_5H_5WO_2C_{14}H_8^+?$
269(?)	4	$C_5H_5MoNC_6H_4O^+$	437	2	?
268(?)	4	$C_5H_5MoNC_6H_3O^+$	429(?)	1	$C_{10}H_{10}WO_2C_7H_4^+?$
252	9	$C_5H_5MoNC_6H_3$	427(?)	2	?
242(?)	3	$C_5H_5MoNC_5H_4^+?$	413	2	$C_{10}H_{10}OC_7H_4^+?$
228	100	$C_{10}H_{10}Mo^+$	330	4	$C_{10}H_{10}WO^+$
202	5	$C_5H_5MoC_3H_3^+$	314	130	$C_{10}H_{10}W^+$
200	6	$C_8H_6Mo^+?$	288	23	$C_8H_8W^+$
189	4	$C_5H_5MoCO^+?$	261	26	$C_{10}H_{10}WO_2C_{14}H_8^{++}$
167.5	5	$C_{10}H_{10}MoNHC_6H_4O^{++}$	239	22	$C_3H_3WO^+$
163	4	$C_5H_5Mo^+$	216	9	WO_2^+
98	3	Mo^+	194	11	(organic)?
80	2	$C_5H_4O^+$	189	5	(organic)?
78	2	$C_5H_4N^+$	180	6	$C_{13}H_8O^+?$
66	2	$C_5H_6^+$	165	9	(organic)?
65	2	$C_5H_5^+$	152	7	$C_{12}H_8^+?$
			95	7	(organic)?
			91	17	(organic)?
			70	10	(organic)?
			66	13	$C_5H_6^+$
			65	11	$C_5H_5^+$
(other organic peaks of lower m/e)			(other organic peaks of lower m/e)		

Table 12 - continued

[$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{O}_2\text{C}_5\text{H}_7)]^+\text{Cl}^-$ ^a			$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OCOC}_6\text{H}_5)_2$ ^a		
m/e	rel.int. ^c	assignment ^d	m/e	rel.int. ^c	assignment ^d
397(?)	0.7	$\text{C}_{10}\text{H}_{10}\text{MoO}_2\text{C}_5\text{H}_7\text{Cl}^+?$	470	3	$\text{C}_{10}\text{H}_{10}\text{Mo}(\text{OCOC}_6\text{H}_5)_2^+$
355	0.4	$\text{C}_{10}\text{H}_{10}\text{MoC}_3\text{H}_5\text{OC}_2\text{H}_5^+?$	405	100	$\text{C}_5\text{H}_5\text{Mo}(\text{OCOC}_6\text{H}_5)_2^+$
312	0.8	$\text{C}_{10}\text{H}_{10}\text{MoCH}_2\text{Cl}_2^+?$	350	39	$\text{C}_{10}\text{H}_{10}\text{MoH}(\text{OCOC}_6\text{H}_5)^+$
263	100	$\text{C}_{10}\text{H}_{10}\text{MoCl}^+$	301	8	$\text{C}_5\text{H}_5\text{MoOH}(\text{OCOC}_6\text{H}_5)^+$
228	40	$\text{C}_{10}\text{H}_{10}\text{Mo}^+$	284	0.6	$\text{C}_5\text{H}_5\text{Mo}(\text{OCOC}_6\text{H}_5)^+$
198	60	$\text{C}_5\text{H}_5\text{MoCl}^+$	254	5	?
172	10	$\text{C}_3\text{H}_3\text{MoCl}^+$	244	25	$\text{C}_{10}\text{H}_{10}\text{MoO}^+$
131.5	6	$\text{C}_{10}\text{H}_{10}\text{MoCl}^{++}$	228	16	$\text{C}_{10}\text{H}_{10}\text{Mo}^+$
114	4	$\text{C}_{10}\text{H}_{10}\text{Mo}^{++}$	214	2	$\text{C}_9\text{H}_8\text{Mo}^+?$
100	180	$\text{C}_5\text{H}_8\text{O}_2^+$	179	7	$\text{C}_5\text{H}_5\text{MoO}^+$
85	200	$\text{CH}_3\text{COCH}_2\text{CO}^+$	153	1	$\text{C}_3\text{H}_3\text{MoO}^+$
72	33	$\text{CH}_3\text{COCH}_2\text{CH}_3^+$	122	76	$\text{C}_6\text{H}_5\text{COOH}^+$
66	8	C_5H_6^+	105	400	$\text{C}_6\text{H}_5\text{CO}^+$
58	20	$\text{CH}_3\text{COCH}_3^+$	77	75	C_6H_5^+
43	325	CH_3CO^+	65	2	C_5H_6^+
			51	17	C_4H_3^+
			44	16	CO_2^+
			39	5	C_3H_3^+

Table 12 - continued

$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCOCF}_3)_2^b$			$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCCCF}_3)_2^b$ - cont.		
m/e	rel.int. ^c	assignment ^d	m/e	rel.int. ^c	assignment ^d
657	0.1	$\text{C}_{10}\text{H}_{10}\text{W}_2\text{F}_5\text{O}_4^+$	303	18	$\text{C}_5\text{H}_5\text{WOF}_2^+$
641	1	$\text{C}_{10}\text{H}_{10}\text{W}_2\text{F}_5\text{O}_3^+$	286	71	$\text{WO}_4\text{F}_2^+?$
609(?)	0.4	$\text{C}_{10}\text{H}_{10}\text{W}_2\text{F}_5\text{O}^+$	284	74	$\text{C}_5\text{H}_5\text{WOF}^+$
590	0.5	$\text{C}_{10}\text{H}_{10}\text{W}_2\text{OF}_4^+$	258	14	$\text{C}_3\text{H}_3\text{WOF}^+$
540	100	$\text{C}_{10}\text{H}_{10}\text{W}(\text{OCOOFF}_3)_2^+$	213.5	2	$\text{C}_{10}\text{H}_{10}\text{W}(\text{OCOCF}_3)^{++}$
522	3	?	200	1	WO^+
508	0.2	$\text{C}_{10}\text{H}_{10}\text{W}(\text{OCCF}_3)_2^+$	184	0.2	W^+
506	0.2	?	174.5	0.7	$\text{C}_{10}\text{H}_{10}\text{WOF}^{++}$
475	1	$\text{C}_5\text{H}_5\text{W}(\text{OCOCF}_3)_2^+$	166.5	13	$\text{C}_{10}\text{H}_{10}\text{WF}^{++}$
462	3	?	157	4	$\text{C}_{10}\text{H}_{10}\text{W}^{++}$
443	11	$\text{C}_5\text{H}_5\text{W}(\text{OCCF}_3)_2^+$	143	2	$\text{WO}_4\text{F}_2^{++}?$
427	42	$\text{C}_{10}\text{H}_{10}\text{W}(\text{OCOCF}_3)^+$	69	25	CF_3^+
409	0.5	?	65	15	C_5H_5^+
400	1	?	39	31	C_3H_3^+
397	3	$\text{C}_5\text{H}_5\text{W}(\text{OCOCF}_3)\text{OF}^+$			
381	15	$\text{C}_{10}\text{H}_{10}\text{WO}_3\text{F}^+$			
378	12	$\text{C}_{10}\text{H}_{10}\text{WO}_4^+?$			
365	1	$\text{C}_{10}\text{H}_{10}\text{WO}_2\text{F}^+$			
349	5	$\text{C}_{10}\text{H}_{10}\text{WOF}^+$			
333	64	$\text{C}_{10}\text{H}_{10}\text{WF}^+$			
314	4	$\text{C}_{10}\text{H}_{10}\text{W}^+$			
306	14	$\text{C}_5\text{H}_5\text{WF}_3^+$			

Table 12 - continued

$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OCOCF}_3)_2^a$			$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OCOCF}_3)_2^a - \text{cont.}$		
m/e	rel.int. ^c	assignment ^d	m/e	rel.int. ^c	assignment ^d
550	0.6	$(\text{C}_{10}\text{H}_{10}\text{Mo})_2\text{CF}_2\text{CO}_2^+$	201	88	$\text{C}_5\text{H}_5\text{MoF}_2^+$
500	0.3	$(\text{C}_{10}\text{H}_{10}\text{Mo})_2\text{CO}_2^+$	182	44	$\text{C}_5\text{H}_5\text{MoF}^+$
454	100	$\text{C}_{10}\text{H}_{10}\text{Mo}(\text{OCOCF}_3)_2^+$	170.5	2	$\text{C}_{10}\text{H}_{10}\text{Mo}(\text{OCOCF}_3)^{++}$
436	3	?	153	16	$\text{C}_3\text{H}_3\text{MoO}^+$
389	6	$\text{C}_5\text{H}_5\text{Mo}(\text{OCOCF}_3)_2^+$	123.5	23	$\text{C}_{10}\text{H}_{10}\text{MoF}^{++}$
357	1	$\text{C}_5\text{H}_5\text{Mo}(\text{OCCF}_3)_2^+$	114	14	$\text{C}_{10}\text{H}_{10}\text{Mo}^{++}$
341	94	$\text{C}_{10}\text{H}_{10}\text{Mo}(\text{OCOCF}_3)^+$	98	6	Mo^+
323	1	?	69	25	CF_3^+
295	48	$\text{C}_{10}\text{H}_{10}\text{MoO}_3\text{F}^+$	65	20	C_5H_5^+
247	121	$\text{C}_{10}\text{H}_{10}\text{MoF}^+$	44	19	CO_2^+
228	17	$\text{C}_{10}\text{H}_{10}\text{Mo}^+$	39	35	C_3H_3

- a - data based on isotope ^{98}Mo .
b - data based on isotope ^{184}W .
c - relative intensity of peaks.
d - probable assignment.

Chapter V

REACTIONS OF BIS- π -CYCLOPENTADIENYL SULPHUR COMPOUNDS OF MOLYBDENUM AND TUNGSTEN

The preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{SH})_2$, ($\text{M} = \text{Mo}, \text{W}(\text{A3})$), led to attempted reactions involving the coordinated thiol groups. Harris (A124) tried several reactions, including deuterium exchange, reaction of diazomethane, reaction of dimethyl sulphate and the reaction of phenylacetylene, but in no case could characterisable compounds be isolated.

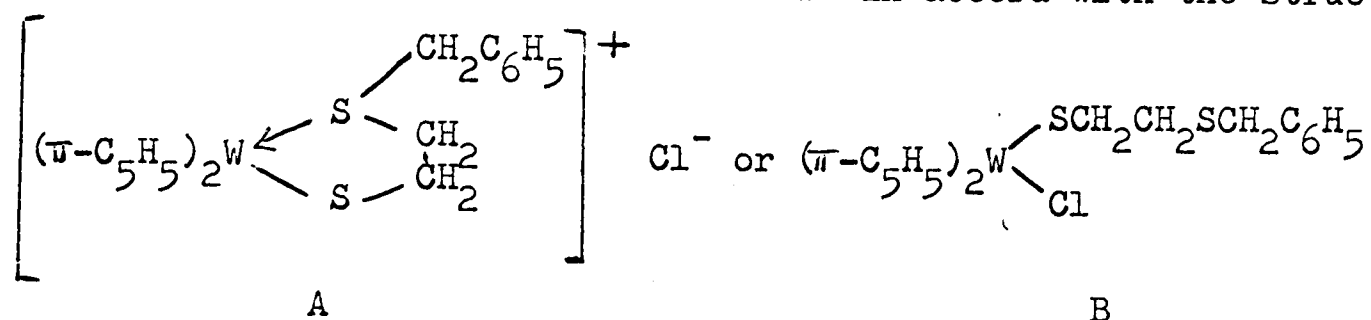
Cleavage of the thio-ligands in $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_6\text{H}_5)_2$ with hydrogen chloride gas to give the parent dichloride, $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ has been shown (A3). Harris noted that methyl iodide reacted with $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_2\text{H}_5)_2$ and suggested that $(\pi\text{-C}_5\text{H}_5)_2\text{MoI}_2$ had been formed (A124). Harris also noted that CF_3COOH reacted with $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_2\text{H}_5)_2$ to give a green product which was probably the trifluoroacetato complex reported in Chapter IV. Other reported reactions of sulphur complexes of molybdenum and tungsten have been few. It was noted that the reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_2(\text{CN})_2)$ with a mixture of nitric acid and hydrochloric acid gave mono-chloro paramagnetic complexes and finally led to the formation of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^+$ cations (A3). Phenyl azide was noted to react with $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_2\text{H}_5)_2$ to give an unknown product (A124).

A. Reactions of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$

a) The compound $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ reacted with benzyl chloride on warming to give an orange, crystalline product ($d \sim 185^\circ\text{C}$) which elemental analysis showed to have a stoichiometry consistent with the formula

$(\pi\text{-C}_5\text{H}_5)_2\text{W}((\text{SCH}_2)_2\text{CH}_2\text{C}_6\text{H}_5)\text{Cl}$. The infra-red spectrum showed typical $(\pi\text{-C}_5\text{H}_5)$, aromatic and aliphatic C-H frequencies. The $^1\text{H.M.R.}^*$ spectrum in liquid sulphur dioxide showed a singlet peak of relative intensity 10 assignable to $(\pi\text{-C}_5\text{H}_5)$ protons, a peak at $\tau = 2.55$ of relative intensity 5 assignable to phenyl protons and 3 peaks each of relative intensity 2; the 2 high field peaks of the latter were basically triplets and may be assigned to the $-\text{CH}_2-\text{CH}_2-$ system of the sulphur ligand.

The $^1\text{H.M.R.}$ and the other data are in accord with the structures:



It must be noted that the triplets of the resonances of the $-\text{CH}_2-\text{CH}_2-$ system were slightly distorted (this was seen more clearly in the spectrum of the related complex $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{CH}_3]\text{I}$ (see below) which was run on the Perkin Elmer Spectrometer and not the J.E.O.L. Spectrometer) and this would be in accord with structure A since the $-\text{CH}_2-\text{CH}_2-$ system is held in a ring without a plane of symmetry in the plane of the ring thus making the protons inequivalent.

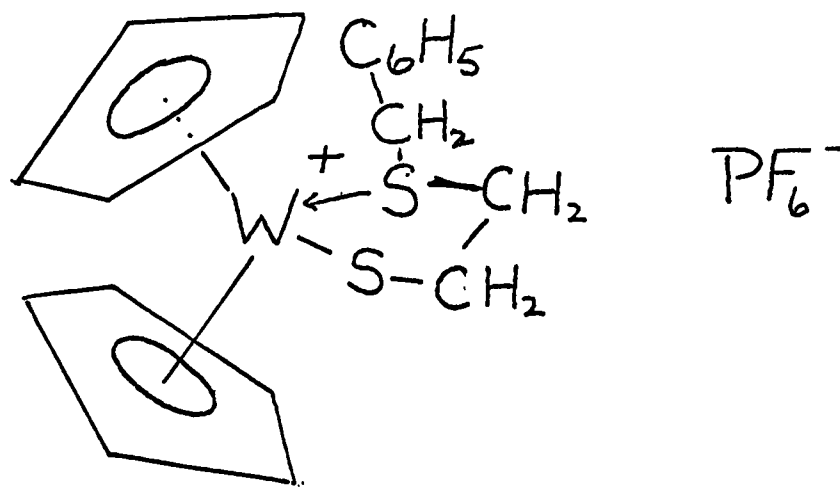
The conductivity of the compound was also high and supported structure A. The value ($\Lambda = 68.2 \text{ ohm}^{-1} \text{ cm}^2$) approached the value expected for a 1:1 electrolyte ($\Lambda \sim 85\text{-}95 \text{ ohm}^{-1} \text{ cm}^2$ in nitromethane (B4)). However it must be noted that the conductivity was appreciably lower than that found for any

* See Table 13 for all $^1\text{H.M.R.}$ spectra of compounds described in Chapter V.

of the other similar complexes reported in this section ($\lambda \sim 90$) and it might be inferred that some interaction between the chlorine ion and the metal occurs.

The compound was slightly soluble in dichloromethane, from which it was recrystallised, but soluble in water and liquid sulphur dioxide.

The solution of $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{CH}_2\text{C}_6\text{H}_5]\text{Cl}$ in water gave a precipitate with aqueous NH_4PF_6 solution to give an orange compound ($d \sim 190^\circ\text{C}$) which analysis showed to have a stoichiometry required for the formula $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{CH}_2\text{C}_6\text{H}_5]\text{PF}_6$. The conductivity ($\lambda = 84.4 \text{ ohm}^{-1} \text{ cm}^2$) was around the value expected for a 1:1 electrolyte and was higher than the value for the related chloride indicating less covalent type interaction between the PF_6^- anion and the cation than between Cl^- and cation. The $^1\text{H.M.R.}$ spectrum of the PF_6^- complex was similar to that of the Cl^- complex. However it was noted that under high resolution the resonance due to $(\pi\text{-C}_5\text{H}_5)$ protons was a doublet with a splitting of $\sim 1.7 \text{ c/s}$. This is consistent with a ring structure which would make the two $(\pi\text{-C}_5\text{H}_5)$ rings inequivalent since 3 coordinate sulphur will assume trigonal-pyramidal symmetry:



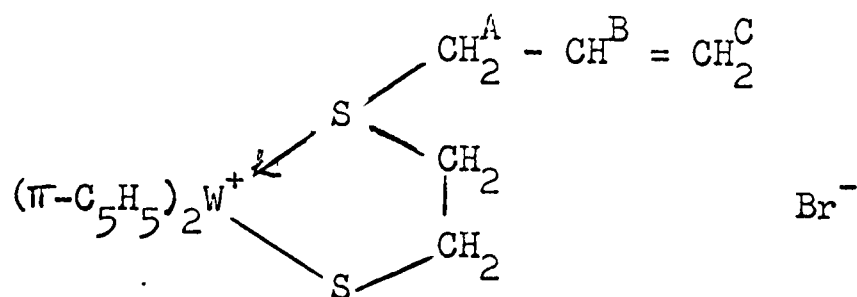
This splitting was not observed in the spectrum of the Cl^- salt. This latter fact may be due to bad resolution or poor spinning of the sample

recorded but could be a consequence of Cl^- interaction with the complex.

Another point concerning the PF_6^- complex was its readiness to include SO_2 in its crystalline lattice. The SO_2 could be pumped off under vacuum after washing with ether but this resulted in destruction of the crystal lattice.

The reaction of a solution of iodine in dichloromethane on a dichloromethane solution of $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{CH}_2\text{C}_6\text{H}_5]\text{Cl}$ gave no product with an E.S.P. signal. However reaction must have occurred since the iodine solution was discoloured. Thus iodine was added until no more discolouration occurred. Some of the product which separated from the solution was shown to be soluble in liquid sulphur dioxide. After 3 recrystallisations from liquid sulphur dioxide, pale yellow needle shaped crystals were obtained which had an infra red spectrum similar to that of the starting material, $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{CH}_2\text{C}_6\text{H}_5]\text{Cl}$, and analysis (Found C, 36.3; H, 3.3; I, 22.35%) indicates that this was probably an impure sample of the corresponding iodide ($\text{C}_{19}\text{H}_{21}\text{S}_2\text{IW}$ requires C, 36.6; H, 3.4; I, 20.3%). However other products were formed since black material, insoluble in liquid sulphur dioxide, was also obtained.

b) Allyl bromide reacted with $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ to give orange crystals (d $\sim 200^\circ\text{C}$) of stoichiometry corresponding to $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{C}_3\text{H}_5]\text{Br}$. The infra-red spectrum shows typical $(\pi\text{-C}_5\text{H}_5)$ and alkyl CH frequencies and a weak band at 1632 cm^{-1} assignable, probably, to C=C in plane vibration. The conductivity ($\Lambda = 88.4$) is consistent with a 1:1 electrolyte. The $^1\text{H.M.R.}$ spectrum in liquid sulphur dioxide is also consistent with the above formula.



The bands due to the $-\text{CH}_2-\text{CH}_2-$ system (essentially two triplets) and the $(\pi\text{-C}_5\text{H}_5)$ protons are distinct. Also the doublet due to CH_2^A protons and the multiplet due to CH^B are clear. However, the resonance due to the vinyl CH_2^C protons appears very close to the $(\pi\text{-C}_5\text{H}_5)$ proton resonance signal and is partly obscured by the latter but appears to be approximately a doublet with, probably, further splitting, since cis and trans protons are inequivalent.

This complex is negligibly soluble in dichloromethane but soluble in water and sulphur dioxide. The solution in water gives a precipitate with NH_4PF_6 . This PF_6^- derivative can be recrystallised from liquid sulphur dioxide to give red crystals but these contain SO_2 of crystallisation and pumping on a vacuum line removes this to give an orange solid (d. $210\text{-}212^\circ\text{C}$) of stoichiometry corresponding to $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{C}_3\text{H}_5]\text{PF}_6$. The conductivity ($\Lambda = 90.8$) is consistent with a 1:1 electrolyte. The infra-red is similar to that of the bromide complex except for additional bands assignable to PF_6^- ($870\text{-}800$, 557 cm^{-1}).

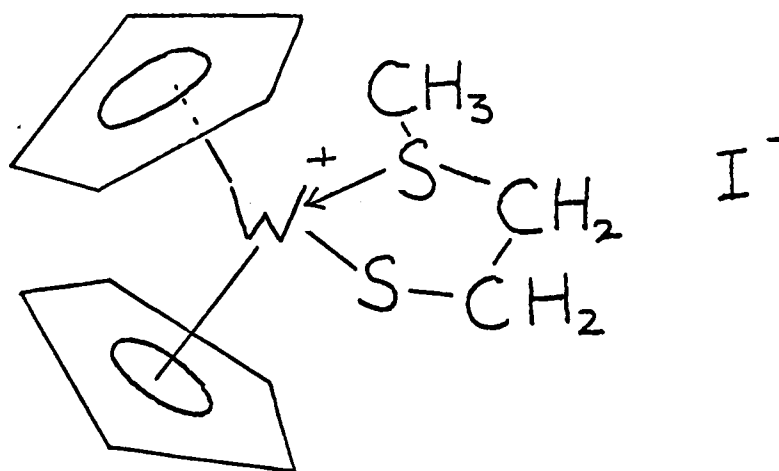
The $^1\text{H.M.R.}$ spectrum of the PF_6^- derivative was similar to that of the Br^- derivative. No splitting of the $(\pi\text{-C}_5\text{H}_5)$ proton resonance peak was observed but this was probably obscured by the overlapping of $(\pi\text{-C}_5\text{H}_5)$ and vinyl CH_2^C resonance bands.

c) The reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ with methyl iodide in dichloromethane gave a similar complex (orange crystals d. $216\text{-}220^\circ\text{C}$) with stoichiometry

corresponding to $[(\pi-C_5H_5)_2W(SCH_2)_2CH_3]I$ and the conductivity of a 1:1 electrolyte. The complex was negligibly soluble in organic solvents but dissolved in water from which the hexafluorophosphate $[(\pi-C_5H_5)_2W(SCH_2)_2CH_3]PF_6$ could be formed (orange solid d.217-220°C) which was also characterised by analysis and shown to have the conductivity of a 1:1 electrolyte.

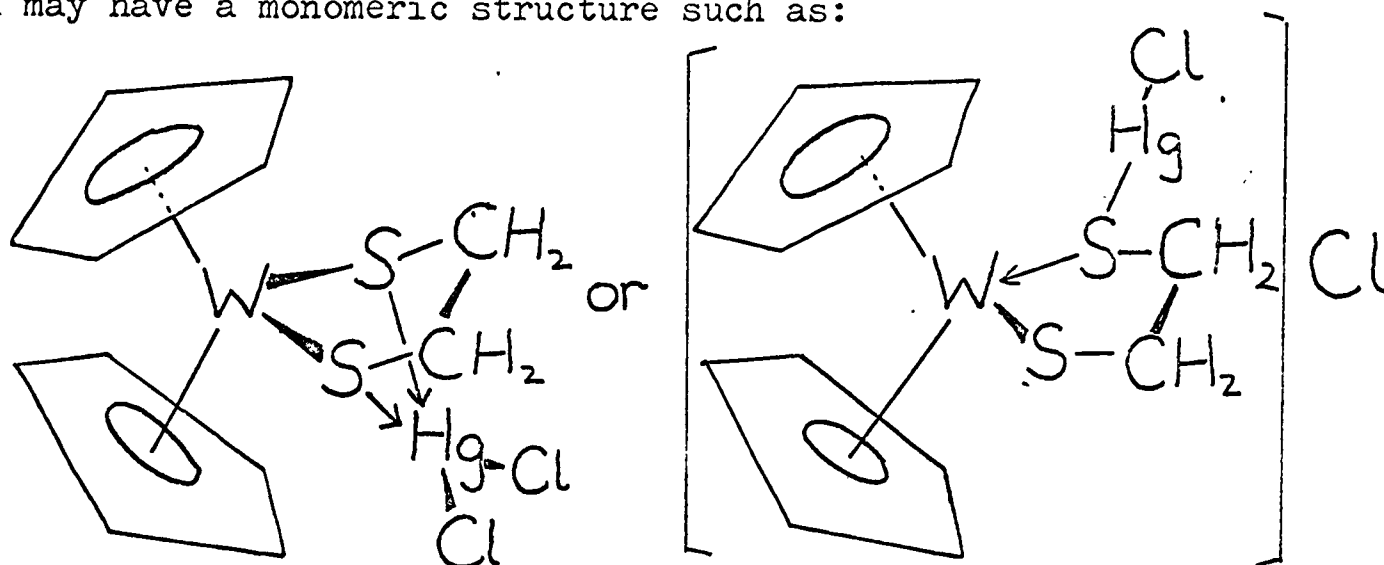
The infra-red spectra of both complexes showed $(\pi-C_5H_5)$ and alkyl CH frequencies and the latter complex showed vibrations assignable to PF_6^- .

Both complexes were soluble in liquid sulphur dioxide and $^1H.M.R.$ spectra run in this solvent were essentially the same. Bands of relative intensities 10 and 3 assignable to $(\pi-C_5H_5)$ and CH_3 protons and two distorted triplets each of relative intensity 2 assignable to the $-CH_2-CH_2-$ system were observed. However under high resolution and scale expansion the $(\pi-C_5H_5)$ resonance of $[(\pi-C_5H_5)_2W(SCH_2)_2CH_3]I$ was shown to be a doublet of splitting ~ 0.5 c/s. This would be expected for a structure:



(No splitting was noticed for the PF_6^- derivatives but this was probably due to lower resolution.) The splitting is smaller than that found for the compound $[(\pi-C_5H_5)_2W(SCH_2)_2CH_2C_6H_5]PF_6$ as would be expected since the presence of a methyl group will cause less inequivalence of the cyclopentadienyl rings than the presence of a bulky benzyl group.

d) The compound $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ in dichloromethane reacted with HgCl_2 to give an orange compound ($d \sim 200^\circ\text{C}$) which was found to be insoluble in common solvents. However analysis showed this to have a stoichiometry consistent with the formula $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{HgCl}_2$, and this formula was also supported by the infra-red spectrum which showed typical $(\pi\text{-C}_5\text{H}_5)$ and alkyl CH frequencies. Since the compound was insoluble $^1\text{H.N.R.}$ studies could not be made. The compound must be similar to those complexes detailed above, but its insolubility may mean that it is greater than a monomer. However the presence of Hg may reduce the solubility and the complex may have a monomeric structure such as:



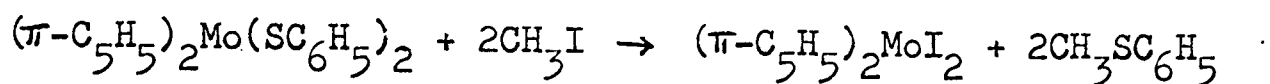
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ was also shown to react with $\text{BF}_3\text{Et}_2\text{O}$ to give a yellow compound which was hydrolytically unstable. No reaction occurred between $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ and $\text{C}_2\text{H}_5\text{Br}$ or $\text{C}_6\text{F}_5\text{Cl}$ at room temperature or with gentle heating.

B. Reactions of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SR})_2$ compounds

a) When $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_6\text{H}_5)_2$ was dissolved in dichloromethane and excess methyl iodide added a smooth reaction took place over several minutes, during which time the solution became green in colour and then green crystals were deposited. These crystals after recrystallisation from liquid sulphur

dioxide were shown by infra-red spectrum and analysis to be $(\pi\text{-C}_5\text{H}_5)_2\text{MoI}_2$.

Thus the reaction:



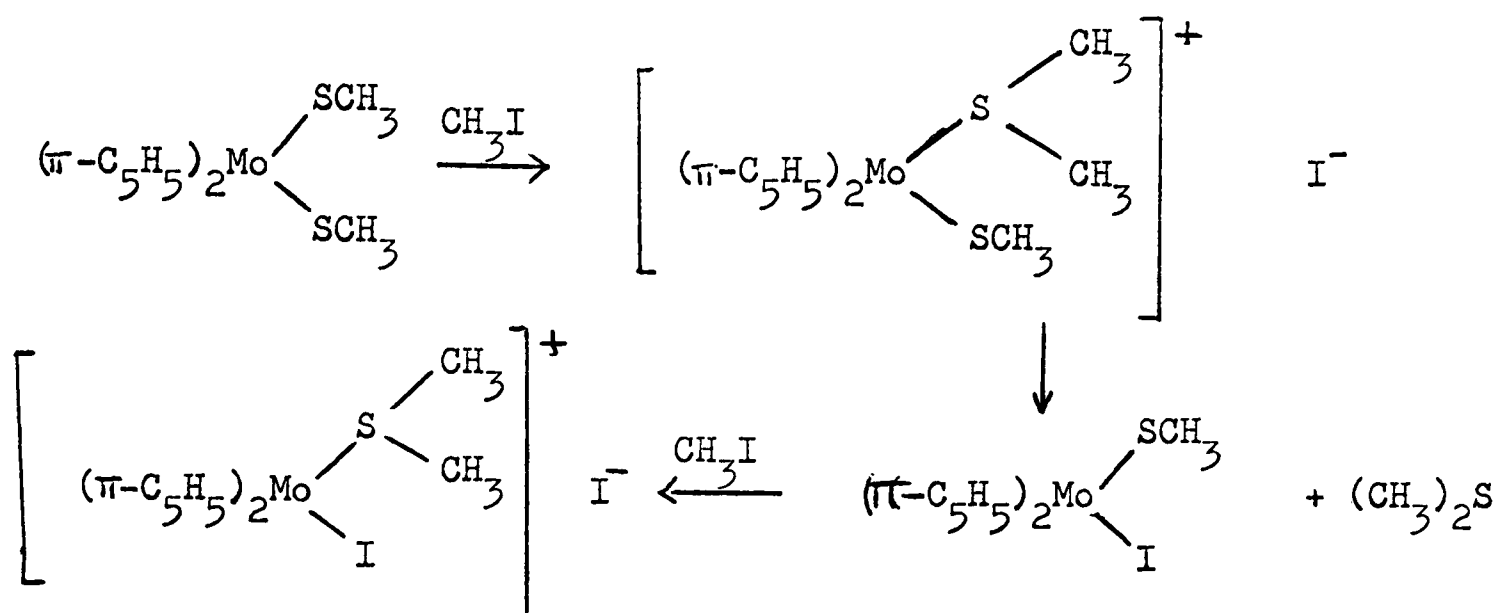
took place and no intermediate product was isolable. It was also noted that $(\pi\text{-C}_5\text{H}_5)_2\text{Mo(SC}_6\text{H}_5)_2$ reacted with iodine in dichloromethane solution to give a green solid - probably $(\pi\text{-C}_5\text{H}_5)_2\text{MoI}_2$.

b) $(\pi\text{-C}_5\text{H}_5)_2\text{Mo(SCH}_3)_2$ in dichloromethane solution reacted with excess methyl iodide to give a green crystalline solid. This solid could be recrystallised from dimethyl sulphoxide to give needle shaped crystals ($d \sim 250^\circ\text{C}$) with the stoichiometry corresponding to $[(\pi\text{-C}_5\text{H}_5)_2\text{MoS(CH}_3)_2\text{I}]\text{I}$. This complex was readily soluble in water (unlike $(\pi\text{-C}_5\text{H}_5)_2\text{MoI}_2$), fairly soluble in dichloromethane and soluble in dimethyl sulphoxide and liquid sulphur dioxide. However recrystallisation from the latter solvent generally caused the product to separate as an oil which was analytically impure.

The conductivity in nitromethane was consistent with that of a 1:1 electrolyte. The infra-red spectrum showed typical $(\pi\text{-C}_5\text{H}_5)$ and alkyl CH frequencies. The $^1\text{H.M.R.}$ in $(\text{D}_3\text{C})_2\text{SO}$ showed two singlet peaks in approximate intensity ratios 10:6 (presence of a little undeuterated dimethyl sulphoxide made intensity measurements difficult) assignable to $(\pi\text{-C}_5\text{H}_5)$ and CH_3 proton resonances respectively.

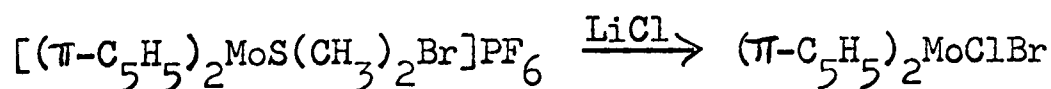
The solution of this complex in water gave a strong precipitate with NH_4PF_6 solution indicating the presence of a large cation and the complex formed was probably $[(\pi\text{-C}_5\text{H}_5)_2\text{MoS(CH}_3)_2\text{I}]\text{PF}_6$.

All the evidence points to the formation of the compound by a scheme similar to:



The compound $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_6\text{H}_5)_2$ with methyl iodide must go through a similar displacement process but go further to give the di-iodide. It is to be noted that $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ showed no reaction with methyl iodide at room temperature.

The compound $[(\pi\text{-C}_5\text{H}_5)_2\text{MoS}(\text{CH}_3)_2\text{Br}]\text{PF}_6$ (prepared from the compound $[(\pi\text{-C}_5\text{H}_5)_2\text{MoS}(\text{CH}_3)\text{Br}]\text{Br}$ analogous to the above iodo-compound by reaction with NH_4PF_6 (G9)) reacted with a less than molar proportion of dry LiCl to give a green product which could be recrystallised from liquid sulphur dioxide. Analysis and infra-red suggested that it was a mixed halide formed by the displacement of dimethylthioether by Cl^- .



Oxidation of this green complex with nitric acid, precipitation with NH_4PF_6 solution and recrystallisation from liquid sulphur dioxide gave purple crystals. The E.S.R. spectrum of these crystals in dimethyl sulphoxide solution (or acetone) gave one signal consisting of a central band split into 4 lines ($g = 2.025$, $A_{\text{Br}} = 15.9$ gauss, in D.M.S.O.) and molybdenum

satellites, due to $^{95}\text{Mo}/^{97}\text{Mo}$, ($A_{\text{Mo}} \sim 32$ gauss), similarly split, which probably arises from the cation $(\pi\text{-C}_5\text{H}_5)_2\text{MoClBr}^+$ (compare exchange experiments in strong acids, Chapter VII). However another signal of lower intensity at $g = 1.999$, split into 7 lines ($A \sim 3$ gauss), which must be assigned to $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^+$ (A2) was present. This indicates that either the neutral mixed halide was slightly impure or that halogen exchange takes place on oxidation and that the purple crystals were a mixture of $(\pi\text{-C}_5\text{H}_5)_2\text{MoClBrPF}_6$ with a smaller amount (ca. 10-20%) of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2\text{PF}_6$. Oxidation of the green neutral mixed halide with bromine in a chloroform suspension led to the production of a cationic product that had signals due to $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^+$, $(\pi\text{-C}_5\text{H}_5)_2\text{MoClBr}^+$ and $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2^+$ in its E.S.R. spectrum.

C. Oxidation of sulphur compounds

It was found that most sulphur compounds did not oxidise readily but were decomposed by excess nitric acid.

However, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$, when suspended in water and oxidised with nitric acid gave a violet solution which gave a precipitate with aqueous NH_4PF_6 . (N.B. further oxidation to a yellow species also readily occurred and had to be avoided.) Purple crystals were obtained, after recrystallisation from liquid sulphur dioxide, which had a stoichiometry consistent with the formula $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)]\text{PF}_6$. The infra-red spectrum of this complex showed typical $(\pi\text{-C}_5\text{H}_5)$ and PF_6^- frequencies and bands at 1584 cm^{-1} and 1524 cm^{-1} which are probably aromatic frequencies (C=C in plane vibrations) but aromatic bands in the region $750\text{-}810\text{ cm}^{-1}$ were probably obscured by PF_6^- absorption. $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ shows a band at 797 s ,

cm^{-1} (A3)).

The compound was paramagnetic and showed a single E.S.R. signal at $g = 1.994$ in acetone solution. A similar signal was obtained by electrolytic oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ in 1,2-dimethoxyethane at $g = 1.994$. This suggests the compound is the same as the electrolytically formed species.

The analogous molybdenum complex, $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ was oxidised by nitric acid and a precipitate was obtained from the solution with HSbCl_6 which gave an E.S.R., $g = 2.009$ in D.M.S.O., but the complex was not characterised. Electrolytic oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ also gave a single signal, $g = 2.009$, in 1,2-dimethoxyethane.

The action of a solution of iodine in dichloromethane on $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ gave dark coloured crystals which were paramagnetic, with single E.S.R. signal in CH_2Cl_2 , $g = 1.994$, but attempted purification was unsuccessful and they were reduced by acetone on an alumina column to the neutral starting complex. The analytical results on impure product and the E.S.R. result suggest that a complex $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)^+\text{I}_x^-$ was present.

Action of nitric acid on the complex $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ gave a purple coloured cation which could be precipitated with NH_4PF_6 but was not obtained pure. An E.S.R. spectrum of the purple precipitate, recrystallised from liquid sulphur dioxide, gave a signal at $g = 2.046$ in acetone. The infra-red spectrum of the purple crystals showed $(\pi\text{-C}_5\text{H}_5)$ and PF_6^- frequencies (e.g. 3134, 900-800 and 559 cm^{-1}).

D. Discussion

The reaction of alkyl halides with bis- π -cyclopentadienyl sulphur complexes depends upon the nature of the sulphur complex. Thus no ready reaction

occurs with alkyl halides and the aromatic, chelated sulphur ligand complex, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$.

The chelated alkyl sulphur ligand complex $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ react additively with reactive alkyl halides to give cationic species $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{R}]^+\text{X}^-$ ($\text{R} = \text{CH}_3, \text{C}_3\text{H}_5, \text{C}_6\text{H}_5\text{CH}_2$) and no cleavage of metal sulphur bonds occur. However mono-dentate thio complexes under the action of methyl iodide undergo ligand cleavage. The aromatic ligand complex $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_6\text{H}_5)_2$ gives $(\pi\text{-C}_5\text{H}_5)_2\text{MoI}_2$ and the aliphatic ligand complex $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SCH}_3)_2$ gives $[(\pi\text{-C}_5\text{H}_5)_2\text{MoI}(\text{S}(\text{CH}_3)_2)]\text{I}$. The fact that the aromatic complex does not form a complex $[(\pi\text{-C}_5\text{H}_5)_2\text{MoI}(\text{CH}_3\text{SC}_6\text{H}_5)]\text{I}$ may be due to the large ligand $\text{C}_6\text{H}_5\text{SCH}_3$ making such a complex unstable to further cleavage by iodide. It has also been shown that the dimethyl thioether in the complex $[(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}(\text{S}(\text{CH}_3)_2)]\text{PF}_6$ can be displaced by Cl^- ions forming a mixed halide complex $(\pi\text{-C}_5\text{H}_5)_2\text{MoClBr}$ as major product.

The oxidation of sulphur complexes appears to proceed more readily with the aromatic chelated complexes $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ and the only characterised cation has been $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)]\text{PF}_6$. However the chelated complex $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ is noted to oxidise to an uncharacterised cation. This readiness to oxidation is reflected by the difficulty of metal sulphur bond cleavage noted above.

Table 13

PROTON MAGNETIC RESONANCE SPECTRA OF COMPOUNDS DESCRIBED IN CHAPTER V

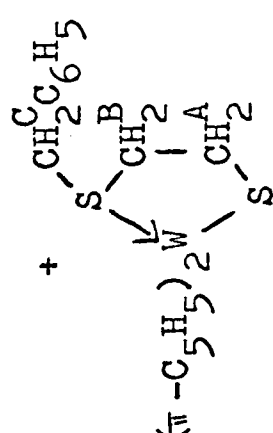
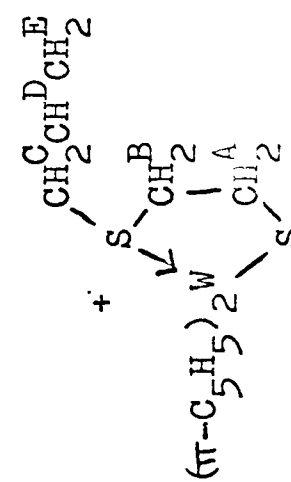
Compound	Solvent	τ value ^a	Intensity ^b	Fine Structure	Assignment
Cl^- 	SO_2	2.53	5	complex	aromatic protons $\pi\text{-C}_5\text{H}_5$ H^{C} H^{B} H^{A}
		4.33	10	singlet	
		5.68	2	singlet	
		7.56	2	triplet, $J \sim 6.5$ c/s	
		8.10	2	triplet, $J \sim 6.5$ c/s	
	SO_2	2.55	5	complex	aromatic protons $\pi\text{-C}_5\text{H}_5$ (inequiv.) H^{C} H^{B} H^{A}
		4.38	10	doublet (~ 1.7 c/s)	
		5.75	2	singlet	
		7.58	2	triplet, $J \sim 6.5$ c/s	
		8.09	2	triplet, $J \sim 6.5$ c/s	
Br^- 	SO_2	3.9	1	complex	H^{D} $\pi\text{-C}_5\text{H}_5$ H^{E} H^{C} H^{B} H^{A}
		4.3	10	singlet	
		~ 4.4	~ 2	multiplet ($J \sim 12$ c/s)	
		6.15	2	doublet, $J \sim 7$ c/s	
		7.4	2	triplet, $J \sim 6$ c/s	
	SO_2	7.95	2	triplet, $J \sim 6$ c/s	
		4.04	1	complex	H^{D} $\pi\text{-C}_5\text{H}_5$ H^{E} H^{C} H^{B} H^{A}
		4.40	10	singlet	
		~ 4.5	~ 2	multiplet ($J \sim 12$ c/s)	
		6.24	2	doublet, $J \sim 7$ c/s	
		7.48	2	triplet, $J \sim 6$ c/s	
	SO_2	8.04	2	triplet, $J \sim 6$ c/s	H^{A}

Table 13 - continued

Compound	Solvent	τ value ^a	Intensity ^b	Fine Structure	Assignment
$ \begin{array}{c} \text{CH}_3 \\ \\ \text{S} \diagup \text{CH}_2 \text{B} \\ \\ \text{CH}_2 \text{A} \\ \\ \text{S} \diagdown \text{CH}_2 \\ \\ \text{W} \\ \\ (\pi\text{-C}_5\text{H}_5)_2 \end{array} + \text{I}^- $	SO ₂	4.31	10	doublet (~ 0.5 c/s)	$\pi\text{-C}_5\text{H}_5$ (inequiv.)
		7.07	3	singlet	CH ₃ B
		7.41	2	triplet, J = 6-7 c/s	H ^A
		7.98	2	triplet, J = 6-7 c/s	H ^A
$ \begin{array}{c} \text{CH}_3 \\ \\ \text{S} \diagup \text{CH}_2 \text{B} \\ \\ \text{CH}_2 \text{A} \\ \\ \text{S} \diagdown \text{CH}_2 \\ \\ \text{W} \\ \\ (\pi\text{-C}_5\text{H}_5)_2 \end{array} + \text{PF}_6^- $	SO ₂	4.42	10	singlet	$\pi\text{-C}_5\text{H}_5$
		7.15	3	singlet	CH ₃ B
		7.47	2	triplet, J ~ 7 c/s	H ^A
		8.02	2	triplet, J ~ 7 c/s	H ^A
$ \begin{array}{c} \text{CH}_3 \\ \\ \text{S} \diagup \text{CH}_2 \text{B} \\ \\ \text{CH}_2 \text{A} \\ \\ \text{S} \diagdown \text{CH}_2 \\ \\ \text{W} \\ \\ (\pi\text{-C}_5\text{H}_5)_2 \end{array} + \text{S}(\text{CH}_3)_2 $	(D ₃ C) ₂ SO	4.13		singlet	$\pi\text{-C}_5\text{H}_5$
		7.48		singlet	CH ₃
	SO ₂ ^c	4.20	10	singlet	$\pi\text{-C}_5\text{H}_5$
		7.41	6	singlet	CH ₃

a - τ value relative to T.M.S. as internal standard.

b - relative intensity ($\pi\text{-C}_5\text{H}_5 \equiv 10$)

c - decomposition in this solvent (other smaller peaks observed - one at $\tau = 4.32$ assignable to $(\pi\text{-C}_5\text{H}_5)_2\text{MoI}_2$).

Chapter VI

E.S.R. STUDIES ON BIS- π -CYCLOPENTADIENYL COMPOUNDS OF MOLYBDENUM AND TUNGSTEN

Since most organometallic compounds obey the 18 electron rule few have been studied by E.S.R. spectroscopy. However some of the metallocenes are paramagnetic and E.S.R. spectra have been obtained for the triplet molecule, $(\pi\text{-C}_5\text{H}_5)_2\text{V}$, at low temperatures (F1, F2), the ionic compound, $(\pi\text{-C}_5\text{H}_5)_2\text{Mn}$ (F3), and the compounds, $(\pi\text{-C}_5\text{H}_5)_2\text{Rh}$ and $(\pi\text{-C}_5\text{H}_5)_2\text{Ir}$, as glasses at liquid nitrogen temperature (F4).

Bis- π -arene cations of chromium, $(\pi\text{-ArH})_2\text{Cr}^+$, give well resolved spectra even at room temperature showing splittings due to hydrogens of the aromatic rings (F5, F6). The related compounds of molybdenum and tungsten, at lower temperatures (F7), and the neutral complexes, of the type $(\pi\text{-ArH})_2\text{V}$ (F8), also show similar E.S.R. spectra.

Other studies on well characterised organometallic compounds have been few, but isolated examples of spectra obtained from compounds such as $(\pi\text{-C}_5\text{H}_5)_3\text{Ni}(\text{CO})_2$ (F9), $(\pi\text{-C}_5\text{H}_5)_2\text{VCl}_2$ (A21), $(\text{py})_3\text{TiRCl}_3$ (R = alkyl, aryl) (F10) and monomers formed from $[(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ (F11) and $[(\pi\text{-allyl})\text{Fe}(\text{CO})_3]_2$ (F12) have been reported. The E.S.R. spectra of the dihalide cations, $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$ (M = Mo, W), reported by Cooper (A2), have been described earlier and will be discussed later.

Other notable E.S.R. studies on organometallic compounds have been mentioned briefly in the introduction. Thus, several studies on the system $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ —aluminium alkyl or related titanium systems have been made and E.S.R. spectra observed of the resulting Ti(III) complexes which have, in

general, splittings arising from ^{27}Al and alkyl protons (A40, A41, F13, F14). The nitrogen fixing system $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2\text{-RMgBr}$ has been studied by E.S.R. and preliminary reports suggested the formation of a nitrogen complex $[(\pi\text{-C}_5\text{H}_5)_2\text{TiNH}]_2$ (A47) but this has later been thrown in doubt. However a paramagnetic species, probably $[(\pi\text{-C}_5\text{H}_5)_2\text{TiH}_2]^-$, is formed since its E.S.R. spectrum shows triplet splitting by two equivalent hydrogen atoms (A48). Hydrogen splitting by hydrogens of the cyclopentadienyl rings, and by ^7Li , if lithium naphthalide is used as the reducing agent, can also be observed (A49). Ti(III) alkyl complexes of proposed formulae $[(\pi\text{-C}_5\text{H}_5)_2\text{TiR}_2]^-$ or $[(\pi\text{-C}_5\text{H}_5)_2\text{TiR(solv)}]^-$ are also formed from $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2\text{-LiR}$ mixtures and show distinctive E.S.R. signals (A48).

Dessy and co-workers have studied the electrochemical behaviour of numerous organometallic complexes using polarographic techniques (F15, F16, F17), and have shown that, in a lot of cases, electrolytic reduction or, in a few cases, oxidation can take place. The generally unstable species produced were looked at by E.S.R. spectroscopy and it was found that in a few cases signals were obtained. The most extensive and interesting set of signals were derived from bi-metallic transition metal compounds of V, Cr, Mo, W, Fe, Co, Ni with phosphorus or sulphur bridges, e.g.

$[(\pi\text{-C}_5\text{H}_5)\text{V}(\text{S}_2\text{C}_4\text{F}_6)]_2$, $[\text{M}(\text{CO})_4\text{P}(\text{CH}_3)_2]_2$ ($\text{M} = \text{Cr}, \text{W}$) and $[(\pi\text{-C}_5\text{H}_5)\text{MP}(\text{C}_6\text{H}_5)_2]_2$ ($\text{M} = \text{Co}, \text{Ni}$). Other paramagnetic species of unknown nature were formed from acetylenic metal complexes and the E.S.R. spectra of $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}$, $(\pi\text{-C}_5\text{H}_5)\text{VCl}$ and a species formed by the reduction of $(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ (postulated to be $(\pi\text{-C}_5\text{H}_5)_2\text{Ti-SC}_6\text{H}_3\text{CH}_3\text{S}^-$) were also observed. It was reported that $\text{Mo}(\text{CO})_4(\text{dipy})$ gave a complex spectrum on reduction to the

mono-anion.

Biochemical studies of metals in enzymes by E.S.R. have been made but usually little information of the nature of the metallic site is obtained. However for reduced xanthine oxidase, a Mo and Fe containing enzyme, an Mo(V) signal shows a doublet splitting assigned to a unique hydrogen which is interacting with the metal (F18).

In this chapter E.S.R. studies on compounds reported elsewhere in this work will be discussed.

A. Paramagnetic complexes isolated in the solid state

a) Solution Spectra

The ionic complexes, $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2\text{PF}_6$ ($\text{X} = \text{Cl}, \text{Br}; \text{M} = \text{Mo}, \text{W}$), were characterised by Cooper and he also obtained their E.S.R. spectra in solution. The values for the parameters shown in table 14 were run on samples made by Cooper's method and agree, within experimental error, with previous results (A2). The complexes, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})\text{ClPF}_6$ (see p. 54), $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)\text{PF}_6$ (see p.135), $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MCl}(\text{C}_6\text{F}_5)\text{PF}_6$ ($\text{M} = \text{Mo}, \text{W};$ see p. 93) have been characterised and the results of E.S.R. experiments in solution are recorded in table 14, and the spectra of the latter two complexes are shown in figures 7 and 8. The compound $(\pi\text{-C}_5\text{H}_5)_2\text{MoBrClPF}_6$ (see p.134), although not obtained free from $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2\text{PF}_6$, is almost certainly of the formula given and details of its solution spectra are given. Also the complex formed by the reaction of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WH}(\text{C}_6\text{F}_5)$ with bromoform (see p. 93), although not characterised, is probably $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WBr}(\text{C}_6\text{F}_5)\text{-PF}_6$ (compare the analogous chloride and the expected four line spectrum which is observed). The compound precipitated from oxidised

Figure 7.

E.S.R. spectrum of

$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoCl}(\text{C}_6\text{F}_5)\text{PF}_6$
in acetone solution.

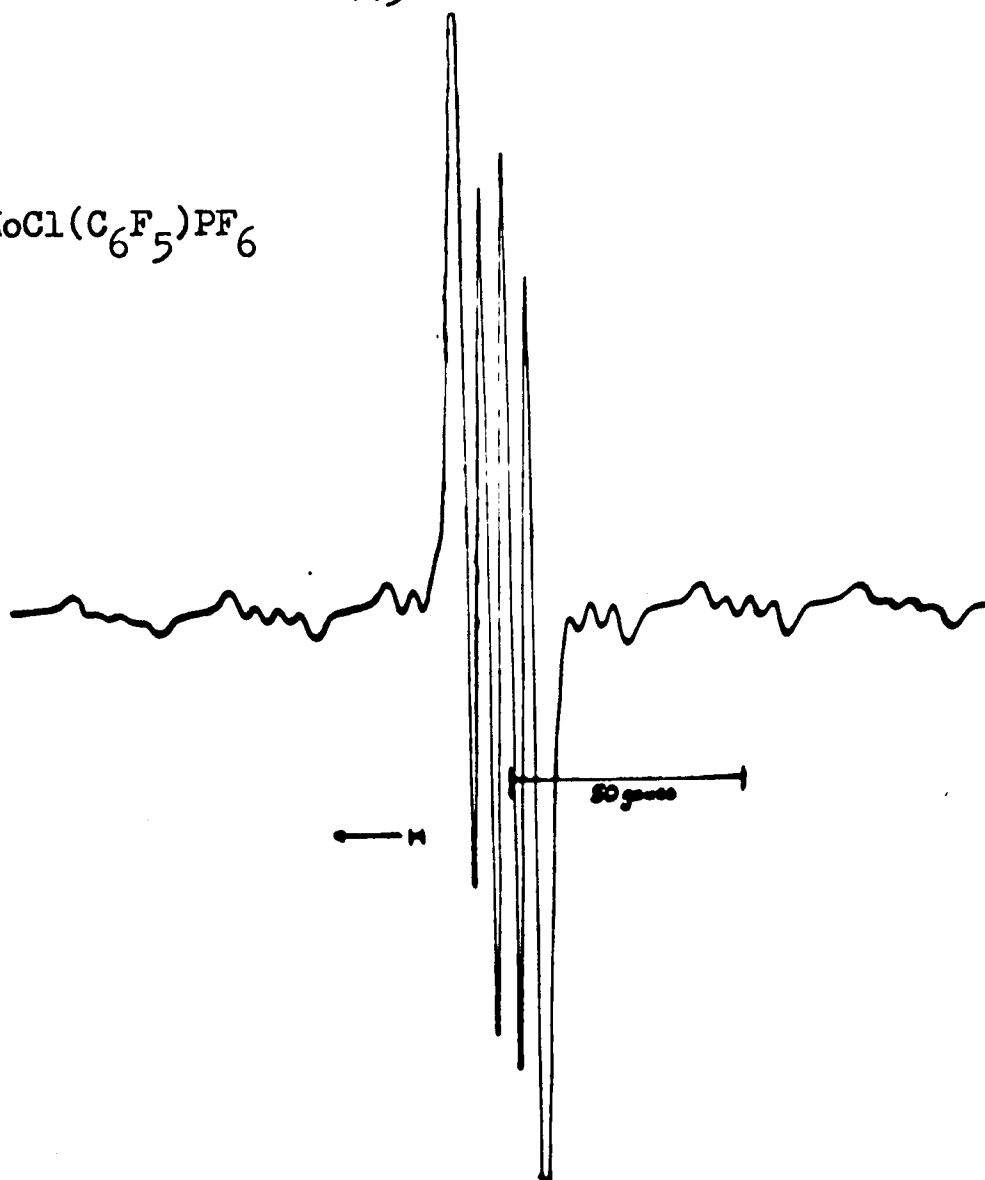


Figure 8.

E.S.R. spectrum of

$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WCl}(\text{C}_6\text{F}_5)\text{PF}_6$
in acetone solution.

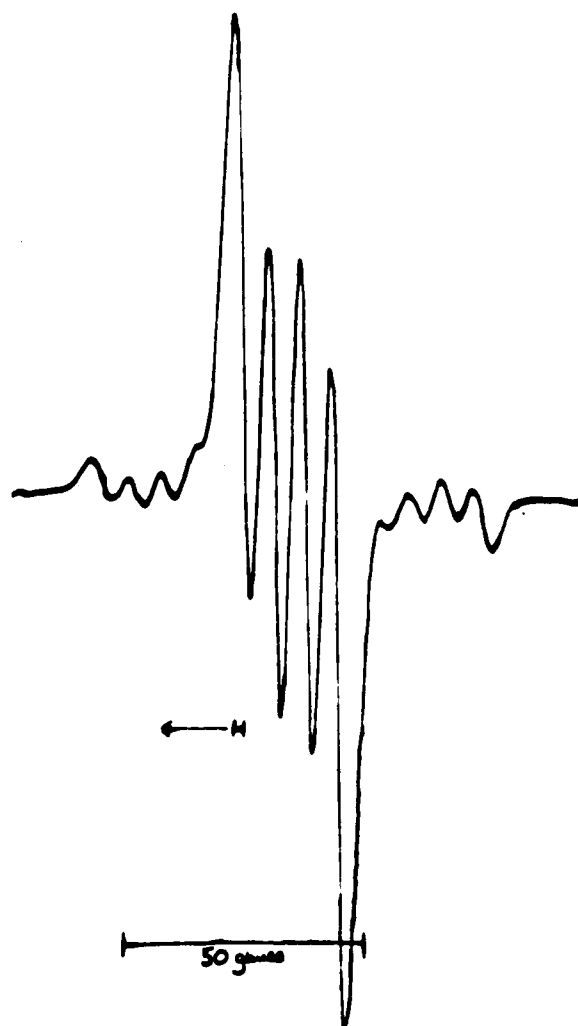


Figure 9.

Frozen solution spectrum of
 $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2\text{PF}_6$ in $(\text{CH}_3)_2\text{SO}$

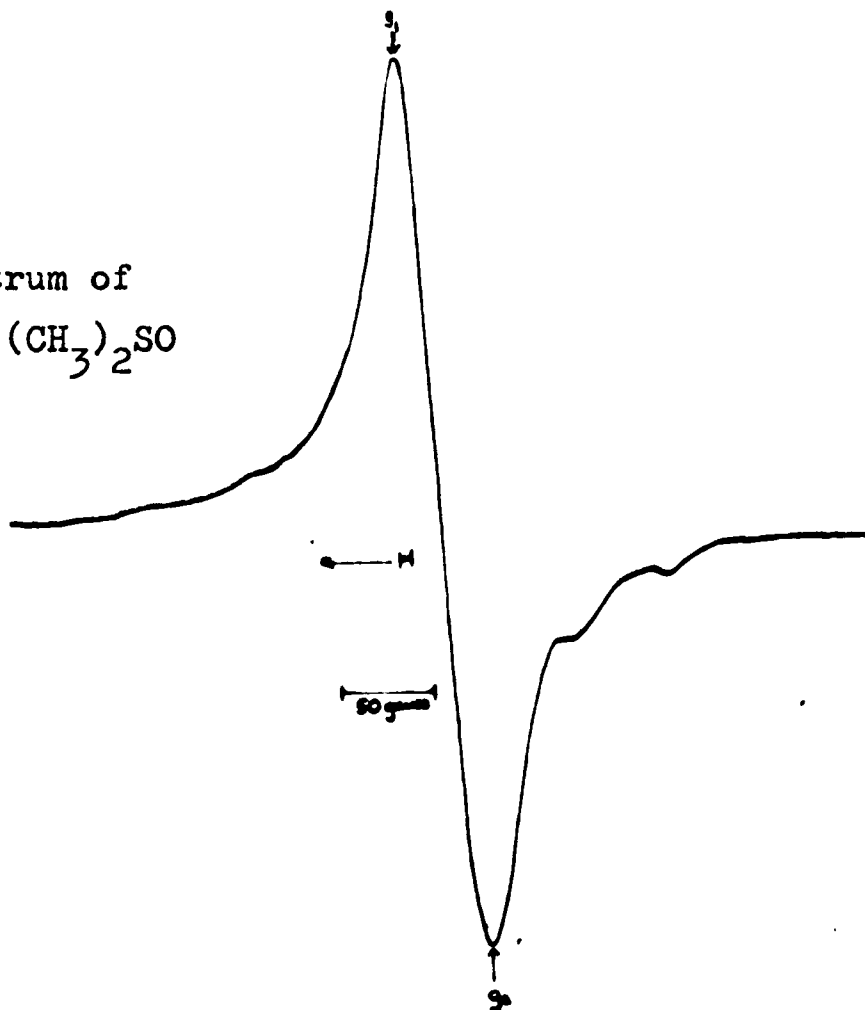


Figure 10.

Frozen solution spectrum of
 $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2\text{PF}_6$
 in $(\text{CH}_3)_2\text{SO}$

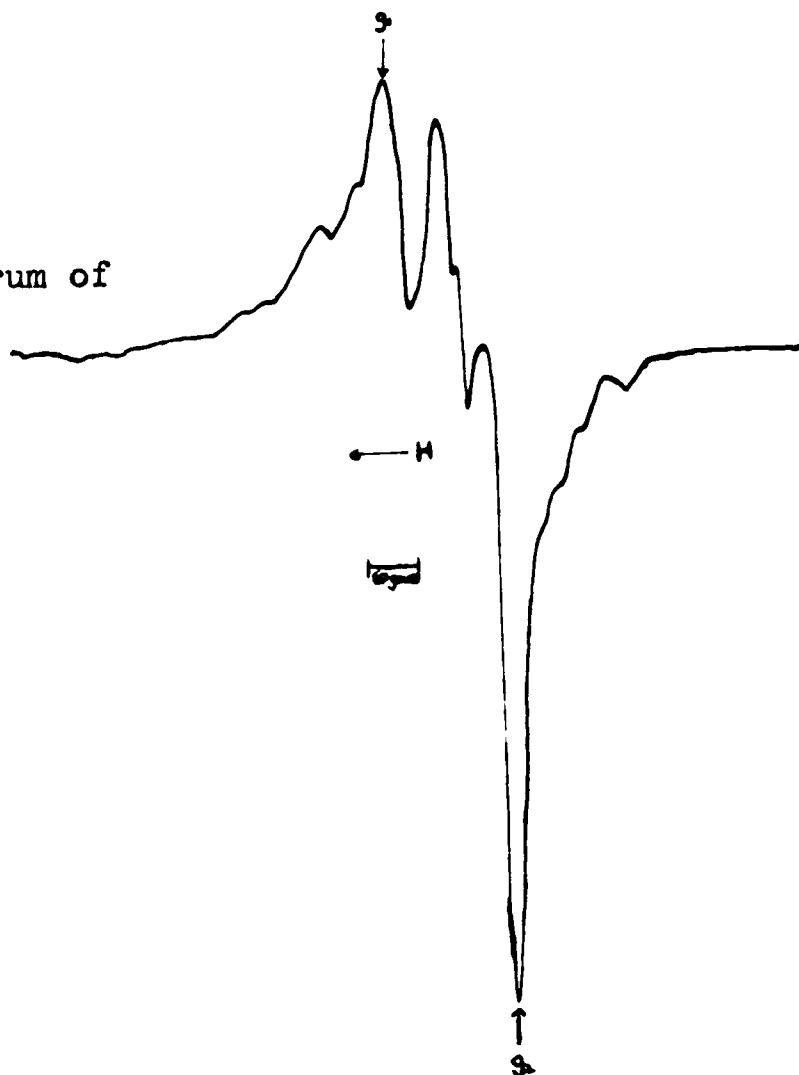


Figure 11.

Frozen solution spectrum of
 $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2\text{PF}_6$ in $(\text{CH}_3)_2\text{SO}$

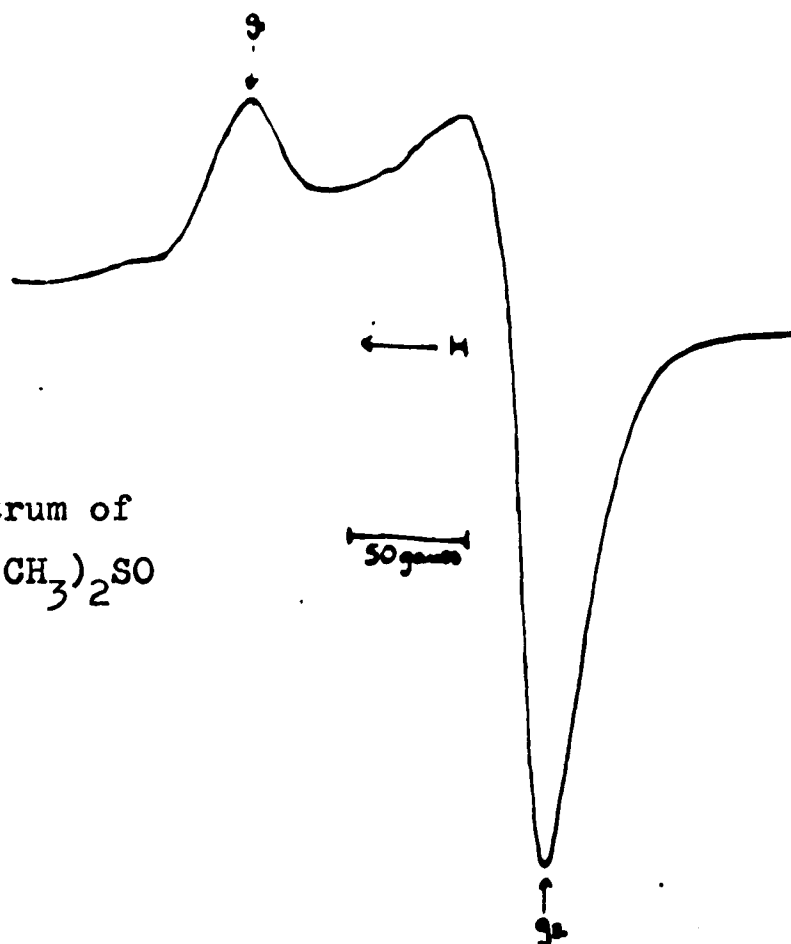
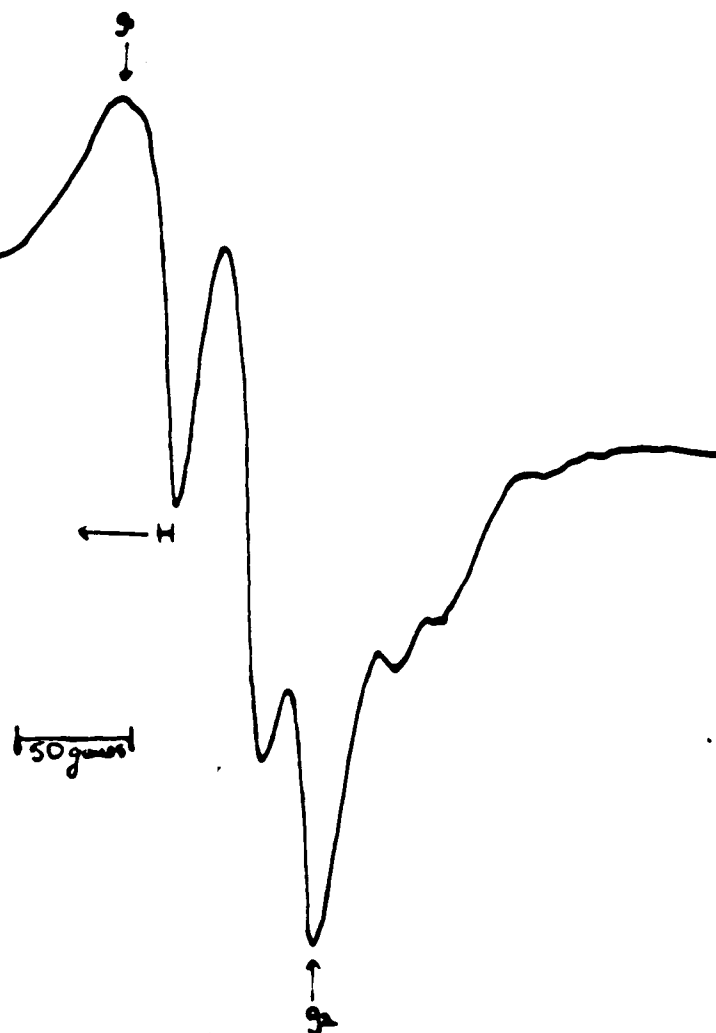


Figure 12.

Frozen solution spectrum of
 $(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2\text{PF}_6$ in $(\text{CH}_3)_2\text{SO}$



$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ by HSbCl_6 was almost certainly $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)\text{-SbCl}_6$, if impure, (see p. 136) and its E.S.R. spectrum is also recorded.

The composition of other species cannot be so definitely assigned. However oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{N}_3)_2$ ($\text{M} = \text{Mo}, \text{W}$; see p. 42) led to unstable ionic complexes which had azide bands in their infra-red spectra and it is probable that these are $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{N}_3)_2\text{PF}_6$. The ionic complexes formed by oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})(\text{SCN})$ (see p. 52) each gave only one major E.S.R. signal and these are also recorded and are assigned tentatively to corresponding hexafluorophosphate salts (compare electrolytic results; table 16). The spectrum of oxidised $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$, possibly $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{PF}_6$ (see p.136) is also recorded.

Since spectra were run in several different solvents, necessitated in some cases by different solubility properties, the influence of the solvent on the solution $\langle g \rangle$ values was considered. The spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2\text{PF}_6$ was recorded in a range of solvents and the results are listed in table 14. The variation in $\langle g \rangle$ value is only in the range 0.002 and almost within the estimated accuracy of any particular $\langle g \rangle$ value in this region (~ 90 gauss from D.P.P.H.), i.e. ± 0.001 . Other $\langle g \rangle$ values measured in more than one solution are also quoted in the table and these are all very close and almost within experimental error so that it may be assumed that any solvent shifts are small and can be neglected when comparing $\langle g \rangle$ values ranging from 1.93-2.05.

Table 14

SOLUTION E.S.R. SPECTRA OF PARAMAGNETIC COMPLEXES ISOLABLE IN THE SOLID STATE

Compound ^a	Solvent	$\langle g \rangle^b$	$a_{\text{iso}} (M)^c$	$a_{\text{iso}} (X)^c$
$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2\text{PF}_6$	glyme ^d CH_2Cl_2 $(\text{CH}_3)_2\text{CO}$ $(\text{CH}_3)_2\text{SO}$ $\text{HCl}(\text{conc})$	1.955 ₅ 1.953 ₉ 1.954 ₄ 1.953 ₇ 1.954 ₇		
$(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2\text{PF}_6$	$(\text{CH}_3)_2\text{SO}$	2.013 ₆		23.3 ± 0.2
$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2\text{PF}_6$	$(\text{CH}_3)_2\text{SO}$ $\text{HCl}(\text{conc})$	1.998 ₈ 1.999 ₁	37.0 ± 0.5	3.3 ± 0.1 3.3 ± 0.1
$(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2\text{PF}_6$	$(\text{CH}_3)_2\text{SO}$ $\text{HBr}(\text{conc})$	2.053 ₅ 2.051 ₁	32.0 ± 3	15.6 ± 0.2 15.5 ± 0.2
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})\text{ClPF}_6$	$(\text{CH}_3)_2\text{CO}$	1.948 ₆		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)\text{PF}_6$	$(\text{CH}_3)_2\text{CO}$	1.993 ₉	~ 32	
$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_2\text{F}_5\text{C}_5\text{H}_4)\text{MoCl}(\text{C}_6\text{F}_5)\text{PF}_6$	glyme $(\text{CH}_3)_2\text{O}$ $\text{HCl}(\text{conc})$	2.005 ₄ 2.005 ₆ 2.005 ₄	34.1 ± 0.5 34.2 ± 0.5 34.1 ± 0.5	4.9 ± 0.2 5.0 ± 0.2 5.1 ± 0.2
$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_6\text{F}_5\text{C}_5\text{H}_4)\text{WCl}(\text{C}_6\text{F}_5)\text{PF}_6$	glyme $(\text{CH}_3)_2\text{CO}$	1.982 ₅ 1.982 ₄	58.5 ± 1 58.7 ± 1	6.8 ± 0.2 6.8 ± 0.2

Table 14 - continued

Compound ^a	Solvent	$\langle g \rangle^b$	$a_{\text{iso}} (M)^c$	$a_{\text{iso}} (X)^c$
$(\pi\text{-C}_5\text{H}_5)_2\text{MoClBrPF}_6$	glyme (CH ₃) ₂ SO	2.025 ₈ 2.025 ₀	32.0 ± 3	15.9 ± 0.5
$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_6\text{F}_5\text{C}_5\text{H}_4)\text{WBr}(\text{C}_6\text{F}_5)\text{PF}_6$	glyme (CH ₃) ₂ SO	2.025 ₈ 2.025 ₃		32.9 ± 1 32.6 ± 0.5
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)\text{SbCl}_6$	(CH ₃) ₂ SO	2.009 ₂	17.4 ± 0.3	
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{N}_3)_2\text{PF}_6 ?$	(CH ₃) ₂ CO	1.986 ₁	33.7 ± 0.5	
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{N}_3)_2\text{PF}_6 ?$	(CH ₃) ₂ CO H ₂ O CH ₃ CN	1.941 ₆ 1.942 ₆ 1.941 ₈		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})_2\text{PF}_6 ?$	(CH ₃) ₂ CO	1.942 ± 0.003		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})(\text{SCN})\text{PF}_6 ??$	(CH ₃) ₂ CO	1.965 ± 0.003		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{PF}_6 ?$	(CH ₃) ₂ CO (CH ₃) ₂ SO	2.046 ₃ 2.045 ₉		

a - Probable formulae are marked with ? (see text).

b - Isotropic g value. Error within 0.001 in all cases unless marked otherwise.

c - Isotropic hyperfine splitting in gauss. M = Mo or W. X = Cl or Br.

d - glyme is 1,2-dimethoxyethane.

b) Glass Spectra

Since solution spectra only give isotropic values for g and a tensors it was decided to run some spectra in glasses to get more information about these values. The spectra of the dihalide and $(\pi-C_5H_5)_2W(NSC)ClPF_6$ complexes were recorded in frozen solution glasses, see figures 9, 10, 11 and 12. The spectra are very complex and one does not obtain the symmetrical well resolved split signals that are observed at room temperature, but this is to be expected, since the highest symmetry possible in any of the complexes is an approximate C_{2V} symmetry and is probably less. Three g values, g_1 , g_2 and g_3 and three metal hyperfine splitting tensors A , B , C (due to $^{95}Mo/^{97}Mo$ or ^{183}W) are to be expected and in addition to these six terms, three values of the superhyperfine splitting by halide ligands will be present and these latter interactions will generally have three different principal axes to the axes of the other tensors.

From the spectra it is virtually impossible to get values of hyperfine splitting constants unless, possibly, computing techniques are used. However 2 probable g values can be obtained fairly accurately from the two peaks marked in the figures 9, 10, 11 and 12. The third g value is difficult to estimate from the spectra although it can be limited to a small range. The third g value however, can be obtained with more accuracy, from the relationship

$$\langle g \rangle = \frac{1}{3}(g_1 + g_2 + g_3)$$

although it is to be noted that the solution measurements were at room temperature and the frozen solution measurements were at $<-100^\circ C$ (N.B.

no change in glass spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2\text{PF}_6$ at -125°C and -165°C .)

Also, the assignment of g_1 and g_2 , although probably correct, may be erroneous due to the presence of ligand hyperfine structure, especially of the bromides.

Table 15

FROZEN SOLUTION SPECTRA OF SOME BIS- π -CYCLOPENTADIENYL COMPOUNDS
OF Mo AND W

Compound	Medium ^a	g_1^b	g_2^b	g_3^c
$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2\text{PF}_6$	$(\text{CH}_3)_2\text{SO}$	1.984	2.015	(1.998)
$(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2\text{PF}_6$	$(\text{CH}_3)_2\text{SO}$	2.015	2.101	(2.045)
$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2\text{PF}_6$	$(\text{CH}_3)_2\text{SO}$	1.904	1.992	(1.966)
$(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2\text{PF}_6$	$(\text{CH}_3)_2\text{SO}$	1.992	2.055	(1.995)
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})\text{ClPF}_6$	CH_3OH	1.879	1.995	(1.972)

a - Glasses formed by freezing the solution to below -100°C

b - Principal g tensor values. No indication of a particular axis is implied. Accuracy is within ± 0.004 (if correct assignment).

c - g values calculated using g_1 , g_2 and $\langle g \rangle$.

B. Exchange Experiments

Experiments were tried to cause substitution of halide ligands in the paramagnetic dihalide complexes, $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$ ($M = \text{Mo}, \text{W}$), to form new paramagnetic species and to observe this process by E.S.R. spectroscopy.

a)' In organic solvents

When $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2\text{PF}_6$ and excess Et_4NBr were dissolved in dimethylsulphoxide solution and the sample put into the E.S.R. cavity at room temperature no change in the spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$ occurred over 2 days

and it was assumed that no reaction had taken place. When $(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2\text{PF}_6$ and excess Et_4NCl were dissolved in $(\text{CH}_3)_2\text{SO}$ the E.S.R. spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2^+$ disappeared over 30-60 minutes and the colour of the solution changed from purple, through green, to colourless. No other E.S.R. signal was observed from the sample and it was shown that $(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2^+$ did not decompose in $(\text{CH}_3)_2\text{SO}$ alone or in a solution of $(\text{CH}_3)_2\text{SO}$ and Et_4NBr . Therefore reaction must have taken place between $(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2^+$ and Et_4NCl but the product was not $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$.

When $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2\text{PF}_6$ was dissolved with excess of Et_4NBr in methyl cyanide the only E.S.R. signal to be observed was that of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^+$ although this decayed slowly and the colour of the solution changed. When $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2\text{PF}_6$ was dissolved in CH_3CN with Et_4NCl there was rapid decay of the $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2^+$ spectrum, although the complex is stable in CH_3CN alone, and no other signal was observed. Mixing $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2\text{PF}_6$ and Et_4NI in CH_3CN led to a yellow solution and no E.S.R. signal was observed.

b) In concentrated acids

$(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$ cations are stable for days in the corresponding concentrated haloacids, HX , or in HClO_4 and give the characteristic E.S.R. signals (e.g. see table 14). However when $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$ ($\text{X} = \text{Cl}$ or Br) is dissolved in HX' ($\text{X}' = \text{Br}$ or Cl , respectively) reaction occurs and this can be observed by E.S.R. spectroscopy. $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2\text{PF}_6$ in HBr reacts over a period of days to show changes in the E.S.R. spectrum (see figures 13, 14 and 15). The initial spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$ slowly decreases in intensity, an intermediate 4 line spectrum appears and then the spectrum characteristic of $(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2^+$, although overlapping of all spectra occurs.

Figure 13.

$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2\text{PF}_6$ in
concentrated HBr after
 $\sim 3\frac{1}{2}$ hours

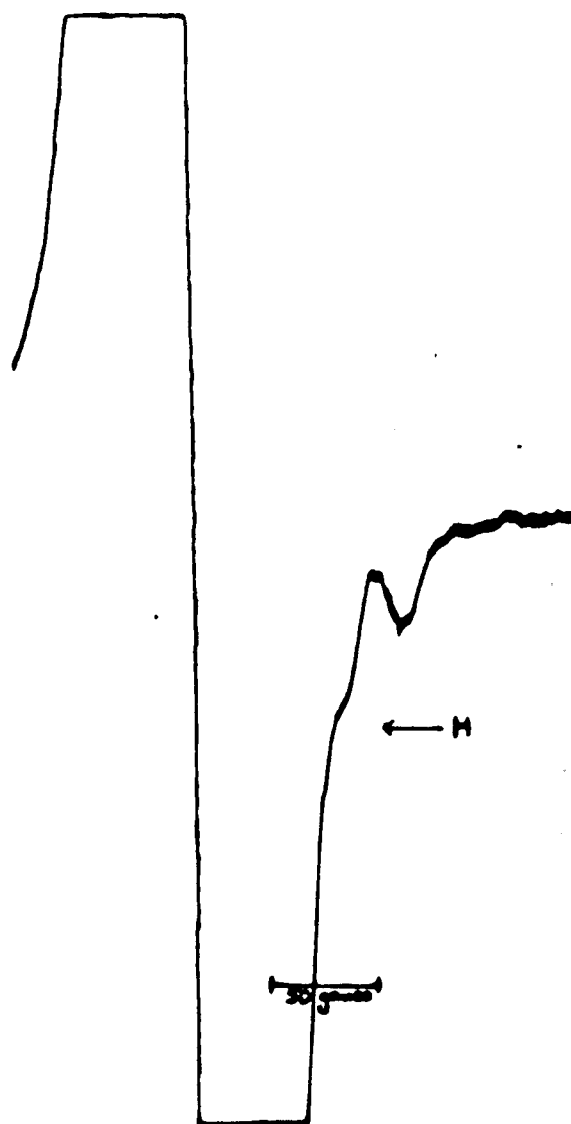


Figure 14.

$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2\text{PF}_6$
in concentrated HBr
after ~ 40 hours

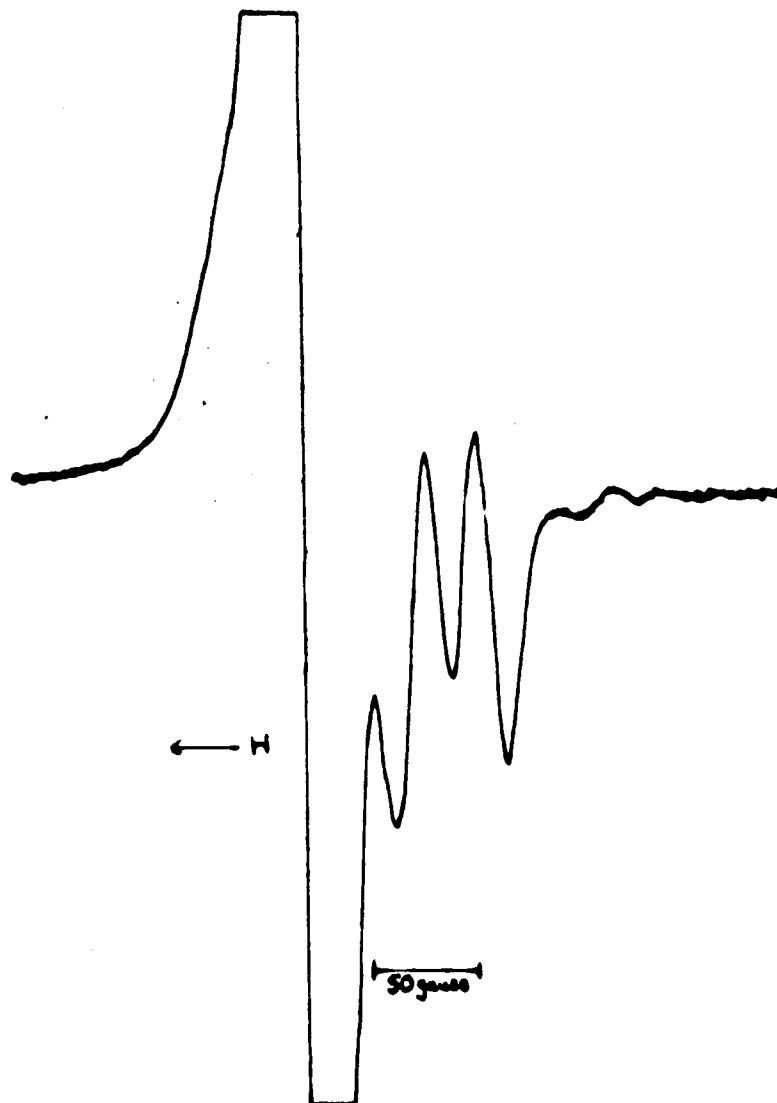


Figure 15.

$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2\text{PF}_6$ in
concentrated HBr
after ~ 114 hours

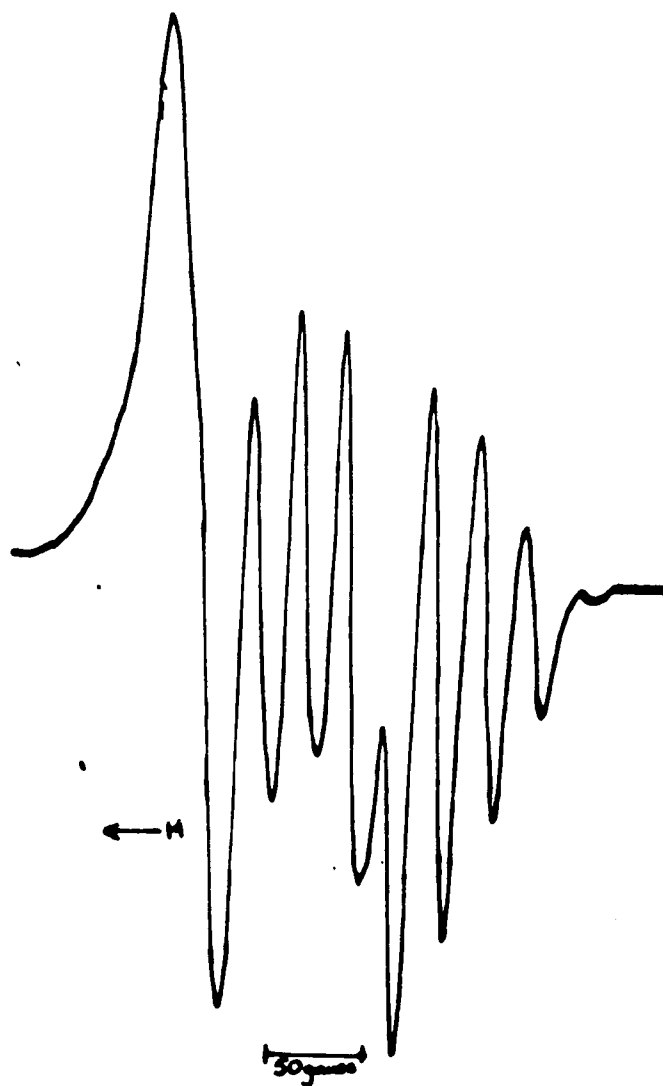


Figure 16.

$(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2\text{PF}_6$ in
concentrated HCl
after ~ 15 minutes

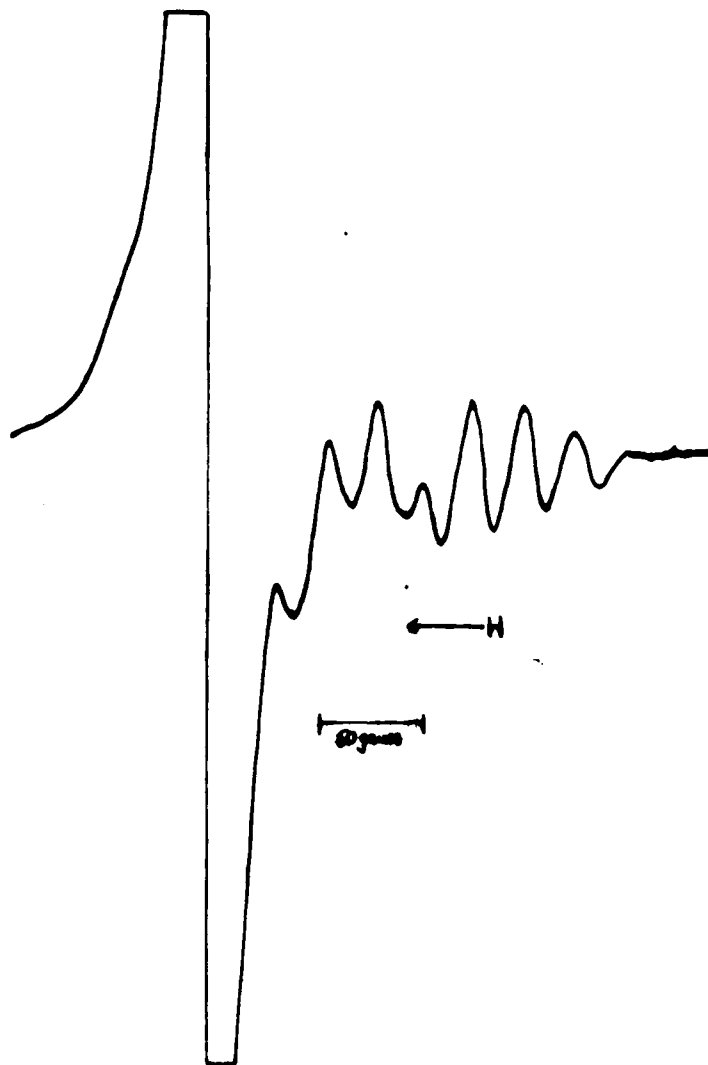


Figure 17.

$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2\text{PF}_6$ in concentrated
HBr after ~ 70 hours

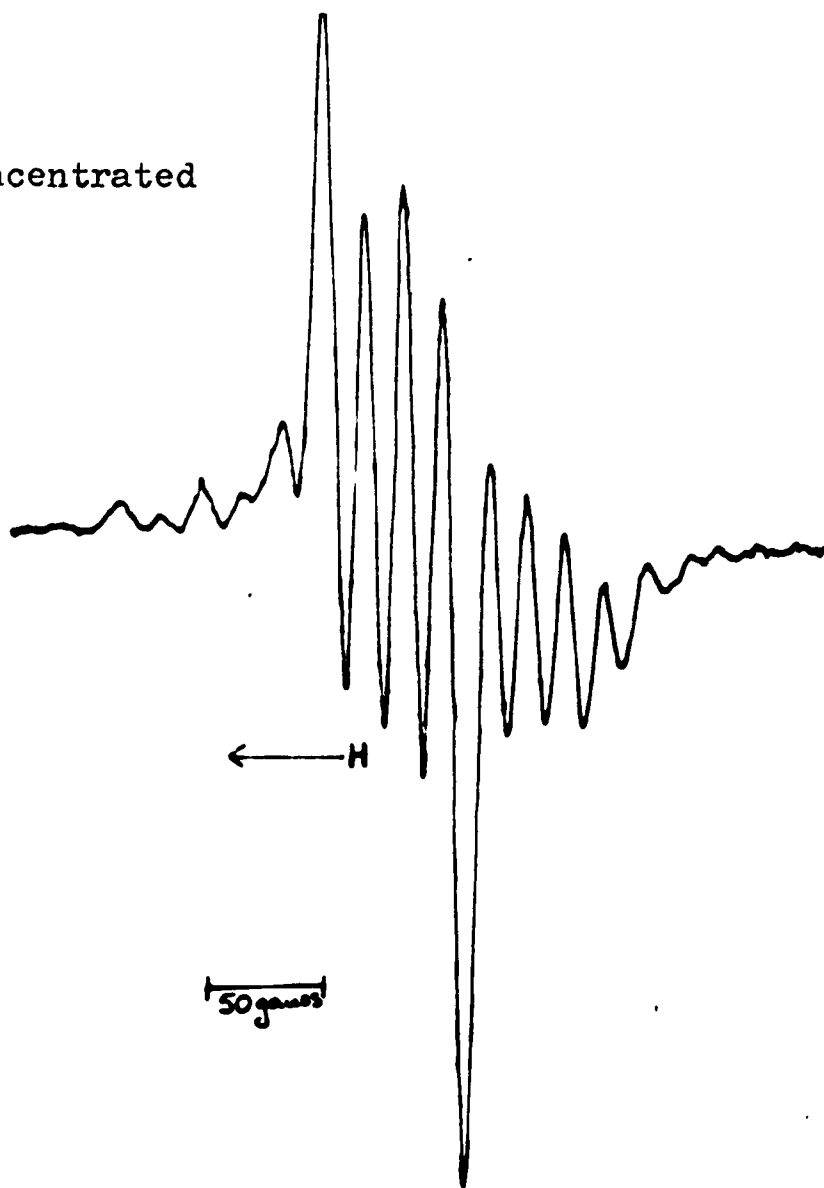
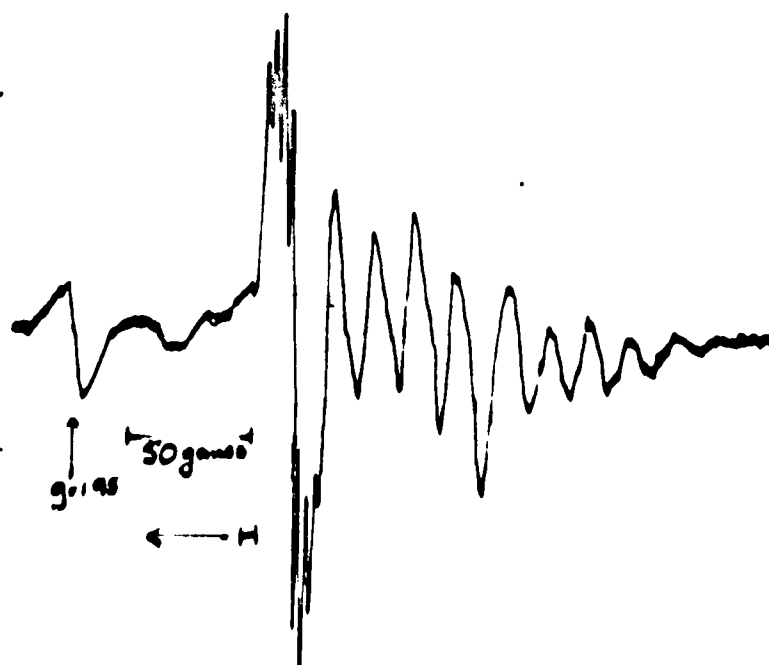
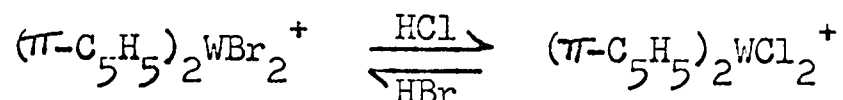


Figure 18. $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2\text{PF}_6$ in concentrated HCl after $\sim 5\frac{1}{2}$ hours



$(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2\text{PF}_6$ in HCl reacts more rapidly and the spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2^+$ goes, again, through an intermediate four line spectrum and then the spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$ is observed (see figure 16 for an intermediate stage).

This indicates a reaction:

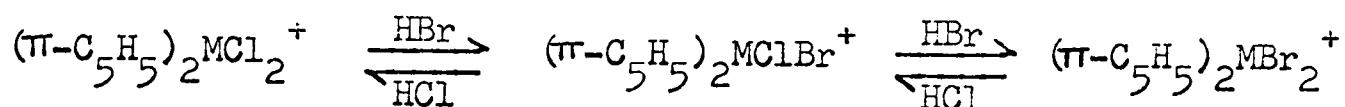


via a common intermediate which is a species with $\langle g \rangle = 1.985 \pm 0.0015$ and four line splitting constant $a_{\text{iso}} = 24.8 \pm 1.5$ gauss (the accuracy of these parameters is lower than usual since there is difficulty in estimating the position of measurement because of overlapping of spectra). The a_{iso} value is similar to that of $(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2^+$ and this suggests it is due to a Br atom and, since the intermediate is formed both from $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$ with HBr and $(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2^+$ with HCl, the signal is almost certainly from the mixed halide $(\pi\text{-C}_5\text{H}_5)_2\text{WBrCl}^+$.

In a similar fashion, $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2\text{PF}_6$ in HBr reacts slowly with HBr to show changes in its E.S.R. spectrum of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^+$ through an intermediate 4 line split signal (with ^{95}Mo and ^{97}Mo satellites similarly split) to give finally the spectrum corresponding to the species $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2^+$ (see figure 17 for intermediate stage in reaction). $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2^+$ in HCl also shows a similar, more rapid, change in its E.S.R. spectrum, going through the same intermediate to give eventually pure $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^+$ (see figure 18). However in this latter case a peak at $g = 1.95$ is observed, from the outset, in concentrated HCl which does not change in form, although it probably decreases in absolute intensity, throughout the experiment. It was shown

that no other signal but that of $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2^+$ was observed from $(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2\text{PF}_6$ in $(\text{CH}_3)_2\text{SO}$ solution but in concentrated HBr a weak resonance was also observed at $g \sim 1.95$. This signal probably arises from a hydroxy species (compare the g values with oxygen complexes in table 16). The intermediate species, $(\pi\text{-C}_5\text{H}_5)_2\text{MoClBr}^+$, has the values $\langle g \rangle = 2.028 \pm 0.0015$ $a_{\text{iso}}(\text{Br}) = 16.8 \pm 0.5$ gauss $a_{\text{iso}}(\text{Mo}) = 34 \pm 3$ gauss (compare the complex in table 14).

The reaction path for both molybdenum and tungsten complexes is, therefore:



The rates of the reactions were not studied very carefully, but anomalous rates seemed to occur. For instance on one occasion $(\pi\text{-C}_5\text{H}_5)_2\text{WBr}_2^+$ in HCl reacted and turned completely to $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$ within 30 minutes, but another similar sample took over a day to show any appreciable change in its spectrum. It was noted also that colour changes, due to the different complexes, occurred more rapidly near the tops of the capillary tubes opened to the air, suggesting that oxygen may be catalytic in the displacement process and that simple nucleophilic attack does not occur.

C. Electrolytic Experiments

Reduction of organic molecules in the E.S.R. cavity has often been used and was pioneered by Maki and Geske (F19) and there is a good review (F20). Little work has been reported of oxidation in the E.S.R. spectrometer.

The electrolytic cell described in chapter VII was designed to enable us to form unstable species in the E.S.R. cavity. Trial oxidation of

$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ to $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^+$ in $(\text{CH}_3)_2\text{SO}$ solution with $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ as supporting electrolyte gave the expected signal of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^+$ which disappeared on current reversal. Also $\text{Mo}(\text{CO})_4(\text{dipy})$ was reduced in 1,2-dimethoxyethane solution at a Hg cathode to give the spectrum reported for the anion (F16) and similar, not previously reported, spectra were obtained from $\text{Mo}(\text{CO})_4(\text{phen})$ and $\text{Cr}(\text{CO})_4(\text{dipy})$.

The spectra listed in table 16 were obtained by oxidation from the parent compound listed. Voltages are not given since in most cases no accurate check of these was made. However most signals appeared at applied potentials in the range 1-3 volts and the signals recorded are the first signals which appeared rapidly when the potential was raised above a particular threshold voltage in the range indicated and, in most cases, these were the only signals observable even if the voltage was raised to the maximum of $4\frac{1}{2}\text{V}$ applied. Most signals were due to unstable species (the toluene dithiol cations being notable exceptions) and the signals decayed with varying rates if the current was switched off. Reversal of current caused more rapid loss of signals in all cases when this was tried (most cases). The usual solvent was 1,2-dimethoxyethane but compounds which were virtually insoluble in this were run in $(\text{CH}_3)_2\text{SO}$ or $(\text{CH}_3)_2\text{CO}$ and it is assumed that no large solvent effects will prevent comparison of results (see section A a), p. 146). It is to be noted that high field broadening, especially of high field ^{95}Mo and ^{97}Mo satellites, sometimes occurred and may be due to too low a tumbling frequency of the complex in solution (F21) or to decomposition.

It is to be noted that the signals obtained from $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})_2$, $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{N}_3)_2$, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}$ (see p. 48, $g = 1.955$),

$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ and $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ are virtually, and within experimental error, the same as signals obtained from chemically oxidised cationic products. This leads to the proposal that all these, and probably the other, signals arise from cations formed by electron removal from the neutral complex. This is certainly the case for $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)$ complexes and is very probably the case with the pseudohalide and the carboxylic acid derivatives.

Whether the signals observed from $(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{SC}_6\text{H}_4\text{NH})$ ($\text{M} = \text{Mo}, \text{W}$), $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OC}_6\text{H}_4\text{NH})$ or $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_{14}\text{H}_8)$ arise from the corresponding cations is not so clear. The signals obtained from these complexes required higher voltages (~ 3 volts applied) and after several hours at this potential other signals appeared. However the data quoted are for the first signal observed and it is a reasonable assumption that these are due to the unstable cationic species.

The spectrum of the compound postulated to be $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})(\text{SCN})$ also requires comment. At $2\text{-}2\frac{1}{2}$ volts applied only one signal was observed for about 30 minutes, but then another signal was observed to grow up, at slightly higher field, and this latter peak grew in intensity to be as large as the first signal after $\sim 2\frac{1}{2}$ hours and no noticeable change from this situation was noted after another hour. Since the first signal appeared rapidly it may be assumed to be due to the corresponding cation and the second signal may be due to a paramagnetic complex formed by rearrangement of the cation - this would explain its slow growth rate.

The hydride $(\pi\text{-C}_5\text{H}_5)_2\text{WH}_2$ did not oxidise under the electrolytic conditions but with the complexes $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MH}(\text{C}_6\text{F}_5)$, ($\text{M} = \text{Mo}, \text{W}$),

Table 16

E.S.R. SIGNALS OF BIS- π -CYCLOPENTADIENYL COMPOUNDS FORMED BY ELECTROLYTIC OXIDATION AT A PLATINUM ELECTRODE

Parent Compound ^a	Solvent	$\langle g \rangle^c$	$a_{iso}(M)^b$
$(\pi-C_5H_5)_2Mo(S_2C_6H_3CH_3)$	glyme	2.008 ₉	17.0 $\pm$ 0.5
$(\pi-C_5H_5)_2W(S_2C_6H_3CH_3)$	glyme	1.994 ₄	~ 32
$(\pi-C_5H_5)_2Mo(N_3)_2$	$(CH_3)_2CO$	1.985 ₉	33.9 $\pm$ 0.5
$(\pi-C_5H_5)_2W(OC_2H_5)CN$	glyme	1.955 ₄	~ 51
$(\pi-C_5H_5)_2Mo(NCS)_2$	$(CH_3)_2SO$	1.985 ₃	35.6 $\pm$ 1.0
$(\pi-C_5H_5)_2W(NCS)_2$	$(CH_3)_2SO$	1.945 ₆	
$(\pi-C_5H_5)_2W(NCS)(SCN)$	$(CH_3)_2SO$	1.966 ₀ 1.962 ₉ ^d	
$(\pi-C_5H_5)_2Mo(OCOCF_3)_2$	glyme	1.980 ₈	39.6 $\pm$ 0.5
$(\pi-C_5H_5)_2W(OCOCF_3)_2$	glyme	1.927 $\pm$ 0.003	
$(\pi-C_5H_5)_2Mo(OCOC_6H_5)_2$	glyme	1.982 ₃	39.4 $\pm$ 0.5
$(\pi-C_5H_5)_2W(OCOC_6H_5)_2$	glyme	1.930 ₃	
$(\pi-C_5H_5)_2Mo(NHC_6H_4S)$	glyme	2.001 ₃	
$(\pi-C_5H_5)_2W(NHC_6H_4S)$	glyme	1.977 ₇	
$(\pi-C_5H_5)_2Mo(NHC_6H_4O)$	glyme	1.971 ₀	
$(\pi-C_5H_5)_2W(O_2C_{14}H_8)$	glyme	1.954 ₄	

a - See text for discussion of paramagnetic species which is suggested to be the cation in all cases.

b - Isotropic hyperfine splitting in gauss. M = Mo or W.

c - Accuracy within ± 0.001 unless otherwise stated.

d - Second signal - see text.

oxidation did occur and a signal grew up very slowly with time (several hours electrolysing were required to obtain a signal of reasonable intensity at high spectrometer gain) and the spectra obtained were those of the corresponding monochloro complexes, $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MCl}(\text{C}_6\text{F}_5)^+$, with parameters the same (within experimental error) as in table 12. Thus the supporting electrolyte $(\text{C}_4\text{H}_9)_4\text{NClO}_4$ in 1,2-dimethoxyethane solution must react slowly with the hydride converting it into the chloride which is subsequently oxidised.

Other species on which attempts were made to form paramagnetic oxidised products included $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_6\text{H}_4)$, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SC}_6\text{H}_5)_2$, $(\pi\text{-C}_5\text{H}_5)_2\text{WI}_2$, $(\pi\text{-C}_5\text{H}_5)_2\text{ReBr}_3$, $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{CH}_2\text{C}_6\text{H}_5\text{Cl}$ but no signals were observed in any of these cases. Trial reduction experiments on several of the bis- π -cyclopentadienyl compounds also gave no signals.

D. Discussion

The solution $\langle g \rangle$ values of molybdenum and tungsten compounds obtained by chemical or electrolytic oxidation are arranged in order of increasing value in table 17 and assigned to a cation with consideration of the earlier discussion. This series is of interest and several general points can be made.

1. There is a general increase in $\langle g \rangle$ as the ligands X in $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$ are changed, which corresponds, roughly, with the change through O, N, Cl, S to Br coordinated atoms of the ligands.
2. The spread of $\langle g \rangle$ values is greater for W than for Mo complexes.
3. The compounds containing the ligand C_6F_5 cannot be directly compared with the other complexes since one π -cyclopentadienyl ring is substituted

Table 17

LIST OF E.S.R. PARAMETERS OF COMPLEXES DISCUSSED IN CHAPTER VI

Complex cation ^a	$\langle g \rangle^b$	$a_{iso}(\text{Mo})^b$	$a_{iso}(\text{W})^b$
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NHC}_6\text{H}_4\text{O})^+$	1.971	n.o. ^c	
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OCOCF}_3)_2^+$	1.981	39.6	
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{OCOC}_6\text{H}_5)_2^+$	1.982	39.4	
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NCS})_2^+$	1.985	35.6	
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{N}_3)_2^+$	1.986	33.9	
$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2^+$	1.999	37.0	3.3
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NHC}_6\text{H}_4\text{S})^+$	2.001	n.o.	
$(\pi\text{-C}_5\text{H}_5)(-\text{C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoCl}(\text{C}_6\text{F}_5)^+$	2.005	34.1	5.0
$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)^+$	2.009	17.2	
$(\pi\text{-C}_5\text{H}_5)_2\text{MoClBr}^+$	2.026	33	16
$(\pi\text{-C}_5\text{H}_5)_2\text{MoBr}_2^+$	2.053	32	15.6
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCOCF}_3)_2^+$	1.927		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OCOC}_6\text{H}_5)_2^+$	1.930		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{N}_3)_2^+$	1.942		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})_2^+$	1.945		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})\text{Cl}^+$	1.949		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_{14}\text{H}_8)^+$	1.954		
$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2^+$	1.954		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{OC}_2\text{H}_5)\text{CN}^+$	1.955		
$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NCS})(\text{SCN})^+ ?$	1.966		

continued...

Table 17 - continued

Complex cation ^a	g^b	$a_{iso}(Mo)^b$	$a_{iso}(X)^c$
$(\pi-C_5H_5)_2W(NHC_6H_4S)^+$	1.978		
$(\pi-C_5H_5)(\pi-C_5H_4C_6F_5)WCl(C_6F_5)^+$	1.982		6.8
$(\pi-C_5H_5)_2WClBr^+$	1.985		25
$(\pi-C_5H_5)_2W(S_2C_6H_3CH_3)^+$	1.994		
$(\pi-C_5H_5)_2WBr_2^+$	2.014		23.3
$(\pi-C_5H_5)(\pi-C_5H_4C_6F_5)WBr(C_6F_5)^+$	2.026		32.6
$(\pi-C_5H_5)_2W(SCH_2)_2^+ ?$	2.046		

a - See text for a discussion of the nature of these complexes.

b - See tables 14, 16 and pp. 155, 156 for accuracy.

c - Not observed.

but it is probable that the change in $\langle g \rangle$ value due to ring substitution is small and the observed $\langle g \rangle$ values would indicate that the ligand C_6F_5 behaves similarly to the ligand, Br.

4. The order of $\langle g \rangle$ values also supports the assignment of N-bonding to the thiocyanato complexes except the product 'A' (referred to on p. 60) and the formula $(\pi-C_5H_5)_2W(NCS)(SCN)^+$ for the cation formed by oxidation of 'A' is in agreement with the higher observed $\langle g \rangle$ value caused by one S-bonded ligand.

5. Another point of interest is the $\langle g \rangle$ values of the mixed ligand complexes. The $\langle g \rangle$ values of the cations $(\pi-C_5H_5)_2MClBr^+$, (M = Mo or W) are observed (within experimental error) at the mean $\langle g \rangle$ values of the two cations $(\pi-C_5H_5)_2MCl_2^+$ and $(\pi-C_5H_5)_2MBr_2^+$ (M = Mo or W). The $\langle g \rangle$ value of $(\pi-C_5H_5)_2W(NCS)Cl^+$ also is observed at the mean value of the two $\langle g \rangle$ values of $(\pi-C_5H_5)_2W(NCS)_2^+$ and $(\pi-C_5H_5)_2WCl_2^+$. This observation suggests that for the $(\pi-C_5H_5)_2MX_2^+$ system, over a small range of $\langle g \rangle$ values, the values are an additive property of the ligands and that it is possible to predict $\langle g \rangle$ values of other mixed ligand complexes.

6. However, a few anomalies do exist in the Mo and W series and in particular the difference in $\langle g \rangle$ value between $(\pi-C_5H_5)_2W(S_2C_6H_3CH_3)^+$ and the compound tentatively assigned the cationic formula $(\pi-C_5H_5)_2W(SCH_2)_2^+$. This may be caused by the properties of the aromatic ligand toluene dithiol, which, like the ligand maleonitrile dithiol, is known to stabilise formally, unusual oxidation states in transition metal complexes. The molybdenum cation, $(\pi-C_5H_5)_2Mo(S_2C_6H_3CH_3)^+$, has a $\langle g \rangle$ value in a comparable position to that of the tungsten complex. It is possible that a π -type interaction is

important in the bonding of these complexes and this will cause an anomalous $\langle g \rangle$ shift.

7. The a_{iso} (Mo) values, which are a measure of the unpaired s-electron density at the nucleus of the Mo atom, also show a general but small decrease in value with the increase in $\langle g \rangle$ value. However again the toluene dithiolato complex is a marked exception. The a_{iso} value arises either from direct s-orbital occupancy or by spin polarisation on the Mo atom, but the calculated $a_{\text{iso}} = 2120$ gauss (F22) for Mo ($4p^6 5s^1$ configuration) shows that only a very small s-contribution is present. Typical values of a_{iso} for Mo(V) complexes, such as MoOCl_5^{2-} and other oxy species (F23), are in the range 40-60 gauss, but the value for $\text{Mo}(\text{CN})_8^{3-}$ is 35 gauss. If other factors remain the same, a decrease in a_{iso} indicates removal of unpaired electron density from the metal and this could arise from increase in metal ligand covalency. The low value of a_{iso} for $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)^+$ (and also the estimated lower value for a_{iso} (^{183}W) for the related tungsten complex compared to other a_{iso} (^{183}W) values - see table 16) may be due to increased covalency, possibly of a π -type as proposed above. A very low a_{iso} (Mo) value of 12.1 gauss has been reported for $\text{Mo}(\text{S}_2\text{C}_2\text{CF}_3)_3^-$, (F22).

8. The observation of ligand hyperfine interaction for the halide complexes is interesting. The values of a_{iso} for one unpaired s-electron in a Cl or Br atom are respectively ~ 1600 gauss and ~ 8000 gauss (F25, the values vary slightly with nuclide), thus for similar s-unpaired electron population an increase of 5 times in a_{iso} is expected for Br compared to Cl and, within experimental error, this is precisely what is seen in the complexes $(\pi\text{-C}_5\text{H}_5)_2\text{MX}_2^+$ or $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MX}(\text{C}_6\text{F}_5)^+$. Also the a_{iso} (Br)

values for the mixed halide cations do not differ much from those of the related dibromide cations. These observations again are consistent with no marked change in bonding although the larger ligand hyperfine coupling constants for the pentafluorophenyl complexes compared to the dihalide complexes may be significant.

9. Perturbation theory, assuming L.S coupling and applying spin-orbit coupling and the effect of the magnetic field (Zeeman interaction) as perturbations to an unperturbed molecule having an orbitally non-degenerate ground state, leads to a general equation for g values (F24, F25)

$$g_q = 2.0023 + \Delta g_q \quad (q = x, y, z)$$

$$\text{where } g_x + g_y + g_z = 3\langle g \rangle$$

$$\Delta g_q = 2 \sum_{m(\neq n)} \frac{\langle \psi_n | L_q \lambda | \psi_m \rangle \langle \psi_m | L_q | \psi_n \rangle}{E_n - E_m}$$

where ψ_n is the ground state molecular orbital containing the unpaired electron of energy E_n

ψ_m is another molecular orbital of the molecule of energy E_m

L is the angular momentum operator

λ is the spin orbit coupling constant of the molecule.

This equation can be reduced by assuming the L.C.A.O. approximation for molecular orbitals

$$\text{i.e. } \psi_n = \sum_i c_{in} \phi_i \quad \text{where } \phi_i \text{ is the atomic orbital of atom } i$$

and that the spin-orbit coupling in the vicinity of the i th atom will be

dependent on the coupling constant of the atom, λ_i . This gives an equation of the form (for one unpaired electron):

$$\Delta g_q = 2 \sum_m \frac{[\sum_{in} c_{jm}^* \lambda_i \langle \phi_m | L_q | \phi_n \rangle][\sum_{in} c_{jm} \langle \phi_n | L_q | \phi_m \rangle]}{E_n - E_m}$$

In this equation the matrix elements between atomic orbitals will either be zero or have a numerical value. Thus the parameters which cause the variation of g values are 1) energy separations of coupled states, 2) spin orbit coupling constants of the atoms which have atomic orbitals involved in bonding and 3) the coefficients involved in setting up L.C.A.O. molecular orbitals.

The series of $\langle g \rangle$ values obtained for $(\pi-C_5H_5)_2MX_2^+$ complexes was examined in the light of this theory to see if any of these parameters predominated in determining the $\langle g \rangle$ values. Since the basic symmetry of the complexes will not change much if X is varied the molecular orbitals ψ_m may be assumed to be similar for all complexes and a molecular orbital diagram should be similar for all complexes. Values of $(E_n - E_m)$ will vary but it has not been possible to measure these for the M(V) species, except in isolated cases, but the visible and ultraviolet spectra of the neutral complexes have been measured (see table 6 and A2, A124). The band positions for the neutral complexes $(\pi-C_5H_5)_2MX_2$ (M = Mo, W; X = Cl, Br) occur at lower energy ($\sim 4KK$) than the corresponding cations, but in the same relative order. No simple relationship was found between $\langle g \rangle$ values and $1/\Delta E$ values using low energy ΔE values obtained from the visible or near ultra violet spectra of the neutral complexes of either Mo or W.

It was found however that, except for sulphur complexes, the $\langle g \rangle$ values showed a fairly good linear correlation with the spin-orbit coupling constant of the ligand. There is no doubt that spin-orbit coupling on the ligand is involved in determining the $\langle g \rangle$ values observed, since some $\langle g \rangle$ values are greater than the free spin values and this could not be predicted without a degree of covalence. However, whether this linear correlation is fortuitous or significant is uncertain.

No C_{jm} values are known and so correlations with these cannot be made. In the light of the general discussion in sections 6 and 7 above, it is probable that there are significant differences in these coefficients for the toluene dithiolato complexes compared to the other complexes. It is probable that other B type ligands with atoms such as Se, P, or As coordinated to the metal will show more resemblance to the S-bonded ligands. The B type ligands will probably have more covalence than the basically A type ligands bonded by O, N, Cl or Br atoms.

10. The glass spectra recorded in table 15 show that fairly large differences exist between the three principal g tensors. However on changing the ligands of the complexes one g tensor is fairly constant at $g = 1.992$ for $(\pi-C_5H_5)_2WX_2^+$, (X = Cl, Br), or $g = 1.995$ for $(\pi-C_5H_5)_2W(NCS)Cl^+$ and, similarly, $g = 2.015$ for $(\pi-C_5H_5)_2MoX_2^+$ (X = Cl, Br). These single g tensors for the complexes are probably from related principal axes which are not affected by the ligands. The other g tensors vary in a similar fashion to $\langle g \rangle$ with ligand change.

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Chapter VII

EXPERIMENTAL SECTION

All preparations, reactions and purifications were carried out under nitrogen or vacuum unless otherwise stated. The general techniques employed in experiments are similar to those reviewed in references (G1, G2).

Tetrahydrofuran and ether were dried either by treatment with n-butyl Grignard reagent followed by distillation or by refluxing with finely ground calcium hydride followed by distillation. Other solvents were dried, when necessary, using calcium hydride, sodium wire or molecular sieves. Acid washed alumina was dried at 180°C for four hours for chromatographic use. Light petroleum was A.R. petroleum ether boiling at 30-40°C.

Microanalyses were carried out either by Dr. Alfred Bernhardt of the Max-Planck Institut, Mülheim (Ruhr), or by Mr. Derek Chapple of the Inorganic Chemistry Laboratory, Oxford. The former are marked (B) and the latter (C) in the text.

General Preparations

The halides, MoCl_5 and WCl_6 , were made by the action of chlorine on the appropriate metal. Sodium cyclopentadienide, NaC_5H_5 , was made in tetrahydrofuran from sodium sand and cyclopentadiene monomer as reported (G2).

At the outset of this research, bis- π -cyclopentadienyl metal halides of molybdenum and tungsten were made via the hydrides, $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ and $(\pi\text{-C}_5\text{H}_5)_2\text{WH}_2$. The hydrides were isolated by sublimation as pure, yellow solids by a method similar to that reported (A1) using 1,2-dimethoxyethane as a solvent. The dihalides and the related dihalide cations were made

from the hydrides by the method of Cooper (A2).

During the course of this research an improved method for the preparation of the bis- π -cyclopentadienyl dichlorides was found.

Preparation of $(\pi-C_5H_5)_2MoCl_2$ (improved method)

A solution of NaC_5H_5 in 2.5 litres of tetrahydrofuran was made in a 3 litre, 3 necked flask using 100 g. sodium and 300 g. cyclopentadiene. This solution was cooled in an ethanol-dry ice-liquid nitrogen bath to below $-100^\circ C$ and vigorously stirred. 200 g. $MoCl_5$ and 60 g. $NaBH_4$ were added slowly, in alternate portions, to the cooled NaC_5H_5 over a period of $1\frac{1}{2}$ hours.

The flask was then allowed to warm up slowly to room temperature. After approximately 12 hours the mixture was refluxed gently over a water bath for $1\frac{1}{2}$ hours. The solvent was removed using a vacuum line and a large condensing trap. A little water was carefully added to the dried product under a vigorous stream of nitrogen to remove any free sodium. Then a 1:1 concentrated hydrochloric-water mixture, in small portions, was added until the excess sodium borohydride and NaC_5H_5 had decomposed. Finally the mixture was made acid with concentrated hydrochloric acid to form the acid soluble $(\pi-C_5H_5)_2MoH_3^+$ cation. The solution was transferred using a wide bore polythene tube to a large sintered glass, filtering device, the filter pad of which had been covered with a 2 inch layer of finely ground silica gel, and filtered. The tarry insoluble residue was washed well with acid and water and the washings also collected. Washing and filtering was aided by mechanical agitation of the silica layer with a thick glass rod.

The acid filtrate was basified with concentrated aqueous sodium

hydroxide and then, when the hydride, $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$, separated as a brown-yellow solid, the mixture was diluted with water and the hydride was left to settle. Next, the upper layer of basic solution was decanted from the solid using a siphon. This washing process was repeated several times by adding distilled water and decanting the upper layer after the hydride had settled.

Then the hydride was washed on to a pad of alumina (2-3 inches deep) on the frit of a large sintered glass filtering device, filtered free of solution, washed with water and sucked dry. The $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ was then eluted into a clean flask containing some CaCl_2 (anhydrous) using ~ 2 litres dichloromethane as solvent. Again mechanical stirring of the alumina with a glass rod aided this process.

The dichloromethane solution of $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ was shaken with the calcium chloride to remove the small amount of water present, and the solution was refiltered using a sintered frit covered with a small pad of alumina and a little anhydrous calcium chloride. The filter device was again washed well with more dichloromethane.

Chloroform (~ 500 ml) was added to the combined filtrate and washings and then the solution was left to form the chloride, $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$. (The chloride can be formed more quickly by refluxing the solution or by adding carbon tetrachloride.) When the formation of the chloride was completed (approximately twelve hours in chloroform at room temperature) the bulk of the solvent was distilled off and the remainder allowed to cool. The dark green solid $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$, was filtered off and collected. More dichloride could be obtained from the mother liquor on further evaporation and was recrystallised from liquid sulphur dioxide. Total yield 102 g.,

47%. (Found: C, 40.2%, H, 3.5% (C); $C_{10}H_{10}Cl_2Mo$ requires: C, 40.4%, H, 3.4%).

Preparation of $(\pi-C_5H_5)_2WCl_2$

Using a similar procedure to that stated above, from 120 g. WCl_6 and 30 g. $NaBH_4$ using 2 moles of NaC_5H_5 in 1.2 litres of tetrahydrofuran, 43 g. of dark green $(\pi-C_5H_5)_2WCl_2$ were obtained (yield 20%). The only modification was the use of chloroform instead of dichloromethane to elute the hydride from the sintered glass filtering device since $(\pi-C_5H_5)_2WH_2$ does not react so readily with chloroform as does $(\pi-C_5H_5)_2MoH_2$.

Experimental details for Chapter II

Preparation of $(\pi-C_5H_5)_2Mo(N_3)_2$

Lithium azide was prepared from $Li_2SO_4 \cdot H_2O$ and NaN_3 in aqueous alcohol as described (G3) and recrystallised from 96% alcohol. $(\pi-C_5H_5)_2MoCl_2$ (1 g.) and an excess of LiN_3 (~ 0.9 g.) were refluxed in 40 ml. of a 3:1 acetone-ethanol mixture for 1 hour. The blue coloured mixture was allowed to cool and the solvent was removed under vacuum. Chromatography of the residue by addition to an alumina column in dichloromethane solution and final elution with acetone separated a green-blue band. The acetone solution was evaporated to dryness and the product was recrystallised from a dichloromethane-ether mixture. The small, deep blue, diamond shaped crystals formed were washed with ether and dried under vacuum. Yield ca 70%. [Found: C, 38.7 (B), 38.4 (C); H, 3.2 (B), 3.4 (C); N, 26.9 (B), 27.0 (C)%]. $C_{10}H_{10}N_6Mo$ requires: C, 38.7; H, 3.25; N, 27.1%. Infra-red spectrum (mull): 3103 m, 3069 sh, 2605 vw, 2076 s, 2039 sh, 1438 w, 1419 w, 1370 vw,

1333 w, 1281 m, 1110 w, 1080 w, 1018 w, 1000 w, 875 vw, 835 m, 817 m.]

Preparation of $(\pi\text{-C}_{55}\text{H}_{52})\text{W}(\text{N}_3)_2$

In a similar preparation to the above, $(\pi\text{-C}_{55}\text{H}_{52})\text{WCl}_2$ (1 g.) and LiN_3 (0.9 g.) were refluxed for $\frac{1}{2}$ hour in a 5:1 acetone-ethanol mixture. Purification by an analogous method yielded purple, needle shaped crystals in ca 70% yield. Care should be exercised in handling the dry solid since one sample exploded violently when removing some from a flask with a spatula. [Found: C, 30.0; H, 2.8; N, 20.9% (B). $\text{C}_{10}\text{H}_{10}\text{N}_6\text{W}$ requires: C, 30.2; H, 2.5; N, 21.1%. Infra-red spectrum (mull): 3140 vw, 3102 w-m, $\sim$ 2050 s (br), 1428 w, 1357 w, 1332 m, 1278 m, 1103 w, 1080 w, 1004 m, 992 sh, 895 m, 836 m, 800 w.]

It was found that, in the presence of a large amount of ethanol and after refluxing for a longer time, orange-brown coloured reaction mixtures were formed. Evaporation to dryness gave oily products.

Reaction of $(\pi\text{-C}_{55}\text{H}_{52})\text{MoCl}_2$ with KCN

$(\pi\text{-C}_{55}\text{H}_{52})\text{MoCl}_2$ (1 g.) and an excess of KCN ($\sim$ 2 g.) were refluxed in water ($\sim$ 25 ml.) for 15 minutes. A red solution was produced and this was evaporated to dryness. The dried solid residue was extracted with liquid sulphur dioxide to give a yellow solution which was filtered. Addition of dichloromethane to the filtrate gave a yellow solid precipitate which was collected, washed with dichloromethane and dried. Recrystallisation of this solid from liquid sulphur dioxide-dichloromethane mixtures gave yellow crystals. [Found: C, 47.4; H, 3.3; N, 9.1% (C). Infra-red spectrum, main peaks (mull): 3100 m, 2110 s, 1623 w-m, 839 m.]

Preparation of $(\pi-C_5H_5)_2W(OC_2H_5)CN$

$(\pi-C_5H_5)_2WCl_2$ (1 g.) and an excess of NaCN (1-2 g.) were refluxed in a 1:1 acetone-ethanol mixture for 30 minutes to give an orange-brown coloured reaction mixture. This mixture was evaporated to dryness and the residue chromatographed on alumina using acetone with a small amount of ethanol (approximately 10:1 volume ratio) as eluant. An orange band separated to give a deep orange-red solution. Evaporation to dryness gave an orange solid which was recrystallised from a dichloromethane-ether mixture as prismatic, orange crystals in ca 70% yield. These were washed with ether and dried under vacuum at room temperature. However, as noted in Chapter II, these usually contained a little water. [Found: C, 39.2; H, 4.2; N, 3.6% (average of 5 analyses). Λ , $1.5 \text{ ohm}^{-1} \text{ cm}^2$. Infra red spectrum (KBr disc): 3459 s (br), 3340 sh (br), 3275 m (br), 3144 w, 3103 m, 3080 m, 2972 sh, 2955 w, 2915 w, 2862 w, 2839 w, 2700 vw, 2116 s, 1679 m, 1432 m, 1377 m, 1367 sh, 1262 vw, 1155 vw, 1107 m, 1087 w, 1048 s, 1022 m, 989 m, 966 w, 934 w, 884 m, 858 vw, 844 m, 838 m, 832 sh, 803 m, 686 m, 607 sh, 598 m, 571 m, 438 vw.]

Drying by heating in boiling water under vacuum for 3 hours gave a water free sample. [Found: C, 40.6 (B), 40.6 (C); H, 4.5 (B), 4.2 (C); N, 3.5 (B), 3.7 (C)%. M 420 ($CHCl_3$). $C_{13}H_{15}ONW$ requires C, 40.5; H, 3.9; N, 3.6%. M 385. Infra-red spectrum (KBr disc): 3107 sh, 3070 m-s, 2965 m, 2925 sh, 2835 sh, 2820 m, 2700 vw, 2105 s, 1430 m, 1375 m, 1365 m, 1098 m-s, 1044 s, 1021 w, 989 w, 897 w, 875 m, 831 m, 798 w, 683 m, 597 w, 563 m-s.]

Preparation of $[(\pi-C_5H_5)_2W(OC_2H_5)(CN)H]PF_6$

Dissolution of $(\pi-C_5H_5)_2W(OC_2H_5)CN$, see above, in dilute sulphuric acid and addition of an excess of NH_4PF_6 in a saturated aqueous solution gave, immediately, an orange precipitate. This was collected by centrifugation, washed twice with water and dried under vacuum. The solid was recrystallised from liquid sulphur dioxide-ether mixtures to give a yellow microcrystalline solid which was washed with ether and dried. [Found: C, 29.6; H, 3.15; N, 2.7% (C). Λ 91.5 ohm⁻¹ cm². $C_{13}H_{16}ONPF_6W$ requires: C, 29.4; H, 3.0; N, 2.6%. Infra-red spectrum (KBr disc): 3130 s, 2988 m, 2950 sh, 2898 sh, ~2480 vs (br), 2133 s, 1750 s (br), 1446 m, 1426 sh, 1388 w, 1360 w, 1290 w, 1147 w, 1095 w, 1024 s, 996 w, 958 m, 900-800 vs (br), 693 w, 678 w, 595 w, 557 s, 445 m.]

Preparation of $(\pi-C_5H_5)_2W(OCH_3)CN$

$(\pi-C_5H_5)_2WCl_2$ (1 g.) and excess NaCN (2-3 g.) were refluxed in methanol for 30 minutes to give a yellow-orange coloured solution, which was then cooled and evaporated to dryness under vacuum. The solid residue was chromatographed on alumina using acetone containing a small amount of methanol (approx. 20:1 mixture). The orange solid obtained on evaporation was recrystallised twice from dichloromethane-ether mixtures to give small orange coloured crystals which were washed with ether and dried under vacuum. Yield ca 70%. [Found: C, 38.4; H, 3.5; N, 3.8% (C). $C_{12}H_{13}ONW$ requires: C, 38.4; H, 3.5; N, 3.8%. Infra-red spectrum (mull): 3090 m, 3075 m, 3049 sh, 3050 sh, 2920 w, 2883 w, 2840 w, 2777 m, 2111 m-s, 1426 m, 1382 w, 1111 w, 1063 m, 1049 m, 1016 w, 989 w, 881 m, 837 m, 793 vw, 682 w.]

Preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo(NCS)}_2$

$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ (1 g.) was refluxed with a solution of KNCS (3 g.) in 30 ml. water for 1 hour. A purple-pink coloured solid was formed which, when the reaction mixture had cooled to room temperature, was filtered off, washed well with water and dried under vacuum. This solid was recrystallised twice from liquid sulphur dioxide-dichloromethane mixtures to give purple crystals which were washed with dichloromethane and dried. Yield ca 90%. [Found: C, 42.0; H, 3.1; N, 8.0; S, 18.8% (B). $\text{C}_{12}\text{H}_{10}\text{S}_2\text{N}_2\text{Mo}$ requires C, 42.1; H, 2.9; N, 8.2; S, 18.7%. Infra-red spectrum (mull): 3080 m, 2105 vs, 1442 sh, 1422 w-m, 1405 vw, 1360 w, 1068 vw, 1013 w, 991 w, 950 vw, 837 m, 826 sh. For lower region see Chapter II.]

Reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with KNCS in water

$(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ (1 g.) was refluxed in a solution of KNCS (2 g.) for 15 minutes to give a deep red solid insoluble in boiling solution. This mixture was allowed to cool and the solid collected by filtration, washed with water and dried under vacuum.

The solid was then digested with acetone to give a pink solution which was separated from the insoluble residue by centrifugation. This process of extraction was repeated until the acetone was no longer coloured. The acetone solution was evaporated to dryness to give a pink solid, 'A'. The acetone insoluble material, 'B', was washed well with more acetone and dried under vacuum.

Solid 'A' was chromatographed on alumina using acetone as eluant. The solid residue left after removal of solvent was recrystallised from a chloroform-ether mixture washed with ether and dried to give pink micro-

crystals in ca 40% yield. [Found: C, 33.4; H, 2.3; N, 6.5; S, 14.7% (B). $C_{12}H_{10}S_2N_2W$ requires: C, 33.5; H, 2.3; N, 6.5; S, 14.9%. Infra-red spectrum (mull): 3125 sh, 3095 m, 2121 s, 2104 s, 2094 s, 1430 m, 1360 w, 1258 w, 1009 w, 994 sh, 951 vw, 900 w, 842 m, 815 w. For lower region see Chapter II.]

Solid 'B' was recrystallised twice from liquid sulphur dioxide-dichloromethane mixtures to give a purple microcrystalline solid which was washed well with acetone and ether and, then, dried under vacuum. Yield ca 40%. [Found: C, 33.4; H, 2.2; N, 6.4; S, 14.8% (B). $C_{12}H_{10}S_2N_2W$ requires C, 33.5; H, 2.3; N, 6.5; S, 14.9%. Infra-red spectrum (mull): 3099 sh, 3078 m, 2928 w, 2119 s, 2107 vs, 1448 sh, 1423 w, 1357 w, 1325 vw, 1143 vw, 1009 w, 997 sh, 988 sh, 960 vw, 940 vw, 896 vw, 840 m, 818 sh. For lower region see Chapter II.]

Preparation of $(\pi-C_5H_5)_2W(NCS)Cl$

A mixture of $(\pi-C_5H_5)_2WCl_2$ (1 g.) and KSCN (3 g.) in a suspension of acetone (30 ml.) was refluxed for 3 hours to give a purple coloured solution. The mixture was cooled, evaporated to dryness and then chromatographed by adding in a dichloromethane solution to an alumina column. Elution for a time with dichloromethane caused slow separation of a mauve band from brown material but final elution was achieved with acetone to give a deep mauve solution. [N.B. Acetone also caused brown band to move and on one occasion rechromatography was found necessary.] The residue obtained on evaporating the eluate to dryness was recrystallised from a dichloromethane-ether-light petroleum mixture to give mauve coloured, prismatic microcrystals in ca 70% yield. [Found: C, 32.5 (B), 32.3 (C); H, 2.5 (B), 3.0 (C);

N, 3.6 (C); S, 7.75 (B); Cl, 8.7 (B)%. $C_{11}H_{10}NSClW$ requires: C, 32.4; H, 2.5; N, 3.4; S, 7.9; Cl, 8.7%. Infra-red spectrum (mull): 3015 sh, 3093 m, 2120 s, 1424 m, 1355 w, 1074 w, 1010 w, 995 w, 956 vw, 940 vw, 889 vw, 874 vw, 834 m, 815 w.]

Preparation of $(\pi-C_5H_5)_2W(NCS)ClPF_6$

An aqueous suspension of $(\pi-C_5H_5)_2W(NCS)Cl$ (see above) (0.3 g.) in 10 ml. water was oxidised by adding several drops of concentrated nitric acid to give a deep magenta coloured solution. This solution was centrifuged and then an excess of NH_4PF_6 in a saturated aqueous solution was added to the separated, clear solution. A purple precipitate formed immediately and this was centrifuged off, washed well with water and dried under vacuum. Recrystallisation twice from liquid sulphur dioxide-dichloromethane mixtures gave purple needle-like crystals which were washed with dichloromethane and dried. Yield ca 80%. [Found: C, 23.9; H, 1.8; N, 2.35% (C). Λ , 87.5 $ohm^{-1} cm^2$. $C_{11}H_{10}SNClPF_6W$ requires: C, 24.0; H, 1.8; N, 2.5%. Infra-red spectrum (mull): 3134 m, 2920 vw, 2226 vw, 2126 vw, 2044 s, 1434 m, 1126 w, 1012 w (br), 982 vw, 890-810 vs (br), 567 s.]

Preparation of $(\pi-C_5H_5)_2Mo(OCONH_2)_2$

$(\pi-C_5H_5)_2MoCl_2$ (1 g.) was added to a solution of $NaOCN$ (3 g.) in water and refluxed for $1\frac{1}{2}$ hours to give a red coloured solution. This solution was evaporated to dryness under vacuum and the residue was extracted with liquid sulphur dioxide. The sulphur dioxide extract was filtered and the filtrate evaporated to dryness to give a purple-pink solid residue. This solid was recrystallised twice from hot ethanol to give deep red needle shaped crystals which were washed successively with ethanol and ether and

then dried. Yield ca 80%. [Found: C, 41.4, 41.5 (C); H, 4.15, 4.3 (C); N, 7.9, 8.0 (C); O, 18.1 (B); Mo 27.6 (B)%. $C_{12}H_{14}N_2O_4Mo$ requires: C, 41.6; H, 4.1; N, 8.1; O, 18.5; Mo 27.7%. Infra-red spectrum (KBr disc): 3436 s (br), $\sim$ 3318 s (br), $\sim$ 3200 s(br), 3118 sh, 3100 m, 1670 m, 1620 s, 1593 s, 1442 m, 1427 m, 1369 vw, 1277 s, 1116 vw, 1029 w, 1017 w, 1005 vw, 954 vw, 936 vw, 885 vw, 836 sh, 829 m, 816 sh, 787 vw, 750 w, 682 vw, 585 w, 526 w.]

Reaction of $(\pi-C_5H_5)_2WCl_2$ with NaOCN

- a) As in the above reaction $(\pi-C_5H_5)_2WCl_2$ (1 g.) was refluxed with NaOCN (3 g.) in 30 ml. water for $1\frac{1}{2}$ hours. The purple coloured solution (separated from a small amount of solid) was evaporated to dryness and the residue was purified in a similar fashion to the molybdenum product to give red-brown needle shaped crystals in ca 70% yield. [Found: C, 32.0, 32.05; H, 3.6, 3.3; N, 6.5, 6.0% (C). $C_{12}H_{16}N_2O_5W$ requires: C, 31.9; H, 3.6; N, 6.2%. Infra-red spectrum (KBr disc): 3438 vs (br), 3317 s (br), $\sim$ 3190 s (br), 3132 sh, 3108 m, 1670 sh, 1632 s, 1593 s, 1449 sh, 1423 m, 1363 w, 1278 m-s, 1167 vw, 1111 w, 1028 w, 1018 w, 958 w, 928 w, 887 w, 838 m, 828 m, 811 sh, 770 m, 679 w, 633 w, 580 w, 528 w.]
- b) If the quantities used were the same as in a) but if the solution was refluxed for only 10 minutes a water insoluble purple product was also formed, which was filtered off, washed well with water and dried. Recrystallisation from liquid sulphur-dioxide ether mixtures (2x) gave deep red, prismatic crystals in up to 20% yield. [Found: C, 34.5, 34.8; H, 2.7, 2.7; N, 6.2, 6.3% (C). $C_{10}H_{12}N_2O_3W$ requires: C, 34.6; H, 2.9; N, 6.7%. Infra-

red spectrum (mull): 3600-3000 (br), 3575 w, 3122 m, 3106 sh, ~ 2260 s (br), ~1630 w (br), 1432 m, 1360 sh, 1335 m, 1106 vw, 1080 vw, 1060 vw, 1014 w, 988 vw, 941 vw, 909 w, 861 w, 839 w-m, 810 vw, 597 w, 577 w.]

Experimental details for Chapter III

Preparation of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_6\text{F}_5)$

n-Butyl lithium was made from n-butyl bromide and lithium metal in dry ether by the standard method (G4) and standardised by titration using Gilman's method (G5). Pentafluorophenyl lithium was made by slowly adding $\text{C}_6\text{F}_5\text{Br}$ (3.3 g.) (or $\text{C}_6\text{F}_5\text{Cl}$ (2.7 g.)) in dry ether (20 ml.) to a stoichiometric quantity of the standardised $\text{C}_5\text{H}_9\text{Li}$ in ether (30 ml.), cooled to -70°C and stirred magnetically as described (G6).

$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ (2 g.) was added to this, stirred, cold, $\text{C}_6\text{F}_5\text{Li}$ solution and the reaction mixture was allowed to warm up slowly to room temperature. The mixture turned yellow-brown in colour and was left stirring overnight. The product was then filtered through a sintered frit and the filtrate was evaporated to dryness to give an oily, brown residue. The residue was dissolved in the minimum amount of benzene and chromatographed roughly using benzene as eluant on an alumina column. A yellow-brown band was collected and the brownish-solution evaporated to give a brown oil, 'A'. Another, smaller, yellow-brown band was eluted using an ether-dichloromethane mixture, or dichloromethane alone, which on evaporation also gave a yellow-brown oily product, 'B'.

The product 'A' was rechromatographed by adding to a column in the minimum amount of benzene, washing the column well with petrol (~300 ml.)

to remove less polar impurities and then eluting the main yellow band with a 1:1 mixture of light petroleum-benzene mixture (on some occasions it was necessary to increase the concentration of benzene to get sufficient movement of the band). Again an oily residue was obtained on evaporation of the solution. This could then be rechromatographed (the product usually became less oily with rechromatography) or, after pumping at high vacuum for several hours, after which time it became more solid, the product could be crystallised. Crystallisation from an ether-light petroleum mixture, by cooling in a dry ice-acetone bath, gave a yellow microcrystalline solid. This was recrystallised from ether-light petroleum, washed with a little petroleum and dried in vacuo. Yield ca 15%. [Found: C, 47.2, 46.7; H, 2.0, 2.0; F, 33.9% (B). M, 571 (CHCl_3), $\text{C}_{22}\text{H}_{10}\text{F}_{10}\text{Mo}$ requires: C, 47.2; H, 1.8; F, 33.7%. M, 560. Infra-red spectrum (mull): 3146 sh, 3132 w-m, 1926 w, 1721 vw, 1629 m, 1531 s, 1497 s, 1445 s, 1432 s, 1374 m, 1340 w, 1327 w, 1263 w, 1244 w, 1224 sh, 1214 w, 1139 w, 1109 vw, 1092 m, 1076 w, 1058 s, 1047 s, 1011 w, 1005 w, 978 s, 958 s, 926 w, 900 w, 868 w, 844 w, 840 vw, 812 w, 784 m, 769 m, 752 m, 600 w.] It was also found possible to recrystallise the compound from a) hot petroleum (100-120°) at approximately 100°C on cooling and larger (though still small) crystals were obtained this way, or b) from a methanol-water mixture. [Found: C, 47.4; H, 2.1% (B).]

Rechromatography of product 'B' using an ether-dichloromethane (1:1) mixture as eluant gave an oily yellow-brown product on evaporation. This was transformed to a yellow-brown solid by crystallisation from an ether-light petroleum mixture on cooling. [Found: C, 45.4; H, 1.5; F, 38.5% (B).]

Attempted reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ with $\text{C}_6\text{F}_5\text{MgBr}$

Pentafluorophenyl magnesium bromide was prepared from $\text{C}_6\text{F}_5\text{Br}$ (1.5 ml.) and Mg metal (0.3 g.) in dry ether as described (G7). The solution of $\text{C}_6\text{F}_5\text{MgBr}$ was transferred to a suspension of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ in a little ether and the mixture warmed in a water bath, left to reflux, while stirred, for 6-7 hours and then left stirring at room temperature overnight. The mixture was then filtered to give a dark green solid and an ethereal solution which was slightly discoloured. The green solid was shown to be unchanged $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ and the ethereal solution yielded only unreacted Grignard reagent with a little organic solid probably formed by Grignard coupling.

Attempted reactions of $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ with C_6F_6

- i) A solution of $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ (~0.3 g.) in hexafluorobenzene was refluxed for 2 hours. A yellow solid was obtained on evaporation which was judged from its infra-red spectrum to be unreacted $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$.
- ii) $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ (0.3 g.) in hexafluorobenzene was irradiated with ultra violet light overnight. Evaporation, again, yielded unreacted $(\pi\text{-C}_5\text{H}_5)_2\text{MoH}_2$ as indicated by its infra-red spectrum.

Attempted reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WH}_2$ with SiF_4

$(\pi\text{-C}_5\text{H}_5)_2\text{WH}_2$ in benzene was evacuated while cooling in liquid nitrogen. After isolating the evacuated system and allowing it to warm up SiF_4 was admitted to the stirred solution. The yellow solution became darker in colour but, after 1-1½ hours, evaporation to dryness led to the isolation of $(\pi\text{-C}_5\text{H}_5)_2\text{WH}_2$ as the major product. The product was identified by its infra-red spectrum.

Preparation of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WH}(\text{C}_6\text{F}_5)$

$\text{C}_6\text{F}_5\text{Li}$ was made as detailed above and reacted in dry ether in a 2:1 molar ratio with $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ (3 g.) by stirring overnight as in the similar preparation with $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$. After filtration and evaporation of the filtrate to dryness, the oily product was chromatographed, initially using benzene as eluant and then again using 1:1 benzene-light petroleum as eluant to give a basically solid, yellow residue. This was recrystallised twice from ether-light petroleum mixtures or from light petroleum alone on cooling to give an orange microcrystalline compound in ca 10% yield.

[Found: C, 40.9, 40.8; H, 1.3, 2.1; F, 29.55, 29.0; W, 28.2% (B).

M, 679 (C_6H_6). $\text{C}_{22}\text{H}_{10}\text{F}_{10}\text{W}$ requires: C, 40.8; H, 1.6; F, 29.3; W, 28.4%.

M, 648. Infra-red spectrum (mull): 3155 sh, 3139 sh, 3123 w-m, 2009 vw, 1645 sh, 1623 m, 1603 sh (w), 1590 sh (w), 1527 s, 1500 s, 1444 sh, 1432 s, 1373 m, 1344 w, 1312 w, 1303 w, 1260 w, 1234 w, 1211 vw, 1194 vw, 1151 vw, 1138 vw, 1117 sh, 1107 sh, 1086 s, 1067 s, 1058 s, 1043 s, 1002 s, 988 sh, 982 s, 958 s, 954 sh, 916 m, 898 w, 874 w, 850 w, 838 w, 817 m, 777 sh, 767 m, 756 m, 599 vw, 590 vw.]

Other compounds were formed in this reaction but none in large scale and although other bands could be eluted from the column with more polar solvents no other compounds were characterised.

Preparation of $(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoCl}(\text{C}_6\text{F}_5)$

$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{MoH}(\text{C}_6\text{F}_5)$ (~0.3 g.), prepared as stated above, was dissolved in carbon tetrachloride (~50 ml.) and left at room temperature for approximately 15 hours. A brownish solid separated and the CCl_4 was then taken off under vacuum and the solid washed three times with diethyl ether,

collected and dried. This was recrystallised three times from liquid sulphur dioxide-ether mixtures, washed once with dichloromethane and then well with ether and dried to give green microcrystals in ca 60% yield.

[Found: C, 44.1; H, 1.9; Cl, 5.8; F, 32.0% (B). $C_{22}H_9F_{10}ClMo$ requires: C, 44.4; H, 1.5; Cl, 6.0; F, 31.95%. Infra-red spectrum (KBr disc): 3158 w, 3137 w, 3102 m, 3085 m, 1629 m, 1587 vw, 1529 s, 1504 s, 1442 sh, 1427 s, 1409 sh, 1374 w, 1341 w, 1322 w, 1251 w, 1222 w, 1140 w, 1115 vw, 1098 m, 1082 w, 1059 s, 1018 vw, 1007 vw, 986 s, 958 s, 918 w, 888 vw, 871 m, 862 w, 849 m, 837 m, 824 m, 778 m, 744 m, 708 vw, 686 w, 668 vw, 601 vw, 588 vw.]

Preparation of $(\pi-C_5H_5)(\pi-C_5H_4C_6F_5)WCl(C_6F_5)$

In a similar reaction to the above, $(\pi-C_5H_5)(\pi-C_5H_4C_6F_5)WH(C_6F_5)$ was reacted with carbon tetrachloride overnight and the product purified as above to give brownish-yellow coloured microcrystals in ca 60% yield.

[Found: C, 38.9; H, 1.4; Cl, 5.1% (B). $C_{22}H_9F_{10}ClW$ requires: C, 38.7; H, 1.3; Cl, 5.2%. Infra-red spectrum (KBr disc): 3158 w, 3129 w, 3107 m, 3092 m, 2927 w, 1629 m, 1588 sh, 1528 s, 1503 s, 1443 sh, 1424 s, 1382 w, 1371 w, 1342 w, 1316 w, 1248 w, 1218 w, 1139 w, 1115 w, 1098 m, 1082 m, 1063 s, 1056 sh, 1046 sh, 1014 w, 1005 w, 985 s, 958 s, 918 w, 885 sh, 874 m, 855 m, 836 m, 819 m, 777 m, 774 sh, 748 m, 734 sh, 709 vw, 701 vw, 684 w, 668 vw, 656 vw, 600 vw, 587 w.]

Preparation of $[(\pi-C_5H_5)(\pi-C_5H_4C_6F_5)MoCl(C_6F_5)]PF_6$

$(\pi-C_5H_5)(\pi-C_5H_4C_6F_5)MoCl(C_6F_5)$ (~ 0.2 g.) was dissolved in concentrated nitric acid (~ 1 ml.) to give a red-purple solution. This was centrifuged

and an excess of a saturated aqueous solution of NH_4PF_6 was added to the clear solution to cause precipitation. Ether was added and the mixture shaken. The ethereal layer, which was red-purple in colour, was separated and evaporated to dryness. The oily product obtained was taken up again in ether and the clear ethereal solution was evaporated to dryness. The purple residue was recrystallised twice from liquid sulphur dioxide-ether mixtures to give a purple microcrystalline compound which was washed with ether (in which it was now virtually insoluble) and dried. [Found: C, 36.4; H, 3.6% (B). $\text{C}_{22}\text{H}_9\text{F}_{10}\text{ClPF}_6\text{Mo}$ requires: C, 35.7; H, 1.2%. Infra-red spectrum (KBr disc): 3120 m, 2917 w, 2848 w, 1651 sh, 1624 m, 1526 sh, 1502 m-s, 1435 m-s, 1346 w, 1324 w, 1278 w, 1118 w, 1059 m, 982 w, 952 m-s, 875-810 s-vs (br), 788 w, 750 w, 560 m.]

Preparation of $[(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WCl}(\text{C}_6\text{F}_5)]\text{PF}_6$

$(\pi\text{-C}_5\text{H}_5)(\pi\text{-C}_5\text{H}_4\text{C}_6\text{F}_5)\text{WCl}(\text{C}_6\text{F}_5)$ (~0.2 g.) was dissolved in concentrated nitric acid (~2 ml.) to give a deep red coloured solution. The solution was centrifuged and an excess of saturated aqueous NH_4PF_6 solution was added to the clear solution. The precipitate which formed was centrifuged off washed with water and dried. The solid was recrystallised from a mixture of dichloromethane and petrol to give a small quantity of a red microcrystalline compound. [Found: C, 31.6; H, 1.4% (C). $\text{C}_{22}\text{H}_9\text{F}_{10}\text{ClPF}_6\text{W}$ requires: C, 31.9; H, 1.1%. Infra-red spectrum (KBr disc): 3138 m, 2921 vw, 2837 vw, 1660 sh, 1636 m, 1598 sh, 1535 m, 1504 s, 1491 s, 1441 s, 1375 w, 1354 w, 1328 w, 1266 w, 1229 w, 1127 w, 1100 w, 1073 s, 1051 m, 1026 vw, 1010 vw, 993 s, 965 s, 880 s, 855-825 vs (br), 784 m, 758 m, 736 w, 675 w, 556 m-s.]

Reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ with LiC_6H_5

Lithium phenyl was made by the normal method (G4) from $\text{C}_6\text{H}_5\text{Br}$ and Li metal in diethyl ether. The stoichiometric amount of $\text{C}_6\text{H}_5\text{Li}$ required to give an approximately 2:1 molar ratio with $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ (3 g.) was added to a suspension of the dihalide in ether. The mixture was stirred overnight and became orange-brown in colour. The reaction mixture was evaporated to dryness to give a deep brown-purple coloured oily residue. This residue was chromatographed by addition to an alumina column in benzene. Elution with benzene moved a red-orange coloured band which gave a red solution and a red-brown oily solid, 'A', on evaporation of the solvent. A yellow band was left on the column which was eluted next, with a benzene-ether (1:1) mixture. This band, on evaporation of the resulting solution to dryness, yielded an oily yellow-brown product 'B'. (N.B. One preparation done under similar conditions yielded only the yellow compound 'B'.)

Product 'A' was rechromatographed using benzene as eluant, and the oily solid obtained after pumping off the solvent was recrystallised twice from ether-light petroleum mixtures, with cooling, to give a red-brown micro-crystalline solid which was washed with a little light petroleum and dried. Yield ca 15% (variable). [Found: C, 69.9 (C); H, 5.1 (C); Mo, 25.2 (B)%. $\text{C}_{22}\text{H}_{20}\text{Mo}$ requires: C, 69.5; H, 5.3; Mo, 25.2%. Infra-red spectrum (mull): 3097 m, 3045 m, 3031 sh, 2987 vw, 2953 vw, 1592 vw, 1559 m, 1466 m, 1452 sh, 1418 w, 1366 w, 1352 sh, 1253 w, 1232 w, 1149 vw, 1109 w, 1066 w, 1006 m, 934 vw, 908 vw, 860 sh, 849 w, 833 m, 821 vw, 807 vw, 792 m, 735 s, 702 m, 628 w.]

Rechromatography of product 'B' on alumina with benzene gave a yellow

oily solid on evaporation of the solution. This was recrystallised from an ether-light petroleum mixture to give a yellow solid which was washed with a little petroleum ether and dried. Yield variable (up to ca 10%).

[Found: C, 69.7 (C), 68.4 (B); H, 5.3 (C), 5.3 (B); Mo, 25.95 (B)%.

$C_{22}H_{20}Mo$ requires C, 69.5; H, 5.3; Mo, 25.2%. Infra-red spectrum (KBr disc): 3160 w-m, 1815 m-s, 1599 m, 1573 w, 1507 w, 1490 vw, 1448 m, 1410 vw, 1392 vw, 1380 vw, 1319 vw, 1273 w, 1259 w, 1180 vw, 1151 vw, 1100 w, 1086 w, 1072 w, 1029 m, 1010 sh, 932 vw, 917 sh, 901 m, 889 m, 837 w, 808 w, 769 w, 753 s, 691 m, 637 w, 538 w, 502 m.]

Reaction of $(\pi-C_5H_5)_2WCl_2$ with C_6H_5Li

This reaction was carried out in an analogous manner to the above, using C_6H_5Li and $(\pi-C_5H_5)_2WCl_2$ (3 g.) in an approximately 2:1 molar ratio in ether. Chromatography using benzene yielded only one, separable, yellow band which gave an oily yellow residue on evaporation of the solvent. Chromatography was repeated and the resulting product was recrystallised from an ether-light petroleum mixture with cooling in dry ice-acetone bath to give a microcrystalline yellow solid in variable yields up to ca 15%. [Found: C, 56.5; H, 4.45; W, 39.2% (B). $C_{22}H_{20}W$ requires: C, 56.4; H, 4.3; W, 39.3%. Infra-red spectrum (mull): 3103 w, 3049 m, 3022 sh, 2958 w, 2920 w, 1598 m, 1563 w, 1504 vw, 1466 w, 1448 w, 1406 w, 1363 vw, 1340 vw, 1268 vw, 1104 w, 1072 w, 1028 w, 1010 w, 891 vw, 835 w, 802 w, 759 m, 732 m, 698 m.]

Experimental details for Chapter IV

Preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NHC}_6\text{H}_4\text{S})$

$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ (1 g.) and o-aminothiophenol, $\text{C}_6\text{H}_4(\text{NH}_2)\text{SH}$, (1 ml.), were suspended in a solution of NaOH (1.5 g.) in 30 ml. of a 5:1 ethanol-water mixture. The mixture was refluxed for 1.5 hours to give a purple coloured solution which, after cooling, was then partitioned between dichloromethane and aqueous 2N sodium hydroxide solution. The purple dichloromethane layer was separated and chromatographed on alumina. A 1:1 mixture of dichloromethane-tetrahydrofuran eluted a purplish-brown coloured band which gave a purple solution and a purple solid on evaporation of the solvent. This solid was recrystallised from dichloromethane-ether mixtures to give purple needle-like crystals which was washed in ether and dried. Yield ca 70%.

[Found: C, 55.3; H, 4.2; N, 4.1; S, 9.0% (B). M, 391 $((\text{CH}_3)_2\text{CO})$ (N.B. mass spectrum parent ion peak 349 for ^{96}Mo). $\text{C}_{16}\text{H}_{15}\text{NSMo}$ requires: C, 55.0; H, 4.3; N, 4.0; S, 9.2%. M, 349. Infra-red spectrum (mull): 3326 m, 3110 sh, 3094 m, 3040 w, 1561 m, 1467 m, 1434 m, 1344 w, 1304 m, 1271 vw, 1111 w, 1056 w, 1024 m, 997 w, 915 w, 828 m, 807 m, 793 sh, 754 s, 726 w, 675 w.]

Preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{NHC}_6\text{H}_4\text{S})$ and other products

An excess of o-aminothiophenol (2 ml.) was added to a suspension of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ (1 g.) in a solution of NaOH (1.5 g.) in 30 ml. of a 5:1 ethanol-water mixture. The mixture was refluxed for 20-30 minutes to give a deep red-brown coloured product, which was then cooled and the liquid was decanted into a separating funnel - a small amount of dark coloured solid was left behind and this was washed several times with dichloromethane and

the washings added, also, to the separating funnel. The solution was then partitioned between dichloromethane and 2N aqueous sodium hydroxide solution. The dichloromethane layer was separated and the contents chromatographed using dichloromethane on an alumina column. An orange-brown band gave a deep red coloured solution which, on evaporation, gave a red solid. The solid was recrystallised twice from dichloromethane-ether mixtures to give deep red, needle shaped crystals which were washed with ether and dried. Yield ca 50%. [Found: C, 44.1, 43.8; H, 3.5, 3.2; N, 3.4, 3.3; S, 7.4% (B). $C_{16}H_{15}SNW$ requires: C, 44.0; H, 3.5; N, 3.2; S, 7.3%. Infra-red spectrum (mull): 3336 m, 3102 m, 3043 w, 1608 w, 1565 m, 1467 m, 1438 m, 1418 sh, 1350 w, 1301 m, 1279 w, 1259 w, 1157.vw, 1113 w, 1056 w, 1024 m, 1016 sh, 997 w, 917 w, 850 m, 840 m, 829 m, 804 w, 784 w, 752 m, 740 sh, 722 w, 692 w, 652 w, 637 w.]

Other bands were eluted from the column with more polar solvents. Acetone eluted a purplish coloured band which yielded a little orange-red solid after precipitation of a solution of the evaporated residue in dichloromethane by light petroleum. Another preparation using an excess of $C_6H_4(SH)NH_2$ and refluxing the mixture for more than 1 hour yielded more of this later product as judged by its identical infra-red spectrum. This was probably $(\pi-C_5H_5)_2W(SC_6H_4NH_2)_2$, although not obtained pure. [Found: C, 45.7; H, 3.5; N, 4.5% (C). $C_{22}H_{22}N_2S_2W$ requires: C, 47.0; H, 3.9; N, 5.0%.]

Another reaction using $(\pi-C_5H_5)_2WCl_2$ (1 g.), $C_6H_4(SH)NH_2$ (~1 g.) and heating the basic solution to reflux for several minutes gave a large quantity of the dark red-brown solid, only slightly soluble in water and

insoluble in organic solvents. A recrystallisation of this, after separation, washing with dichloromethane and drying, from a liquid sulphur dioxide-ether mixture gave red-brown crystals. These crystals were recrystallised 5 times from liquid sulphur dioxide-ether mixtures but could not be obtained entirely analytically pure, although the compound was almost certainly

$(\eta\text{-C}_5\text{H}_5)_2\text{W}(\text{SC}_6\text{H}_4\text{NH}_2)\text{Cl}$. [Found: C, 39.3; H, 3.4; S, 6.8; Cl, 7.8% (B).

$\text{C}_{16}\text{H}_{16}\text{NSClW}$ requires: C, 40.6; H, 3.3; S, 6.8; Cl, 7.5%. The infra-red spectrum (mull) included: 3122 w, 3085 w, 3062 w, 3000 m, 2907 m, 1600 w-m, 1468 m, 1442 w-m, 1265 m, 849 m, 752 m, 743 m.]

Preparation of $(\eta\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NHC}_6\text{H}_4\text{O})$

A solution of NaOH (1.5 g.) in 30 ml. of a mixture of 5:1 ethanol-water was added to $(\eta\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ (1.2 g.) and o-aminophenol (0.8 g.) in a side armed flask. The mixture was refluxed for 1.5 hours to give a purple coloured solution. After cooling, the mixture was evaporated to dryness and chromatographed on alumina. After elution of a yellow band with tetrahydrofuran, a 2:1 tetrahydrofuran-ethanol solution eluted a purple coloured band giving a purple coloured solution. On evaporation to dryness an oily product was obtained. This product was recrystallised from a dichloromethane-light petroleum mixture to give purple needle-like crystals which were washed with petrol and dried under vacuum. Yield ca 70%. [Found: C, 57.4 (C), 58.3 (B); H, 4.5 (C), 5.4 (B); N, 4.2 (C), 4.0 (B); O, 4.7 (B)%. M, 343 (CHCl_3). $\text{C}_{16}\text{H}_{15}\text{ONMo}$ requires: C, 57.7; H, 4.5; N, 4.2; O, 4.8%. M, 333. Infra-red spectrum (KBr disc): 3355 m, 3115 m, 3060 w, 3000 vw, 2921 w, 2858 w, 1577 vw, 1556 vw, 1487 s, 1447 sh, 1432 sh, 1368 w, 1291 m, 1271 s, 1239 s, 1112 w, 1090 w, 1065 w, 1019 m, 920 w, 867 sh, 829 m, 797 m, 735 s,

682 w, 644 w, 626 m, 526 m, 443 w, 417 w.]

Reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ with o-C₆H₄(NH₂)₂

Several reactions involving refluxing $(\pi\text{-C}_5\text{H}_5)_2\text{WCl}_2$ (~1.5 g.) with o-phenylenediamine, C₆H₄(NH₂)₂, (~1 g.) in solutions of NaOH (1-2 g.) in 5:1 ethanol-water for periods of $\frac{1}{2}$ -2 hours gave essentially the same result. A green to red-brown coloured reaction mixture was produced. Chromatography similar to the above reactions yielded an orange product, eluted with dichloromethane, which on recrystallisation from dichloromethane-petrol mixtures gave mainly unchanged C₆H₄(NH₂)₂ but on one occasion gave a very small quantity of a red-brown product with a mass spectrum parent peak corresponding to $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{NHC}_6\text{H}_4\text{NH})$ and infra-red absorption frequencies of typical $(\pi\text{-C}_5\text{H}_5)$ and NH groups. Ethanol eluted a blue band from the column which gave a purple solid on evaporation which readily decomposed on attempted purification.

Reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ and KNC₄H₄

Potassium pyrrolide, KNC₄H₄, was made by the action of potassium (1-2 g.) on a solution of pyrrole in petrol. This salt was dissolved in tetrahydrofuran and transferred to $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ (1 g.) and left stirring overnight. The reaction mixture became brown in colour and much solid remained undissolved. The solution was decanted and worked up using chromatography as in the above reactions, but no pure product could be obtained. Recrystallisation of the residue from liquid sulphur dioxide-ether mixtures proved it to be unreacted $(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ as judged by its infra-red spectrum and crystal form.

Preparation of $(\pi\text{-C}_{55}\text{H}_{52})_2\text{W}(\text{O}_2\text{C}_{14}\text{H}_8)$

9,10-Phenanthroquinone was reduced to 9,10-phenanthrohydroquinone, $\text{C}_{14}\text{H}_8(\text{OH})_2$, by passing sulphur dioxide gas through a warmed suspension of the quinone in alcohol, containing a little water, for 1.5 hours (cf. G8). This sample was centrifuged and then colourless phenanthrohydroquinone was precipitated from the separated clear, yellow solution by the addition of excess water. This was recrystallised from aqueous ethanol.

$(\pi\text{-C}_{55}\text{H}_{52})_2\text{WCl}_2$ (1 g.) was suspended in a small quantity of water and phenanthrohydroquinone in 30 ml. aqueous $2\bar{\text{N}}$ sodium hydroxide solution, under nitrogen, was added to this. The mixture was refluxed for 1.5 hours to give a red-brown coloured aqueous solution with a little sandy coloured solid. The cooled solution was decanted into a separating funnel and partitioned between dichloromethane and $2\bar{\text{N}}$ aqueous sodium hydroxide solution. The red dichloromethane layer was separated and the contents chromatographed using dichloromethane as eluant. A yellow band gave a red solution which yielded yellow-brown solid on evaporation. Recrystallisation from a dichloromethane-ether mixture gave dark red crystals; addition of light petroleum to the mother liquor gave more dark coloured material with the same infra-red spectrum. These crystals were washed with ether and dried under vacuum. Total yield ca 70%. [Found: C, 55.0, 55.2; H, 3.4, 3.4; O, 6.3; W, 34.6% (B). $\text{C}_{24}\text{H}_{18}\text{O}_2\text{W}$ requires: C, 55.2; H, 3.5; O, 6.1; W, 35.2%. Infra-red spectrum (mull): 3103 sh, 3090 w, 3048 vw, 3020 w, 1608 w, 1588 m, 1556 vw, 1508 vw, 1481 w, 1441 w, 1416 m, 1399 vw, 1366 m-s, 1332 m, 1281 vw, 1236 w, 1223 w, 1171 w, 1112 m, 1056 s, 1033 m, 1013 sh, 1006 m, 995 sh, 940 sh, 896 m, 867 m, 829 m, 791 m, 755 m, 721 m, 687 m, 675 vw, 666 vw, 634 vw,

569 m, 540 w.]

Reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_6\text{H}_4)$ with iodine

$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{O}_2\text{C}_6\text{H}_4)$ was prepared as described (A3) and 0.2 g. were dissolved in dichloromethane (10 ml.). A solution of iodine (~ 0.2 g.) in dichloromethane was added to the solution of the tungsten complex. After 10 minutes green crystals had been deposited from the solution. These crystals were separated, washed with dichloromethane and ether, and dried. The infra-red spectrum was taken at this stage and shown to be different to that of $(\pi\text{-C}_5\text{H}_5)_2\text{WI}_2$. However recrystallisation from a liquid sulphur dioxide-ether mixture gave green crystals (leaving a yellow coloured mother liquor). These crystals were identified as $(\pi\text{-C}_5\text{H}_5)_2\text{WI}_2$ by their infra-red spectrum.

Preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{O}_2\text{C}_5\text{H}_7)\text{Cl}\cdot\text{H}_2\text{O}$

$(\pi\text{-C}_5\text{H}_5)_2\text{MoCl}_2$ (1 g.), acetyl-acetone (5 ml.) and NaOH (1.5 g.) in 5 ml. water were refluxed for 30 minutes to give a deep red-brown coloured solution which, after cooling, was evaporated to dryness. The oily residue was extracted with liquid sulphur dioxide and filtered, using a sintered glass funnel, under sulphur dioxide pressure. After evaporating the sulphur dioxide solution to dryness the oily product was chromatographed by adding to an alumina column with dichloromethane. Acetone first eluted a small pink coloured band and then, ethanol eluted a yellow-brown band which gave a deep coloured solution. The yellow-brown solid obtained by evaporating the ethanolic solution to dryness was recrystallised twice from dichloromethane-ether mixtures to give yellow needle shaped crystals on cooling, which were separated, washed with ether and dried under vacuum,

ca 80%. [Found: C, 47.6 (C); H, 5.1 (C); Cl, 9.4 (B), O, 12.6 (B)%.

$C_{15}H_{19}O_3ClMo$ requires: C, 47.6; H, 5.1; Cl, 9.4; O, 12.7%. Infra-red spectrum (mull): 3500 m-s, 3328 m, 3227 w, 3130 vw, 3098 w, 3063 m, 3030 w, 2849 vw, 1642 sh, 1624 w, 1579 m, 1560 m, 1520 m, 1423 w, 1363 m, 1346 sh, 1278 m, 1193 vw, 1029 w, 996 w, 934 w, 906 w, 874 w, 838 w, 786 m, 680 m, 595 w.]

Preparation of $[(\pi-C_5H_5)_2Mo(O_2C_5H_7)]BF_4$

The compound, $(\pi-C_5H_5)_2Mo(O_2C_5H_7)Cl \cdot H_2O$ (0.5 g.), prepared as detailed above, was dissolved in a small quantity of water (~ 10 ml.) and an excess of a saturated solution of $NaBF_4$ in water was added dropwise. A pale brown precipitate formed which was separated, washed twice with water (~ 10 ml.) and dried. The solid was recrystallised twice from hot water. Deep red needle crystals formed on cooling which were separated, washed with small quantity of water, methanol and then ether and then dried, ca 90%. [Found: C, 43.75 (B), 43.5 (C); H, 3.9 (B), 4.0 (C); F, 18.6 (B)% Λ , $94.6 \text{ ohm}^{-1} \text{ cm}^2$. $C_{15}H_{17}O_2F_4BMo$ requires: C, 43.7; H, 4.2; F, 18.4%. Infra-red spectrum (mull): 3119 m, 1562 s, 1521 s, 1428 m, 1357 m, 1340 sh, 1285 m, 1192 w, 1105 s, 1055 vs (br), 1034 vs, 997 sh, 964 w, 948 w, 889 w, 839 m-s, 803 m, 668 m, 600 m, 518 m, 448 m.]

Preparation of $(\pi-C_5H_5)_2Mo(OCOCF_3)_2$

A 1:1 mixture of acetone-ethanol containing sodium trifluoroacetate (2-3 g.) and $(\pi-C_5H_5)_2MoCl_2$ (1 g.) was refluxed for 30 minutes. A green coloured reaction mixture resulted which, after cooling, was evaporated to dryness. The product was chromatographed on alumina using acetone as eluant.

A green coloured band gave a greenish-blue eluate which was evaporated to dryness. (A small lime green band left on the column and eluted with ethanol gave a small quantity of oily solid.) Recrystallisation of the green solid obtained from the acetone fraction, using an acetone-ether-light petroleum mixture gave a green microcrystalline product which was separated, washed with ether and dried, ca 80%. [Found: C, 37.3; H, 2.3; F, 25.4% (B). $C_{14}H_{10}O_4F_6Mo$ requires: C, 37.2; H, 2.2; F, 25.2%. Infra-red spectrum (mull): 3133 m, 2920 w, 1720 sh, 1694 s, 1587 w, 1432 w, 1403 m, 1367 sh, 1286 vw, 1186 vs (br), 1138 vs (br), 1068 vw, 1001 w, 838 s, 792 m, 728 s, 700 γ w, 688 vw.]

Preparation of $(\pi-C_5H_5)_2W(OCOCF_3)_2$

A mixture of $(\pi-C_5H_5)_2WCl_2$ (1 g.) and $NaOCOCF_3$ (2 g.) in ethanol was refluxed for 30 minutes and using a similar chromatographic purification as in the above reaction a purple solid was obtained. Recrystallisation from dichloromethane gave small, purple, plate-like crystals, ca 40%. [Found: C, 31.0; H, 1.9; F, 21.3% (B). $C_{14}H_{10}O_4F_6W$ requires: C, 31.1; H, 1.9; F, 21.1%. Infra-red spectrum (mull): 3130 m, 2922 w, 2848 w, 1797 vw, 1727 sh, 1700 s, 1582 w, 1428 m, 1405 s, 1360 w, 1281 vw, ca 1190 vs (br), 1142 vs (br), 1082 vw, 1068 vw, 1009 m, 999 sh, 951 vw, 899 w, 842 s, 810 vw, 791 m, 729 s, 685 w, 618 w.]

Other side reactions occurred and another band could be eluted from the column with an acetone-methanol mixture to give a yellow solid which was not characterised.

Preparation of $(\pi-C_5H_5)_2Mo(OCOC_6H_5)_2$

A mixture of $(\pi-C_5H_5)_2MoCl_2$ (1.5 g.) and an excess of sodium benzoate (3-4 g.) in 30 ml. of a 1:1 mixture of acetone and ethanol was refluxed for approximately 1 hour until the solution turned blue in colour. The mixture was evaporated to dryness and the solid residue was extracted with dichloromethane-acetone mixtures which were added to an alumina column. Elution with acetone gave a blue coloured band and a purple solution was collected. Evaporation of the solution to dryness and recrystallisation of the resulting solid from a dichloromethane-ether-light petroleum mixture gave deep purple needle crystals which were washed in ether and dried, ca 80%. [Found: C, 61.6; H, 4.4% (C). M, 490 (CHCl₃). (N.B. mass spectrum parent peak, 468 for ⁹⁶Mo.) C₂₄H₂₀O₄Mo requires: M, 468. Infra-red spectrum (mull): 3130 sh, 3119 w, 3078 m, 3020 w, 2935 w, 1916 vw, 1630 sh, 1614 s, 1578 m, 1558 sh, 1540 sh, 1527 sh, 1488 w, 1451 m, 1428 m, 1344 s, 1320 s, 1296 sh, 1264 sh, 1166 m, 1133 w, 1066 w, 1021 w, 848 sh, 833 m, 811 sh, 728 m, 713 m, 687 sh, 668 s, 572 w.]

Preparation of $(\pi-C_5H_5)_2W(OCOC_6H_5)_2$

A similar method to that described above was employed, using $(\pi-C_5H_5)_2WCl_2$ (1 g.) and NaOCOC₆H₅ (3 g.) in ethanol. This was refluxed for 30 minutes. Chromatography using acetone or an acetone-ethanol mixture as eluant and recrystallisation from a dichloromethane-ether-petrol mixture gave purple needle crystals, ca 70%. [Found: C, 51.4; H, 3.7% (C). C₂₄H₂₀O₄W requires: C, 51.8; H, 3.6%. Infra-red spectrum (mull): 3135 sh, 3120 m, 3097 m, 3079 sh, 3060 sh, 3020 w, 2958 w, 1648 s, 1628 sh, 1607 sh, 1586 m, 1555 vw, 1527 vw, 1486 w, 1453 m, 1430 m, 1349 s, 1324 s, 1300 sh,

1260 sh, 1163 m, 1127 m, 1065 m, 1024 m, 994 sh, 946 w, 859 sh, 833 m, 813 sh (br), 731 m, 713 m, 683 sh, 676 m.]

Experimental details for Chapter V

Preparation of $[(\pi-C_5H_5)_2W(SCH_2)_2CH_2C_6H_5]Cl$

$(\pi-C_5H_5)_2W(SCH_2)_2$ was prepared from $(\pi-C_5H_5)WCl_2$ and $HSCH_2CH_2SH$ in alcoholic sodium hydroxide solution by the reported method (A124). This was purified by chromatography and recrystallisation.

$(\pi-C_5H_5)_2W(SCH_2)_2$ (0.5 g.) was dissolved in dichloromethane (~ 5 ml.) and benzylchloride (~ 2 ml.) was added. The mixture was warmed over a water bath at $\sim 60^\circ C$ and after several minutes large orange-yellow crystals formed. When no more crystals appeared, (~ 30 minutes), the crystals were centrifuged off, washed well with dichloromethane and ether and dried.

[Found: C, 42.7; H, 4.1; S, 11.8% (B).] The compound is slightly soluble in dichloromethane and could be recrystallised from dichloromethane-ether mixtures to give small orange-yellow crystals which were washed and dried.

[Found: C, 42.5; H, 4.2; S, 11.8; Cl, 6.65% (B). Λ , $68.2 \text{ ohm}^{-1} \text{ cm}^2$.

$C_{19}H_{21}S_2ClW$ requires: C, 42.8; H, 4.0; S, 12.0; Cl, 6.65%. Infra-red spectrum (mull): 3520 w, 3395 w, 3100 sh, 3074 m, 3042 m, 2951 w, 2899 sh, 1492 w, 1453 sh, 1430 m, 1366 vw, 1280 w, 1235 w, 1156 vw, 1114 w, 1075 w, 1055 w, 1026 sh, 1015 m, 1005 w, 986 w, 960 vw, 939 w, 924 vw, 891 w, 874 m, 846 s, 842 sh, 834 m, 830 sh, 823 sh, 774 m, 742 w, 708 s.]

Preparation of $[(\pi-C_5H_5)_2W(SCH_2)_2CH_2C_6H_5]PF_6$

$[(\pi-C_5H_5)_2W(SCH_2)_2CH_2C_6H_5]Cl$, prepared as above, was dissolved in water and centrifuged to give a clear solution. An excess of a saturated solution

of NH_4PF_6 in water was added to the yellow solution and a pale yellow precipitate was immediately formed. This precipitate was centrifuged off, washed twice with water and dried. The solid was recrystallised from a liquid sulphur dioxide-ether mixture to give orange-red crystals which were washed with ether and dried on vacuum. However these smelled of sulphur dioxide and analysis [Found: C, 33.2; H, 2.05; S, 13.5% (B)] showed that they contained sulphur dioxide of crystallisation. Therefore the crystals were washed very thoroughly by grinding in ether and dried by pumping on a vacuum line overnight to give an orange powder, ca 95%. [Found: C, 35.4; H, 3.35; S, 9.9% (B). Λ , $84.4 \text{ ohm}^{-1} \text{ cm}^2$. $\text{C}_{19}\text{H}_{21}\text{S}_2\text{F}_6\text{PW}$ requires: C, 35.5; H, 3.3; S, 10.0%. Infra-red spectrum (mull): 3131 m, 3043 vw, 2909 w, 2832 vw, 1493 w, 1434 sh, 1413 m, 1360 vw, 1274 w, 1246 w, 1233 vw, 1164 sh, 1157 w, 1119 vw, 1074 w, 1030 sh, 1021 w, 996 w, 937 w, 876 sh, 870-800 vs (br), 775 m, 741 w, 707 s, 684 vw, 638 w, 557 m.]

Preparation of $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{CH}_2\text{CHCH}_2]\text{Br}$

In a similar method to above allyl bromide (1 ml.) was added to a dichloromethane solution of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ ($\sim 0.5 \text{ g.}$) and after a few minutes at room temperature orange crystals formed. These were separated, washed well with dichloromethane and dried, ca 90%. [Found: C, 34.4; H, 3.5; S, 12.1% (B). Λ , $88.4 \text{ ohm}^{-1} \text{ cm}^2$. $\text{C}_{15}\text{H}_{19}\text{S}_2\text{BrW}$ requires: C, 34.2; H, 3.6; S, 12.2%. Infra-red spectrum (mull): 3425 w, 3357 w, 3100 w, 3080 sh, 3052 m, 2952 w, 2898 w, 2831 vw, 1632 w, 1431 m, 1418 m, 1403 m, 1375 w, 1362 vw, 1349 vw, 1278 w, 1249 w, 1232 w, 1085 w, 1058 w, 1021 m, 1006 w, 990 w, 975 vw, 935 m, 907 w, 886 m, 863 w, 849 m, 840 m, 831 w, 746 w.]

Preparation of $[(\pi-C_5H_5)_2W(SCH_2)_2CH_2CHCH_2]PF_6$

Addition of excess of a saturated NH_4PF_6 solution in water to an aqueous solution of $[(\pi-C_5H_5)_2W(SCH_2)_2CH_2CHCH_2]Br$ gave an immediate light orange-yellow precipitate. This was centrifuged off, washed well with water and dried. Recrystallisation from a liquid sulphur dioxide-ether mixture gave red crystals. These crystals, however, contained sulphur dioxide of crystallisation and, after washing with ether and drying on a vacuum line overnight, sulphur dioxide was removed and an orange amorphous powder was left, ca 95%. [Found: C, 30.2; H, 3.2; S, 10.9% (B). Λ , $90.8 \text{ ohm}^{-1} \text{ cm}^2$. $C_{15}H_{19}S_2F_6PW$ requires: C, 30.4; H, 3.2; S, 10.8%. Infra-red spectrum (mull): 3138 sh, 3126 m, 3093 sh, 2980 vw, 2916 w, 2853 vw, 1731 w, 1633 w, 1438 sh, 1425 sh, 1417 m, 1406 sh, 1358 vw, 1294 vw, 1278 w, 1248 w, 1076 w, 1018 w, 1000 m, 960 w, 934 m, 877 sh, 870-800 vs (br), 778 vw, 757 sh, 739 w, 557 m.]

Preparation of $[(\pi-C_5H_5)_2W(SCH_2)_2CH_3]I$

Prepare in a similar manner to $[(\pi-C_5H_5)_2W(SCH_2)_2CH_2CHCH_2]Br$ using methyl iodide instead of allyl bromide to give orange crystalline solid, ca 90%. [Found: C, 28.6; H, 3.3; S, 11.7; I, 23.0% (B). Λ , $92.8 \text{ ohm}^{-1} \text{ cm}^2$. $C_{13}H_{17}S_2IW$ requires: C, 28.5; H, 3.1; S, 11.7; I, 23.0%. Infra-red spectrum (mull): 3111 sh, 3100 sh, 3072 m, 2983 w, 2966 w, 2946 vw, 2903 w, 2829 vw, 1443 m, 1420 w, 1380 vw, 1360 vw, 1329 w, 1280 w, 1148 w, 1075 vw, 1055 w, 1016 w, 993 sh, 986 m, 935 w, 861 sh, 848 s, 830 sh, 665 w.]

Preparation of $[(\pi-C_5H_5)_2W(SCH_2)_2CH_3]PF_6$

As in the preparation of $[(\pi-C_5H_5)_2W(SCH_2)_2CH_2CHCH_2]PF_6$, NH_4PF_6

solution was added to an aqueous solution of $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{CH}_3]\text{I}$ and the precipitate washed and dried. A liquid sulphur dioxide-ether mixture was used for recrystallisation but the product generally separated as an oil due to sulphur dioxide inclusion. However, the oil was separated, washed well with ether and dried for a long period under vacuum to give an orange amorphous solid. [Found: C, 27.8; H, 3.1; S, 11.3% (B).

Λ , $91.4 \text{ ohm}^{-1} \text{ cm}^2$. $\text{C}_{13}\text{H}_{17}\text{S}_2\text{F}_6\text{PW}$ requires: C, 27.6; H, 3.0; S, 11.3%.

Infra-red spectrum (mull): 3133 m, 2919 w, 2841 w, 1443 m, 1421 m, 1382 vw, 1357 vw, 1318 w, 1272 w, 1239 w, 1151 w, 1120 w, 1072 w, 1021 w, 999 w, 971 w, 932 w, 875 sh, 870-800 vs (br), 775 vw, 740^j w, 556 m.]

Preparation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2\text{HgCl}_2$

HgCl_2 ($\sim 0.3 \text{ g.}$) was dissolved in dichloromethane to give a saturated solution and this was added dropwise to a solution of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ (0.5 g.) in dichloromethane. An orange precipitate formed and this was centrifuged off, washed well with dichloromethane and dried, ca 95%.

[Found: C, 21.4; H, 2.1; S, 9.3; Cl, 10.6% (B). $\text{C}_{12}\text{H}_{14}\text{S}_2\text{Cl}_2\text{HgW}$ requires: C, 21.4; H, 2.1; S, 9.5; Cl, 10.5%. Infra-red spectrum (mull): 3098 m, 2948 sh, 2917 w, 2844 vw, 1425 m, 1378 sh, 1365 w, 1290 w, 1263 vw, 1235 w, 1147 vw, 1110 vw, 1067 w, 1020 w, 1008 w, 998 w, 959 vw, 935 vw, 900 vw, 887 vw, 869 m, 853 m, 844 m, 823 w.]

Reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_6\text{H}_5)_2$ with CH_3I

$(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{SC}_6\text{H}_5)_2$ ($\sim 0.3 \text{ g.}$) was prepared, as reported (A3), and dissolved in dichloromethane ($\sim 10 \text{ ml.}$). Methyl iodide ($\sim 1 \text{ ml.}$) was added to this solution and a reaction occurred slowly, at room temperature, over a

period of approximately 15 minutes. The solution became deeper red in colour, and ~~then~~ green, and large olive green crystals precipitated. These were washed with dichloromethane and dried and, then, recrystallised twice from a liquid sulphur dioxide-dichloromethane mixture to give a dark green microcrystalline solid. This solid was collected, washed with ether and dried. It was shown to be $(\pi-C_5H_5)_2MoI_2$ by its infra-red spectrum (A2) and by analysis. [Found: C, 24.7%; H, 1.8% (C). $C_{10}H_{10}I_2Mo$ requires: C, 25.0; H, 2.1%.]

Preparation of $[(\pi-C_5H_5)_2MoS(CH_3)_2I]I$

$(\pi-C_5H_5)_2Mo(SCH_3)_2$ (~0.5 g.), prepared as reported (A124), was dissolved in dichloromethane solution (~10 ml) and an excess of methyl iodide (~1 ml) was added. In the course of one minute the solution turned green and deposited light green crystals. After 10 minutes the crystals were separated, washed with a little dichloromethane, and then ether, and dried. They were recrystallised twice from a dimethyl sulphoxide-dichloromethane-ether mixture to give small green needle shaped crystals which were washed with dichloromethane followed by ether and dried, ca 80%. [Found: C, 26.7; H, 2.95; S, 6.05; I, 47.1% (B).. Λ , $90.5 \text{ ohm}^{-1} \text{ cm}^2$. $C_{12}H_{16}SI_2Mo$ requires: C, 26.6; H, 3.0; S, 5.9; I, 46.8%. Infra-red spectrum (KBr disc): 3130 vw, 3080 m, 3057 m, 2966 w, 2900 w, 1451 w, 1431 m, 1416 sh, 1389 vw, 1370 vw, 1340 w, 1267 w, 1124 vw, 1050 w, 1036 m, 1015 w, 997 m, 942 vw, 920 vw, 887 w, 840 s, 830 sh, 667 w, 594 w, 586 w.]

Reaction of $[(\pi-C_5H_5)_2MoS(CH_3)_2Br]PF_6$ with LiCl

$[(\pi-C_5H_5)_2MoS(CH_3)_2Br]PF_6$ (0.45 g.) (G9), was suspended in 1,2-

dimethoxyethane with less than a molar proportion of dry LiCl (0.03 g.) and the mixture was refluxed for 30 minutes. The green precipitate obtained was separated by centrifuging, dried and then recrystallised from a liquid sulphur dioxide-ether mixture to give green microcrystals. [Found: C, 35.1; H, 3.5% (C). $C_{10}H_{10}ClBrMo$ requires: C, 35.2; H, 2.9%. Infra-red spectrum (mull): 3094 m, 1417 m, 1355 w, 1267 vw, 1157 w, 1118 vw, 1073 vw, 1014 w, 990 w, 906 vw, 876 sh, 827 m-s, 809 sh, 652 w.]

Preparation of $[(\pi-C_5H_5)_2W(S_2C_6H_3CH_3)]PF_6$

$(\pi-C_5H_5)_2W(S_2C_6H_3CH_3)$ was prepared, as reported (A3), from $(\pi-C_5H_5)_2WCl_2$ and 3,4-toluenedithiol, and approximately 0.3 g was suspended in water (5-10 ml). Drops of nitric acid were added to this suspension until a violet coloured solution was formed. The mixture was rapidly centrifuged and the clear solution separated. An excess of NH_4PF_6 in a saturated aqueous solution was added to the violet solution and a brownish-purple precipitate was formed which was collected by centrifugation, washed well with water and dried. The whole operation had to be carried out as carefully and expeditiously as possible as further oxidation occurs in the presence of nitric acid to give a yellow coloured species. The solid was recrystallised three times from liquid sulphur dioxide-ether mixtures to give purple coloured crystals washed well with ether and dried, ca 30%. [Found: C, 32.9; H, 2.6; S, 10.2% (B). $C_{17}H_{16}S_2F_6PW$ requires: C, 33.3; H, 2.6; S, 10.5%. Infra-red spectrum (mull): 3126 m, 2948 sh, 2923 w, 2860 vw, 1584 w, 1524 w, 1430 m, 1423 sh, 1330 w, 1283 vw, 1250 vw, 1209 w, 1149 vw, 1087 w, 1018 w, 968 vw, 898 sh, 876 sh, 862 sh, 842 vs(br), 825 vs(br), 800 w-m, 667 w, 557 m.]

Reaction of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)_2$ with Iodine

$(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)_2$ (~ 0.5 g.) was dissolved in dichloromethane and iodine (~ 0.5 g.), dissolved in dichloromethane, was added. Dark coloured crystals separated after a while which were washed with a little dichloromethane, in which they were fairly soluble, and then with ether. The solid was recrystallised from dichloromethane by cooling in a dry ice-acetone bath to give copper brown coloured crystals which were washed well with ether and dried. [Found: C, 20.9; H, 1.7; I, 31.5% (B).]

Oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$

In a similar manner to the oxidation of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)_2$, nitric acid was added in drops to an aqueous suspension of $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{SCH}_2)_2$ to give a purplish coloured solution and this gave a blue-purple coloured precipitate with NH_4PF_6 solution which could be crystallised from liquid sulphur dioxide-ether mixtures. However further reactions take place when this compound is oxidised with nitric acid and it was found impossible to obtain pure crystals.

Experimental details for Chapter VI

Exchange Studies

a) E.S.R. samples for exchange studies in organic solvents were prepared by dissolving approximately 3 mg. of the dihalide cation in 3 ml organic solvent and then an excess of anhydrous tetra-ethyl ammonium halide (~ 10 mg) was added. The E.S.R. tube, of appropriate size for the dielectric constant of the mixture, was then filled with this solution under nitrogen and placed in

the spectrometer as quickly as possible.

b) E.S.R. samples for studies of exchange reactions in strong acids were made up by dissolving approximately 3 mg of the dihalide cation in 3 ml of the appropriate strong acid. Capillary tubes drawn from quartz tube were dipped into this solution under vacuum and filled by admission of nitrogen.

Electrolytic Experiments

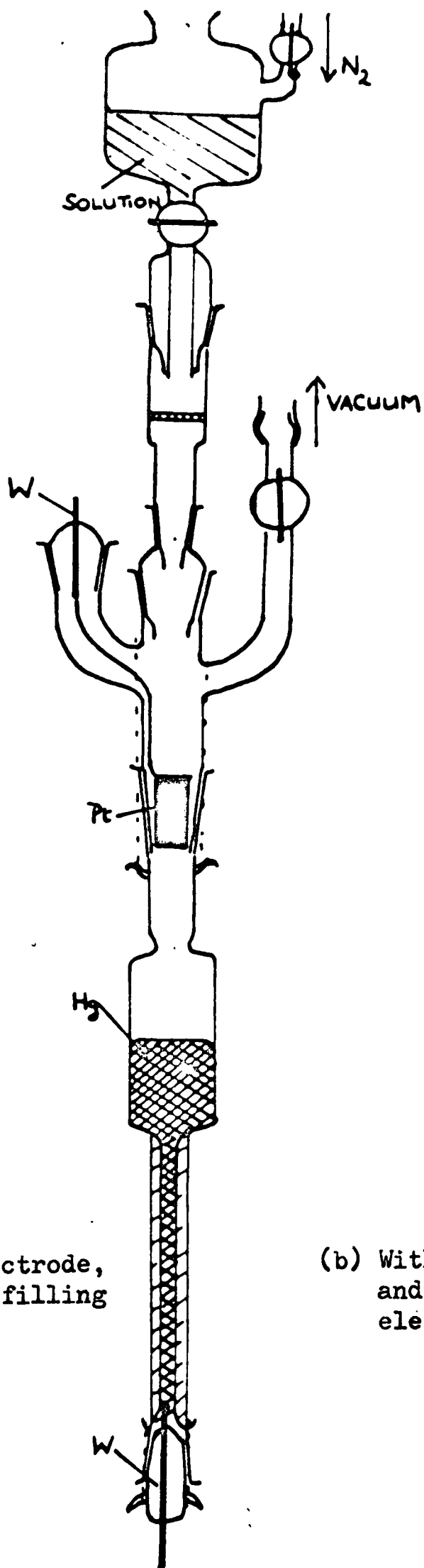
An electrolytic cell was built into an aqueous type, flat E.S.R. cell made from pyrex (since quartz cells could not be evacuated). This is shown in figure 19.

This cell could be used with a mercury or platinum gauze in the centre of the E.S.R. cavity and thus could be used for reduction or oxidation. In the oxidation experiments described the platinum electrode was used. The other electrode was of bright platinum and a third electrode, a standard Ag/AgClO_4 electrode, was also designed for use in controlled potential electrolysis, as shown. This third electrode, however, was rarely used in the experiments described and the third electrode compartment was not inserted since accurate measurements of the potential were not required. The reason for not using the third electrode were a) no accurately known working potential was known for the compounds studied, b) the current passing through the organic solvents used was so small that deviations of working potential from applied potential were also small, and c) convenience of experimentation. Nevertheless use of this third electrode would have given more accurate electrochemical data, if required.

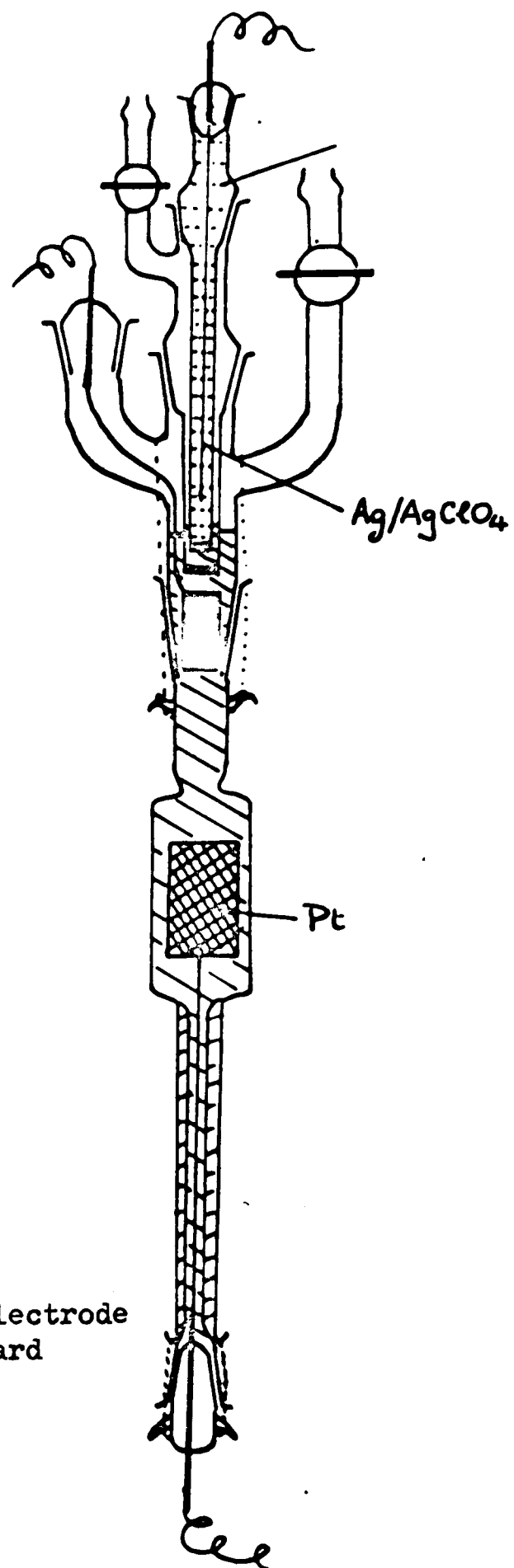
Solutions were made up, usually using 1,2-dimethoxyethane as solvent,

Figure 19.

E.S.R. electro-
lytic cell



(a) With Hg electrode,
set up for filling



(b) With Pt electrode
and standard
electrode

from approximately 15 mg of compound, 500 mg tetrabutylammonium perchlorate (as supporting electrolyte) and 15 ml of solvent. The solution was deoxygenated by bubbling oxygen free nitrogen through it for $\sim \frac{1}{4}$ hour and then admitted to the cell under vacuum using the filter device shown in figure 19a. The evacuated cell, containing solution, was then filled with nitrogen and inserted into the E.S.R. cavity. A $4\frac{1}{2}$ volt dry battery with a variable potentiometer was used as a voltage source. A high vacuum voltmeter was used to measure the potential between the working electrode and the Ag/AgClO_4 electrode when this was present.

The procedure used was to gradually increase the potential until a signal appeared on the cathode ray oscilloscope of the E.S.R. spectrometer and this was then recorded as in normal procedure.

Instrumentation

Proton Magnetic Resonance Spectra

Most spectra were recorded on a Japan Electron Optics Laboratory Co. electromagnet instrument operating at 100 Mc/sec. The spectra were usually recorded at room temperature (25°C) but the variable temperature studies were made on this machine. I am most grateful to Dr. J.C. Green, Mr. J.D. Duncan and Mr. W.J. Murray for running these spectra.

Other spectra were recorded on Perkin Elmer 100 or 60 Mc/s permanent magnet spectrometer at 35°C and I am most grateful to Mrs. Richards of the Dyson Perrins Laboratory for running these.

Fluorine Magnetic Resonance Spectra

These were run on a Varian Associates model HA 100 spectrometer operating at 100 Mc/s or a model 4300B operating at 56.4 Mc/s at room temperature. I am most grateful to Dr. D.F. Evans of Imperial College for running these spectra.

Low Resolution Mass Spectra

These spectra were run on a Perkin Elmer M.S.9. spectrometer and I am most grateful to Dr. Aplin of the Dyson Perrins Laboratory for running these spectra.

Infra-red Spectra

All spectra were recorded on a Perkin Elmer 337 spectrometer either as mulls in nujol and hexachlorobutadiene between NaCl or KBr plates or in KBr discs. The spectra were calibrated with polystyrene at 3060, 1944, 1601, 1154, 1028 and 906 cm^{-1} .

Low range spectra were recorded on a Perkin Elmer 225 spectrometer as CsI discs calibrated with CO_2 at 667 cm^{-1} and H_2O at 303 cm^{-1} . I am most grateful to Miss H.E. Hegedus for running these spectra.

Ultra-violet and Visible Spectra

These were recorded from solutions on a Beckmann D.K.2A ratio recording spectrophotometer calibrated with holmium and didymium filters.

Electron Spin Resonance Spectra

Spectra were recorded on a Japan Electron Optics Laboratory Co. electro-magnet instrument employing 100 Kc/s modulation at room temperature unless

otherwise specified. Calibration of g values was made using diphenyl picryl hydrazyl radical, $g = 2.0036$, with an aqueous N.M.R. field marker in most cases, although Fremy's Salt in aqueous solution, $g = 2.0055$, was used for some spectra.

Conductivity Measurements

These were made at 21-22°C using a Cambridge Instruments Co. Conductivity Bridge to measure the conductance of $\sim 10^{-3}M$ nitromethane solutions of the compounds in a platinum black electrode cell. The cell constant was estimated using $N/100$ KCl solution and the equivalent conductivity values were calculated assuming monomeric formulae.

Molecular Weights

These were determined in solution with a Mechrolab osmometer by members of Dr. Venanzi's group.

Additional references for Chapter VII

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