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REDOX AND SUBSTITUTION REACTIONS OF METAL CARBONYL COMPLEXES

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by

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SUMMARY

The complex $Mo(CO)_2(dpe)_2$ reacts with nitrosonium hexafluorophosphate in the non-coordinating solvents, dichloromethane and nitromethane, to form seven-coordinate molybdenum(II) fluoro complexes. The product formed with dichloromethane as the solvent, originally formulated as *cis*-$[Mo(CO)_2(dpe)_2]PF_6$, is shown to be $[Mo(CO)_2(dpe)_2F]PF_6$. The fluoro-bridged species $[\{Mo(CO)_2(dpe)_2\}_2F](PF_6)_3$, which was originally formulated as *cis*-$[Mo(CO)_2(dpe)_2](PF_6)_2$, is obtained in nitromethane. These complexes have been characterized by conductance measurements, infrared and NMR (^{19}F, ^{31}P) spectroscopy. Low-temperature ^{31}P NMR spectra show that $[Mo(CO)_2(dpe)_2F]^+$ is rigid. The fluoro-bridged complex is cleaved by reaction with fluoride to give $[Mo(CO)_2(dpe)_2F]^+$, while reaction with halide ions (X^- = Cl, Br) yields the dimers $[Mo(CO)_2(dpe)_{1.5}X_2]_2$ in which one dpe molecule bridges the two metal atoms. Treatment of $Mo(CO)_2(dpe)_2$ with nitrosonium hexafluorophosphate in cyano solvents (RCN; R = Me, Ph) yields the nitrile complexes $[Mo(CO)_2(dpe)_2(RCN)](PF_6)_2$, which have been characterized by conductance, infrared and ^1H NMR spectroscopy. The oxidation of $W(CO)_2(dpe)_2$ with nitrosonium hexafluorophosphate in dichloromethane, nitromethane and acetonitrile resulted in the formation of a mixture of complexes. The major components of the reaction mixtures were not characterized, but the minor products are identical to those formed in the reactions of the molybdenum analogue. Similar reactions with $Cr(CO)_2(dpe)_2$ resulted in decomposition to give high oxidation-state products.

The complexes $M(CO)_2(dpe)_2$ (M = Mo, W) react with oxidants (NOCl, Br_2, I_2) in dichloromethane at room temperature to form the seven-coordinate divalent cations $[M(CO)_2(dpe)_2X]^+$ (X = Cl, Br, I). The molybdenum(II) derivatives were also prepared by treating a mixture of $Mo(CO)_2(dpe)_2$ and halide ions (X^- = Cl, Br) with nitrosonium hexafluorophosphate. The products have been characterized by conductance, infrared and ^{31}P NMR

spectroscopy. The low temperature ^{31}P NMR spectra of the molybdenum derivatives suggest that they are non-rigid. The ^{31}P NMR spectra of the neutral complexes $M(CO)_2L_2$ (M = Cr, Mo; L = dpe, dpm) are also discussed. The complexes $[Mo(CO)_2(dpe)_2X]^+$ undergo further substitution with halide ion, displacing a phosphorous atom from the coordination sphere, to give the neutral isomers, $[Mo(CO)_2(dpe)_2X_2]$ (X = Cl, Br); the extent of the reaction increases from chloride to bromide. With iodide this product could not be isolated and instead a dpe molecule is lost and the tricarbonyl complex $Mo(CO)_3(dpe)I_2$ is formed. The tungsten complexes react in a similar manner, but at a much slower rate. The compounds $[Mo(CO)_2(dpe)_2X_2]$ (X = Cl, Br) slowly undergo a self-substitution in solution to give polymeric species of the type $[Mo(CO)_2(dpe)_{1.5}X_2]_n$ with loss of dpe. The reaction of $Mo(CO)_2(dpe)_2$ with NO_2 resulted in the formation of a mixture of complexes, which were not fully characterized. Solvento complexes of the formula $[Mo(CO)_2(dpe)_2Y]^{2+}$ (Y = MeCN, PhCN, $MeNO_2$, $EtNO_2$) are formed when the complexes $[Mo(CO)_2(dpe)_2X]^+$ (X = Br, I) are reacted with silver perchlorate in the appropriate solvent. Treatment of $Cr(CO)_2(dpe)_2$ with bromine in dichloromethane at room temperature resulted in decomposition to give a chromium(III) product.

$Mn(CO)_5Br$ reacts with $AgClO_4$ in dichloromethane at room temperature to give the perchlorato complex $Mn(CO)_5(OClO_3)$. The complex, which has been characterized by infrared and mass spectroscopy, is very stable in the solid state in a dry atmosphere, but absorbs water on exposure to the air. The perchlorato group is readily displaced by solvent molecules (S = MeCN, PhCN, MeOH, $MeNO_2$, Me_2CO, py) yielding $[Mn(CO)_5S]^+$, by phosphines [L = PR_3 (R = Ph, *p*-Tol, *m*-Tol), dpe, dpm] to give $[Mn(CO)_5L]^+$ and by halide ions (X^- = Cl, Br, I) to form $Mn(CO)_5X$. Reaction with fluoride ion yields $Mn(CO)_3F_3$ plus other decomposition products. The complex reacts slowly with dichloromethane and chloroform to give $Mn(CO)_5Cl$, while treatment with water yields the unstable aquo complex $[Mn(CO)_5(H_2O)]^+$. The substituted perchlorato complexes, $Mn(CO)_3L_2(OClO_3)$ ($L = PPh_3$, $P(OPh)_3$; L_2 = bpy), were prepared by stirring the corresponding bromo complexes with excess $AgClO_4$; these derivatives react in a similar manner. Attempts to prepare perchlorato complexes from $[Mn(CO)_4Br_2]^-$ and $[Mo(CO)_5Br]^-$ resulted in decomposition.

The reaction of $Mn(CO)_5Br$ with $AgPF_6$ in dichloromethane results in the hydrolysis of the PF_6^- ion giving the difluorophosphato complex $Mn(CO)_5(PO_2F_2)$ A similar reaction occurred with the substituted complexes $Mn(CO)_3L_2Br$ ($L = PPh_3$, $P(OPh)_3$; L_2 = bpy), giving $Mn(CO)_3L_2(PO_2F_2)$. The difluorophosphato complexes are reasonably stable at low temperatures (*c.* -15°C), but they decompose at room temperature. They have been characterized by infrared, ^{19}F NMR and mass spectroscopy. The difluorophosphato group is more inert than the perchlorato group, with the rate of substitution increasing in the order $P(OPh)_3 \ll \text{bpy} < PPh_3 \approx CO$.

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference is made in the text of this thesis.

F.L. WIMMER

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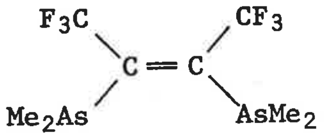
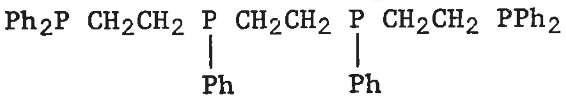
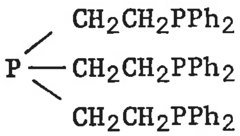
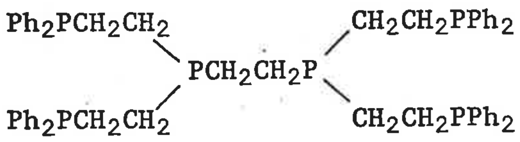
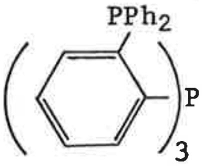
ABBREVIATIONS

The abbreviations listed below have been used throughout the text of this thesis.

as, asy	asymmetric
ax	axial
bpy	2,2'-bipyridyl
Bu	butyl
Cp	cyclopentadienyl
dam	bis(diphenylarsino)methane, methylenebis(diphenylarsine)
def	deformation
diars	*o*-phenylenebis(dimethylarsine)
dmpe	1,2-bis(dimethylphosphino)ethane, ethane-1,2-diylbis(dimethylphosphine)
dpab	1,4-bis(diphenylarsino)butane, butane-1,4-diylbis(diphenylarsine)
dpae	1,2-bis(diphenylarsino)ethane, ethane-1,2-diylbis(diphenylarsine)
dpe	1,2-bis(diphenylphosphino)ethane, ethane-1,2-diylbis(diphenylphosphine)
dpm	bis(diphenylphosphino)methane, methylenebis(diphenylphosphine)
dpsm	bis(diphenylstibino)methane, methylenebis(diphenylstibine)
$E_{\frac{1}{2}}$	half-wave potential
Et	ethyl
eq	equatorial
fars	*cis*-2,3-bis(dimethylarsino)-1,1,1,4,4,4-hexafluorobut-2-ene 
Me	methyl

NBS	N-bromosuccinimide
Pf-Pf-Pf-Pf	hexaphenyl-1,4,7,10-tetraphosphadecane  $Ph_2P\ CH_2CH_2\ \underset{Ph}{\underset{\vert}{P}}\ CH_2CH_2\ \underset{Ph}{\underset{\vert}{P}}\ CH_2CH_2\ PPh_2$
Ph	phenyl
phen	1,10-phenanthroline
$P(Pf)_3$	tris(2-diphenylphosphinoethyl)phosphine 
$P_2(PF)_4$	1,1,4,4-tetrakis(2-diphenylphosphinoethyl)-1,4-diphosphabutane 
py	pyridine
QP	tris(*o*-diphenylphosphinophenyl)phosphine 
RT	room temperature
Saen	N-(2-aminoethyl)salicylaldiminato
str	stretch
sym	symmetric
Tol	tolyl
l-triars	methylbis(dimethylarsino-3-propyl)arsine
o-triars	bis(*o*-dimethylarsinophenyl)methylarsine
ν-triars	tris-1,1,1-(dimethylarsinomethyl)ethane
w.r.t.	with respect to

In reference to the infrared spectra:

br	broad	vs	very strong

m	medium	sh	shoulder
ms	medium strong	shp	sharp
mw	weak medium	w	weak
s	strong	vw	very weak

CHAPTER 1

INTRODUCTION

A major obstacle to the successful production of chlorine by the Solvay process was the very rapid corrosion of the nickel valves in the brick-lined tanks in which ammonium chloride was vapourised. A laboratory study of the corrosion showed that it was due to the presence of small amounts of carbon monoxide in the carbon dioxide stream used to remove ammonia from the tanks.[1] A more elaborate study of the reaction of carbon monoxide with metallic nickel led to the now classical discovery[2] in 1890 of nickel tetracarbonyl.

This was rapidly followed by the preparation of iron pentacarbonyl in 1891.[3,4] In the ensuing fifty years progress was slow. Some of the metal carbonyls discovered in this period were $Co_2(CO)_8$ (1910), $Mo(CO)_6$ (1910), $Cr(CO)_6$ (1926), $Ru(CO)_5$ (1936), $Ir_4(CO)_{12}$ (1940) and $Re_2(CO)_{10}$ (1941) With the resurgence of interest in inorganic chemistry in the early fifties, the number of known carbonyl complexes has increased dramatically. Today a binary carbonyl compound or a carbonyl containing derivative is known for virtually every transition metal.

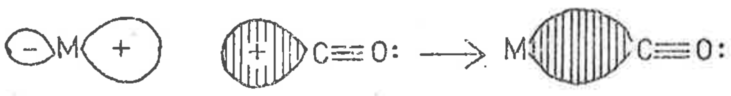
Only nickel and iron react directly with carbon monoxide to give the carbonyls. Most metal carbonyls are prepared by reducing a transition metal compound in the presence of carbon monoxide under pressure. Common reducing agents are sodium, aluminium alkyls or carbon monoxide itself. The methods of preparation, the structure and the properties of the metal carbonyls have been the subjects of a number of reviews.[5-7]

1.1 Bonding in Metal Carbonyls

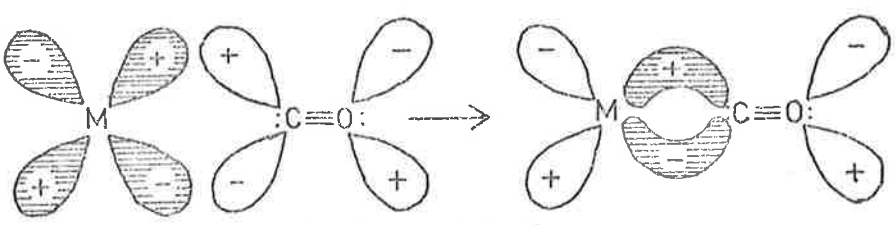
Metal carbonyls belong to a diverse collection of compounds in which the metals have low positive, zero or low negative oxidation states. The ligands giving rise to these compounds include the cyanide ion, isocyanides, nitric oxide, phosphorous trifluoride, unsaturated hydrocarbons as well as carbon monoxide. It is generally agreed that the common property of these ligands to stabilise low oxidation states is related to their ability to form acceptor as well as donor bonds with transition metals.

The bonding in carbon monoxide consists of a σ bond and a doubly degenerate π bond[8]; the result being a triple bond $(\sigma)^2(\pi_x)^2(\pi_y)^2$. In addition, there is a lone pair of electrons on both the carbon and the oxygen atoms. Carbon monoxide does not appear to be basic and the donor power of the lone pair of electrons on the carbon atom can only be slight, as illustrated by the absence of simple complexes with the normal empty orbital acceptors. A sole exception to this is the rather unstable complex[9] $H_3B\,CO$.

In the metal carbonyls, a metal-carbon σ bond is formed by the overlap of the lone pair on the carbon atom with the vacant d orbitals of the metal. In an octahedral complex, these are the e_g orbitals. The filled orbitals on the metal (t_{2g}) can now overlap with the lowlying π^* orbitals of carbon monoxide to form a π bond. This is illustrated in Fig. 1.1.



σ bond M ← CO



π bond M → CO

Fig. 1.1 Representation of M-C bonding in metal carbonyls.

The π bond not only provides an additional bond, but also transfers the excess charge built up on the metal by the σ bond onto the carbon monoxide, which results in more extensive σ bonding. This in turn increases the electron density on the metal which produces more extensive donation to the carbon monoxide and hence stronger π bonding. The two types of bonding are mutually reinforcing or "synergic". The overall result is greater than that which would be produced when the two parts are considered separately, since each tends to cancel out the large unfavourable charge separation which the other would set up.

A major consequence of the presence of electrons in the π^* orbitals of carbon monoxide is the reduction in the C-O bond order. Infrared spectra provide a convenient and useful estimate of this. Table 1.1 shows a set of self consistent bond orders obtained from spectroscopically derived force constants.

TABLE 1.1

Computed Bond Numbers (N)[A]

Complex	N_{CO}	N_{MC}	ΣN
CO	3.00	-	-
$Ni(CO)_4$	2.64	1.33	3.97
$[Co(CO)_4]^-$	2.14	1.89	4.03
$[Fe(CO)_4]^=$	1.85	2.16	4.01

[A] Reference 17

The bonding in mixed carbonyl complexes consists of three types:

(a) Ligands such as amines, amides, alcohols and ketones are structurally unable to accept charge from the metal. Their mixed carbonyl complexes are stabilized to a degree by the ability of the CO groups to accept a part of the charge they donate to the metal.

(b) Ligands which can accept charge through d_π-p_π back-bonding. These have, in addition to a lone pair of electrons, either multiply bonded atoms possessing low lying p_π^* orbitals (e.g. CN^-) or are heterocyclic ring systems (e.g. pyridine or 1,10-phenanthroline) in which back-bonding takes place through the molecular orbitals of the aromatic system.

(c) Ligands such as phosphines, which can accept charge via d_π-d_π back-bonding, because the coordinating atom possesses vacant d orbitals. Phosphines, being strong Lewis bases, are also good σ donors. The extent to which back-bonding occurs depends on the nature of the substituent groups. The overall result, with the exception of PF_3[†], tends to be a net charge donating effect. The relative π acceptor strengths of the substituent groups can be inferred from the carbonyl stretching frequencies.

[†] PF_3 has a π accepting ability similar to CO.

1.2 Infrared Spectroscopy

The technique most frequently used in the study of metal carbonyl complexes is IR spectroscopy, because the carbonyl stretching mode (ν_{CO}) give rise to intense absorptions of characteristic shape in a restricted region of the spectrum (2200 - 1650 cm^{-1}). The numbers and symmetries of the IR (and Raman) active CO stretching fundamentals can be derived from the molecular symmetry of the complex and generally from the local symmetry of the carbonyl groups themselves.[10,11] Band assignments have been made on the basis of relative band positions and intensities,[12,13] through complementary Raman data[11] and through the applications of the "non-rigorous" secular equations of Cotton and Kraihanzel.[10,14]

The presence of electrons in the π^* orbital of carbon monoxide results in a reduction of the CO bond order. Whereas the CO stretching frequency in carbon monoxide itself is about 2155 cm^{-1}, the corresponding values for terminal carbonyl groups lie at considerably lower values, usually around 2000 cm^{-1}. Moreover, the CO stretching frequency decreases as negative charge is added to the metal and increases when it is removed. The isoelectronic and isostructural complexes in Table 1.2 illustrate this point.

TABLE 1.2

Effect of Charge on CO Stretching Frequency

$[V(CO)_6]^-$	$Cr(CO)_6$	$[Mn(CO)_6]^+$
1859^A	1981^A	2090^A
$[Fe(CO)_4]^{2-}$	$[Co(CO)_4]^-$	$Ni(CO)_4$
1786^B	1886^B	2057^B

^{A} Reference 15 ^{B} Reference 16

Negative charge on the metal has the effect of increasing the extent of metal-carbon back-bonding and hence raising the metal-carbon bond order while simultaneously decreasing the carbon-oxygen bond order as shown by the calculated bond orders in Table 1.1. The successive substitution of carbon monoxide from a metal carbonyl by other ligands which are stronger σ donors but weaker π acceptors results in a decrease in the stretching frequencies of the remaining CO groups (see Table 1.3).

TABLE 1.3

Effect of Substitution on CO Stretching Frequency

Complex[A]	ν_{CO} (cm^{-1})[C]
$Mo(CO)_6$[B]	2120, 2020, 1990
$Mo(CO)_5L$	2080, 1993, 1965, 1952
cis - $Mo(CO)_4L_2$	2037, 1945, 1926, 1921
trans - $Mo(CO)_4L_2$	2035, 1972, 1921
mer - $Mo(CO)_3L_3$	1993, 1919, 1890
fac - $Mo(CO)_3L_3$	1977, 1888
cis - $Mo(CO)_2L_4$	1909, 1856
$Mo(CO)\ L_5$	1844

[A] L = $P(OMe)_3$, references 11, 14, 215.

[B] Reference 10.

[C] Saturated hydrocarbon solvent.

Conversely, ligands which tend to inhibit the transfer of electron density from the metal to the π^* orbital of carbon monoxide by placing a positive charge on the metal cause the CO stretching frequency to rise as illustrated in Table 1.4.

TABLE 1.4

Effect of Electronwithdrawing Groups on CO Stretching Frequency

Complex[A]	ν_{CO} (cm^{-1})[B] A_1^{1b}	E	A_1^{1a}
$Mn(CO)_5Cl$	2148	2063	2002
$Mn(CO)_5Br$	2144	2056	2004
$Mn(CO)_5I$	2133	2048	2005
$Mn(CO)_5CH_3$	2116	2015	1991

[A] Ref. 14 [B] CCl_4 solution

Slight changes in the CO stretching frequencies are observed when the groups bonded to the donor atom are changed, as shown in Table 1.5. An increase in the electronegativity of the substituent groups leads to a decrease in the net electron density on the metal. This, in turn, is compensated by less backbonding to the π^* orbitals of carbon monoxide, which leads to the observed increase in ν_{CO}.

TABLE 1.5

Effect of Electronegativity on CO Stretching Frequency

Compound	ν_{CO} (cm^{-1}) A_1	E	medium	reference
$Mo(CO)_3(PF_3)_3$	2090	2055	KBr	14
$Mo(CO)_3(PCl_3)_3$	2040	1989	hydrocarbon	11, 18
$Mo(CO)_3(PPhCl_2)_3$	2016	1943	$CHCl_3$	18
$Mo(CO)_3(PPh_2Cl)_3$	1977	1885	$CHCl_3$	18
$Mo(CO)_3(PPh_3)_3$	1934	1835	mull	11, 18

The metal-carbon stretching vibrations (ν_{m-c}) and the metal-carbon-oxygen bending vibrations (δ_{m-c-o}) occur at low frequencies (700 - 100 cm^{-1}). The number of infrared active bands and their symmetries for octahedral carbonyl derivatives have been calculated.[19,20,21] The metal-carbon stretching modes obey the same selection rules as the carbonyl stretching absorptions. There must also be some mixing between bending and stretching modes of the same symmetry, so that, for example, a ν_{m-c} vibration may be only "essentially" a stretching vibration. Force constant calculations[25,26] for the group VIa metal hexacarbonyls indicate that, at least in these cases, all the ν_{m-c} modes of vibration occur at lower frequencies than the δ_{m-c-o} vibrational modes. Low frequency infrared spectra have been reported for the metal carbonyls, $M(CO)_6$ (M = Cr, Mo, W)[20,26] and $M_2(CO)_{10}$ (M = Mn, Re),[20] the pentacarbonylhalide complexes $[M(CO)_5X]^n$ (n = 0, -1; M = Cr, Mo, W, Mn, Re; X = Cl, Br, I),[20,22] Lewis base derivatives of the type $M(CO)_{6-n}L_n$ (n = 1-4, L = group Vb donor)[11,19,21,23,24] and for $Mn(CO)_{5-n}L_nX$ (n = 1,2; X = Cl, Br; L = py, PPh_3, $AsPh_3$).[20] The δ_{m-c-o} absorptions usually occur in the region 680 - 540 cm^{-1} and ν_{m-c} absorptions in the region 560 - 360 cm^{-1}. Ligand vibrations also occur in this part of the spectrum which makes band identification more difficult. As the degree of substitution of a metal carbonyl increases, both ν_{m-c} and δ_{m-c-o} also increase, because the ligands enhance the extent of metal-carbonyl π bonding in the remaining carbonyl groups. It appears that δ_{m-c-o} modes are more sensitive to the degree of substitution, stereochemistry and oxidation state than ν_{m-c} modes.

The CO stretching frequencies[27(b),29] of most carbonyl complexes together with the bandwidths[27] are solvent dependent. Frequency shifts relative to a given standard such as *n*-hexane are greater for asymmetric vibrations than for the corresponding symmetric vibrations. For a given complex, frequency shifts increase with the polarity of the solvent. The magnitude of the shift (to lower frequencies) increases with the degree of substitution and correlates with the reduction in the CO stretching frequencies themselves.[28] The trends suggest that there is appreciable solvent-solute interaction, probably through a dipole-dipole interaction with the CO groups. However, the phenomenon remains virtually unexplained. Gutmann has proposed a model based on the concept of solvent acceptor numbers.[30] Aromatic, halogenated and polar solvents produce large increases in bandwidths, which can completely destroy any fine structure in the spectrum.[11,27,31] In the solid state, the number of CO stretching bands is determined by the site symmetry and not by the molecular point group.[32] Not only may the symmetry of the site be lower than that of the isolated molecule, but a molecule may also occupy different sites in a unit cell which leads to a splitting of the bands. For this reason, Orgel[13] has completely rejected spectra obtained from solids for the purpose of band assignments.

1.3 Chemistry of the Group VIa Metal Carbonyls

The chemistry of the group VIa metal carbonyls, $M(CO)_6$ (M = Cr, Mo, W) is very extensive and has been the subject of numerous reviews[33-40,42,43] and thus, only a brief account of the chemistry relevant to this work will be given.

(a) Substitution Reactions

Carbonyl anions have been prepared by reduction of the hexacarbonyls[5,37,40,44] and the products are solvent dependent. The anions $[M(CO)_5]^=$ (M = Cr, Mo, W) are formed by reacting the hexacarbonyls with sodium in liquid ammonia or with cesium amalgam in tetrahydrofuran.[44] Reduction with sodium borohydride in liquid ammonia or with sodium amalgam in tetrahydrofuran produces the dimeric anions $[M_2(CO)_{10}]^=$, while sodium borohydride reduction in tetrahydrofuran affords the trimeric anions $[M_3(CO)_{14}]^=$. The various oligomers undergo disproportionation reactions in the presence of carbon monoxide.[40,41] The anions tend to behave as nucleophiles in their reactions.[44,45,46] The hexacarbonyls react with hydroxide ion under various conditions to form anionic derivatives containing hydroxo and/or aquo ligands[37,47-50] and with halide ions (X = F, Cl, Br, I) to form the anions $[M(CO)_5X]^-$.[37,42,50-52]

The reactions of $M(CO)_6$ with Lewis bases have been extensively investigated and reviews have been written specifically on this topic.[33,34,36,38] Complexes containing phosphines, arsines, stibines, bismuthines, amines, ethers and thioethers have been prepared and characterized. The great majority of these complexes have been prepared by direct reaction of the ligand and metal carbonyl by either refluxing in a suitable solvent (sodium borohydride catalyzes the substitution reaction),[53] heating in a sealed tube or by ultraviolet irradiation. However, with monodentate ligands it is often difficult to replace more than two carbonyl groups directly. More highly substituted complexes can be prepared by heating an (arene)metal-

(tricarbonyl) complex with the ligand[58] or by using a coordinating solvent such as diglyme[62,109] or acetonitrile.[54]

Monodentate phosphines ($L = PR_3$) react with $M(CO)_6$ to form derivatives of the type $M(CO)_{6-n}L_n$ ($n = 1 - 6$). The extent of substitution depends on the nature of the R group. If R is bulky or a poor π acceptor, the degree of substitution is low (e.g. $R = n$-Bu or $-CH_2CH_2CN$; $n = 1$). For ligands of reasonable π accepting ability, the extent of substitution can be increased to three (e.g. $L = PPh_3$, $P(OPh)_3$, PPh_2Cl). When the ligand is small or has high π accepting ability (PMe_3, PCl_3, $P(OEt)Cl_2$), tetrasubstituted complexes can be prepared. For instance, the complexes $M(CO)_2L_4$ ($L = PMe_3$, $P(OMe)_3$; $M = Cr$, Mo, W) were prepared from the hexacarbonyls by ultraviolet irradiation and also from $M(CO)_2(1,3\text{-cyclohexadiene})_2$ ($M = Mo$, W).[54] Pentasubstituted derivatives of the type $M(CO)L_5$ ($L = P(OMe)_3$, $PMe(OMe)_2$ and $PMe_2(OMe)$) were formed after extensive irradiation (6 - 21 days) of mixtures of the metal carbonyl and the ligand. Hexasubstituted complexes were obtained when the ligand contained fluorine (i.e. $L = n\text{-}C_3H_7OPF_2$, $(MeO)_2PF$).[215] Phosphorous trifluoride has a greater overall electronwithdrawing effect than carbon monoxide as shown by photoelectron spectroscopy[55] and force constant calculations[14] and will completely substitute $Mo(CO)_6$ to form $Mo(PF_3)_6$. All the derivatives in the series $Mo(CO)_{6-n}(PF_3)_n$ ($n = 1 - 6$) have been isolated.[56]

Bidentate phosphine ligands (L) react under mild conditions to yield initially $M(CO)_5L$[57], which is converted to $M(CO)_4L$.[36,53,58-60] The kinetics of ring closure for the dpe and dmpe complexes show that dpe forms the chelated derivative twice as rapidly as dmpe.[61] Under more vigorous conditions, dicarbonyl complexes, $M(CO)_2L_2$, are formed, usually in the *cis* configuration.[36,58,60] Attempts to completely displace carbon monoxide from these complexes under very drastic conditions failed.[58] Bidentate arsine ligands react in an identical manner, but they have not been investigated to the same extent.[60,62,63] Tridentate phosphine and arsine ligands (L) form tricarbonyl complexes $M(CO)_3L$.[58,64-67,69]

The potentially quadridentate ligand *tris*(*o*-diphenylphosphinophenyl)-phosphine (QP) reacts with the metal carbonyls to give $[M(CO)_3(QP)]$, (M = Cr, Mo, W) in which QP acts as a terdentate ligand. These complexes can be converted into $[M(CO)_2(QP)]$, in which the ligand is quadridentate. Direct reaction of the metal carbonyls with the tetratertiary phosphine ligands Pf-Pf-Pf-Pf and $P(Pf)_3$ produced tricarbonyl derivatives. Tetracarbonyl and dicarbonyl derivatives were prepared by indirect methods.[70] The hexatertiary phosphine, $P_2(Pf)_4$, which resembles ethylenediaminetetraacetic acid, reacts with $M(CO)_6$ (M = Cr, Mo or W) to give the dimeric complexes $P_2(Pf)_4[M(CO)_3]_2$, in which the ligand is fully coordinated.[71]

Complexes containing asymmetric ligands such as $Me_2PCH_2CH_2PPh_2$ or $Ph_2P(CH_2)_2P(Ph)(CH_2)_2PMe_2$ have been synthesized[73] and used in ^{31}P NMR studies.[72] These ligands enable the *cis* phosphorous-phosphorous coupling constant, which is not observed with symmetrical ligands, to be measured. Grim and co-workers[74] prepared a series of carbonyl derivatives containing the unsymmetrical ligands $Ph_2P(CH_2)_nOPPh_2$, (n = 1 or 2) which were used in ^{31}P NMR studies.

The aromatic nitrogen donor ligands, 2,2'-dipyridyl and 1,10-phenanthroline (D), react with the hexacarbonyls to give complexes of the type $M(CO)_4D$[34,53,77] and $M(CO)_2D_2$.[76,77] The tetracarbonyl complexes react under fairly mild conditions with nitrogen donor ligands ($L = NH_3$, py) to form complexes of the type $M(CO)_3(D)L$ (M = Cr, Mo, W)[78] and with Lewis bases ($Y = RPh_3$(R = P, As, Sb), $P(OPh)_3$ etc.) to give the mixed complexes $M(CO)_3(D)Y$ and $M(CO)_2(D)Y_2$.[79-81] The kinetics of the reaction with phosphites have been reported.[82] Reaction of $Mo(CO)_4$(dpe) with monodentate ligands (L = py, MeCN, $P(OPh)_3$, RPh_3 (R = P, As, Sb)) under drastic conditions gave two types of mixed complexes, *cis*-and *trans*-$Mo(CO)_3$(dpe)L and *cis*-$Mo(CO)_2(dpe)L_2$.[83] The mixed donor ligand 8-dimethylarsinoquinoline (As-N) reacts with molybdenum hexacarbonyl to form $Mo(CO)_4(As\text{-}N)$.[84]

(b) Oxidation Reactions

The electrochemistry, including both oxidation and reduction processes, of the metal carbonyls[85,86] and the pentacarbonyhalide anions[87] has been investigated and explains the results of synthetic studies.[42] The halopentacarbonyl anions, $[M(CO)_5X]^-$ (M = Mo, W), are oxidized by halogen to yield the seven-coordinate anions $[M(CO)_4X_3]^-$.[88] Mixed halogen derivatives were also prepared.

The tetracarbonyl complexes $M(CO)_4L$ (M = Mo, W; L = bpy, diars, dpe, dmpe) react with halogens (X = Br, I) to form seven-coordinate metal(II) complexes, which are diamagnetic, as shown by the equations:

$$M(CO)_4L \xrightarrow[CH_2Cl_2]{Br_2} M(CO)_3LBr_2 + CO$$

$$\begin{tikzcd} M(CO)_4L \arrow[r, "I_2", "CH_2Cl_2"'] & {[M(CO)_4LI]I} \arrow[r, "-CO"] \arrow[d, "I_2"] & M(CO)_3LI_2 \\ & {[M(CO)_4LI]I_3} & \end{tikzcd}$$

All bromine oxidations[79,89,90,92] resulted in the direct formation of the neutral tricarbonyl complexes. Controlled oxidation of $W(CO)_4(bpy)$ with iodine gave $[W(CO)_3(bpy)I_2]$.[79] Moreover, iodine reacts with $Mo(CO)_4L$ (L = dpe,[89] diars[90]) with evolution of carbon monoxide to form $[Mo(CO)_3(L)I_2]$. However, iodine oxidation[91] of $Mo(CO)_4(dmpe)$ produces $[Mo(CO)_4(dmpe)I]I$, which can be converted to $[Mo(CO)_3(dmpe)I_2]$ by refluxing in dichloromethane. Oxidation of the tungsten analogues produces $[W(CO)_4(L)I]I$[89,91,92], which is converted to the triiodide salt when more iodine is added. The dpe complex existed only in solution and evolved carbon monoxide over a period of hours to yield the tricarbonyl complex. The dmpe analogue is stable in the dark, but decarbonylates on exposure to daylight and in refluxing dichloromethane, while the diarsine complex appears to be indefinitely stable. The six-coordinate molybdenum(II) complex $[Mo(CO)_2(diars)I_2]$, the metal(III) complexes $[Mo(CO)_2(diars)I_3]$ and $[W(CO)_3(diars)Br_2]Br$ and the tetravalent complex $[Mo(diars)Br_4]$ were prepared under more vigorous conditions.[90,92] The chromium analogues have not been studied to the same extent because facile oxidation to the trivalent oxidation state with the complete loss of carbonyl groups usually occurs, as exemplified by the oxidation of $Cr(CO)_4(diars)$ to $[Cr^{III}(diars)X_3]_2$ (X = Br, I).[93]

Oxidation of the zerovalent complexes containing tridentate tritertiary arsine ligands has been examined using three such ligands. With *o*-triars, complexes of the type $M(CO)_3$(*o*-triars) (M = Cr, Mo, W), when treated with bromine or iodine under controlled conditions, gave ionic products of the type $[M(CO)_3(o\text{-triars})X]X$.[65] The stability of these derivatives decreased in the order W > Mo > Cr and the bromo-chromium compound was not prepared. The molybdenum complexes evolved carbon monoxide when refluxed in methanol to give the neutral compounds $[Mo(CO)_2(o\text{-triars})X_2]$. The chromium(II) complexes readily undergo further oxidation with complete loss of carbon monoxide to form complexes of the type $[Cr(o\text{-triars})X_3]$ (X = Br, I).

Similar reactions were observed using *l*-triars.[64,94] The compounds $M(CO)_3$(*l*-triars) (M = Mo, W) gave on oxidation with bromine or iodine the compounds $[M(CO)_3(l\text{-triars})X]X$. The iodo-molybdenum derivative could be converted into the neutral seven-coordinate complex $[Mo(CO)_2(l\text{-triars})I_2]$ by refluxing in 1-propanol. Bromine oxidation of the molybdenum complex produced a mixture of dicarbonyl and tricarbonyl complexes, even at -70°C. The bromo-tricarbonyl cation is stable in the absence of halide and may be isolated as the tetraphenylborate salt. At room temperature, bromination produces only the neutral dicarbonyl $[Mo(CO)_2(l\text{-triars})Br_2]$. Halogen oxidation of the chromium complex at room temperature leads to complete decomposition. The unstable chromium(II) derivative $[Cr(CO)_3(l\text{-triars})I]BPh_4$ was precipitated from a methanol extract of the low temperature oxidation products.

Somewhat different results were obtained with the derivatives of ν-triars.[94] Oxidation by bromine or iodine of $M(CO)_3(\nu\text{-triars})$ (M = Mo, W) gave the usual seven-coordinate complexes $[M(CO)_3(\nu\text{-triars})X]X$. Perchlorate and tetraphenylborate salts were prepared by metathesis. The molybdenum compounds were rapidly converted to the neutral dicarbonyl-dihalide complexes by heating in methanol at 60°C. The same reaction for the tungsten complexes required temperatures of 100 - 200°C. The dichloro complexes $[M(CO)_2(\nu\text{-triars})Cl_2]$ were prepared by refluxing $[M(CO)_3(\nu\text{-triars})Br]BPh_4$ with lithium chloride in an alcohol. The tungsten chloro complexes $[W(CO)_3(\nu\text{-triars})Cl]SbCl_6$ and $[W(CO)_2(\nu\text{-triars})Cl_2]$ have been prepared by using antimony pentachloride as the oxidant. Iodine oxidation of $Cr(CO)_3(\nu\text{-triars})$ at -70°C gave the stable six-coordinate paramagnetic chromium(II) derivative $[Cr(CO)_2(\nu\text{-triars})I]BPh_4$.

The dicarbonyl derivatives $M(CO)_2D_2$ (M = Mo, W; D = diars,[90,92] bpy, phen[96,97]) react with bromine and iodine to yield diamagnetic seven-coordinate cations of the type $[M(CO)_2D_2X]^+$, which have been isolated as the halide and trihalide salts. The stable chromium(II) derivatives $[Cr(CO)_2(diars)_2X]X$ were formed by halogen oxidation of $Cr(CO)_2(diars)_2$.[93] Treatment with excess halogen did not effect oxidation to chromium(III) species, but simply resulted in the formation of the trihalide salts. The trivalent complex $[Cr(diars)_2I_2]I_3$ was formed after prolonged heating with iodine in carbon tetrachloride.[93] The reactions of the bidentate phosphine complexes $[M(CO)_2L_2]$, (L = dpe, dpm, dmpe) are discussed in section (d).

The dicarbonyl complex $[Cr(CO)_2(QP)]$ reacts with oxidants (I_2, $SbCl_5$)[67] under mild conditions to form the cation $[Cr(CO)_2(QP)]^+$, which was isolated as either the BPh_4^- or $SbCl_6^-$ salt. The chromium(I) complex decomposes fairly rapidly in air with loss of CO. Two carbonyl bands are present in the IR spectrum which suggests that the *cis*-configuration of the zero-valent complex is retained in the cation. Further oxidation of the cation gave the chromium(III) complexes $[CrX_3(QP)]$ (X = Cl, Br) and $[CrI_2(QP)]I_3$. The tungsten analogue $[W(CO)_2(QP)]$ reacts with oxidants (NBS, I_2)[68] to give the seven-coordinate metal(II) cations $[W(CO)_2(QP)X]^+$ (X = Br, I). The chloro complex was also prepared, but could not be obtained analytically pure. The dihalo complexes $[W(CO)(QP)X_2]$ were prepared by heating $[W(CO)_2(QP)X]X$ (X = Br, I) in *vacuo* or by refluxing $[W(CO)_2(QP)X]BPh_4$ (X = Cl, Br) with excess lithium halide in diglyme. $[Mo(CO)_2(QP)]$ reacts in a similar manner, but the products are less stable.

Chloro derivatives are not usually prepared by direct oxidation with chlorine because complete loss of carbon monoxide generally occurs, to produce high oxidation-state products. The milder oxidant, antimony pentachloride, has been used to prepare chloro complexes.[68,95] Moreover, oxidation with excess bromine also results in complete displacement of the carbonyl groups. $Mo(CO)_4(PPh_3)_2$ and $Mo(CO)_3(PPh_3)_3$ react with excess chlorine to yield $Mo^VOCl_3(Ph_3PO)_2$ and with excess bromine to form a mixture of $Mo^VOBr_3(Ph_3PO)_2$ and $Mo^{VI}O_2Br_2(Ph_3PO)_2$. Oxidation of the tungsten analogues yielded mainly the tungsten(VI) complexes $WO_2X_2(Ph_3PO)_2$. Oxidation of $Mo(CO)_4(dpe)$ and $Mo(CO)_2(dpe)_2$ produced a mixture of $Mo^VOX_3(Ph_2P(O)CH_2CH_2P(O)Ph_2)$ and $Mo^{VI}O_2X_2(Ph_2P(O)CH_2CH_2P(O)Ph_2)$, while oxidation of the tungsten analogues gave only the tungsten(V) complexes.[98,99] Halogen oxidation of *cis*-$M(CO)_4L_2$ (M = Mo, W; L = PEt_3, PMe_2Ph, $AsMe_2Ph$) under controlled conditions gave $[M(CO)_3L_2X_2]$ (X = Cl, Br, I), while reaction with excess chlorine or bromine gave complexes of the type *trans*-$[MX_4L_2]$.[100]

(c) Substitution Reactions of the Metal(II) Halocarbonyls

The metal carbonyls (M = Mo or W) react with chlorine and bromine at

-78°C and with iodine at room temperature to form the divalent complexes $M(CO)_4X_2$ (X = Cl, Br, I).[42,43] The complexes are diamagnetic in solution and a dimeric halogen bridged structure was suggested. This has been confirmed by molecular weight measurements.[101] These species provide an alternative route to substituted metal(II) carbonyl complexes and also enable chloro derivatives to be prepared. Addition of RPh_3 (R = P, As, Sb)[‡] to $M(CO)_4X_2$ (X = Cl, Br, I^*) gave seven-coordinate complexes of the type $[M(CO)_3(RPh_3)_2X_2]$. The triphenylphosphine compounds, only, decompose in refluxing dichloromethane to give $[M(CO)_2(PPh_3)_2X_2]$; a reaction which is reversible. Oxidation of $M(CO)_3(PPh_3)_3$ or $M(CO)_4(PPh_3)_2$ with bromine or iodine gave the anions $[M(CO)_3(PPh_3)X_3]^-$.[103] Reaction of nitrogen donor ligands (L = bpy, phen) with $Mo(CO)_4X_2$ (X = Cl, Br) gave the neutral seven-coordinate species $Mo(CO)_3LX_2$ with one mole of ligand and complexes of the type $[Mo(CO)_2L_2X]X$ with excess ligand.[104] On the other hand, reaction with pyridine yields the six-coordinate paramagnetic complexes $Mo(CO)_2(py)_2X_2$ (X = Cl, Br).[104]

Colton and co-workers have extensively investigated the reactions between the dihalotetracarbonylmetal(II) complexes and bidentate phosphine and arsine donors. Treatment of $M(CO)_4X_2$ (X = Cl, Br, I) with a controlled amount of dpe yields the monosubstituted tricarbonyls $M(CO)_3(dpe)X_2$, which are identical to the products obtained from halogen oxidation of $M(CO)_4(dpe)$. Reaction of $M(CO)_4X_2$ with excess dpe at room temperature produces the dpe bridged dimers $[M(CO)_2(dpe)_{1.5}X_2]_2$. A third class of compound, $[M(CO)_2(dpe)_2X_2]$, is prepared by refluxing $M(CO)_4X_2$ or either of the previously described types of complex with excess dpe. The reactions

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[‡] Reaction also proceeds with PMe_2Ph. These types of complexes can also be prepared by direct oxidation, see reference 100.

[*] When M = Mo and X = I, reaction with PPh_3 produces $PPh_3H^+[Mo(CO)_3(PPh_3)I_3]^-$, see reference 102.

are summarized by the following scheme:

$$\begin{tikzcd}
M(CO)_4X_2 \arrow[r, "\text{dpe(stoich.)}", "\text{RT}"'] & M(CO)_3(dpe)X_2 \arrow[d, "\substack{\text{dpe(excess)}\\ \text{RT}}"] \\
{[M(CO)_2(dpe)_2X_2]} \arrow[r, shift right, "\substack{\text{in soln.}\\ \text{RT}}"'] & {[M(CO)_2(dpe)_{1.5}X_2]_2} \arrow[l, shift right, "\substack{\text{dpe(excess)}\\ \text{reflux}}"']
\end{tikzcd}$$

The neutral complexes $[M(CO)_2(dpe)_2X_2]$ (X = Cl, Br) are seven-coordinate and contain one chelated and one monodentate dpe molecule. The iodo derivative is ionic and is thus formulated as $[M(CO)_2(dpe)_2I]I$; however, the workers could not decide between a coordination number of six or seven. The complexes lose dpe on standing in solution to reform the dpe bridged dimers.

Dichlorotetracarbonylmolybdenum(II) and tungsten(II) and also dibromotetracarbonyltungsten(II) react with dpm to give $M(CO)_2(dpm)_2X_2$, which can be isomerized to the ionic complexes $[M(CO)_2(dpm)_2X]X$ by refluxing in chloroform.[106] Dibromotetracarbonylmolybdenum(II) reacts with dpm as shown in the following scheme:

$$\begin{tikzcd}
& Mo(CO)_4Br_2 \arrow[r, "\text{dpm}"] & Mo(CO)_3(dpm)Br_2 \arrow[d, "\text{dpm}"] \\
& {[Mo(CO)_2(dpm)_2Br]Br} & Mo(CO)_2(dpm)_2Br_2 \arrow[l, "\text{CHCl}_3", "\text{reflux}"']
\end{tikzcd}$$

The iodotetracarbonyls react in a similar manner, but the reaction scheme is more complicated.[105] Bridged dimers were not obtained by this method. $[Mo(CO)_4Cl_3]^-$ reacts with dpm at room temperature to give a mixture of $Mo(CO)_2(dpm)_2Cl_2$ and $[Mo(CO)_2(dpm)_{1.5}Cl_2]_2$, whereas the same reaction with $[Mo(CO)_4Br_3]^-$ gives only $[Mo(CO)_2(dpm)_2Br_2]$. The phosphine-bridged dimer $[Mo(CO)_2(dpm)_{1.5}Br_2]_2$ was prepared by mixing $Mo(CO)_4Br_2$ and $Mo(CO)_2(dpm)_2Br_2$. The reaction of $[Mo(CO)_4I_3]^-$ with dpm at room temperature produced only $[Mo(CO)_2(dpm)_2I]I$.[106]

Dichloro- and dibromo-tetracarbonylmolybdenum and tungsten react with dam at room temperature to give complexes of the type $[M(CO)_3(dam)_2X_2]$ in which both dam ligands are monodentate. Mild warming converts these complexes into $M(CO)_2(dam)_2X_2$. This reaction is readily reversed by bubbling carbon monoxide into the system. The reactions of dam with the diiodotetracarbonyls are more complex. Three types of compounds exist and they are all in mutual equilibrium as shown by the equations:

$$M(CO)_3(dam)I_2 + dam \rightleftarrows M(CO)_3(dam)_2I_2 \rightleftarrows M(CO)_2(dam)_2I_2 + CO$$

Complexes of the general formula $Mo(CO)_3(dpae)X_2$ and $[Mo(CO)_2(dpae)_{1\cdot5}X_2]_2$ (X = Cl, Br, I) were prepared by reacting $Mo(CO)_4X_2$ with dpae. The dpae-bridged dimeric complexes are cleaved by carbon monoxide to reform the tricarbonyl complexes and by excess dpae to give $[Mo(CO)_2(dpae)_2X_2]$. The monomeric dicarbonyl complexes are very labile and attempts at isolation resulted in conversion to the dimeric species.[107] The dihalotetracarbonyls react with bis(diphenylstibino)methane at room temperature to yield $M(CO)_3(dpsm)_2X_2$ (M = Mo, W; X = Cl, Br, I). Most of the tricarbonyl complexes lose dpsm and carbon monoxide in refluxing dichloromethane to produce species of the type $M(CO)_2(dpsm)X_2$ in low yield.[108]

(d) Reactions of $M(CO)_2L_2$ (L = dpe, dpm, dmpe)

(I) $M(CO)_2(dpe)_2$

(i) Synthetic Chemistry

The dicarbonyl complexes $M(CO)_2(dpe)_2$ (M = Cr, Mo, W) have been prepared by a number of synthetic routes involving either solid state[58] or solution reactions.[60(a),109] The molybdenum and tungsten complexes are isolated solely as the *cis*-isomers, whereas the chromium analogue is obtained as both the *trans*- and *cis*-isomers depending on the method of preparation. The isomers of $Cr(CO)_2(dpe)_2$ can be interconverted by simply changing the polarity of the solvent.[58]

The neutral complexes are easily oxidized to give octahedral metal(I) cations. The complex *trans*-$Cr(CO)_2(dpe)_2$ undergoes facile oxidation on exposure to air in dichloromethane solution to form *trans*-$[Cr(CO)_2(dpe)_2]^+$.[110] The molybdenum analogue, *cis*-$Mo(CO)_2(dpe)_2$, is oxidized by atmospheric oxygen in mildly acidic solution to give *trans*-$[Mo(CO)_2(dpe)_2]^+$.[110] Treatment of *cis*- $M(CO)_2(dpe)_2$ (M = Mo, W) with iodine (1.5 moles)[89] also produced the cation, *trans*-$[M(CO)_2(dpe)_2]^+$. The reaction of *cis*-$Mo(CO)_2(dpe)_2$ with nitrosonium hexafluorophosphate is solvent dependent. Oxidation in dichloromethane[111] produced initially *trans*-$[Mo(CO)_2(dpe)_2]PF_6$ which isomerized after a period of time to give *cis*-$[Mo(CO)_2(dpe)_2]PF_6$. Oxidation in methanol/toluene is reported[112] to lead exclusively to the *trans*-cation, while the *cis*- monocation is the sole product in acetonitrile.[112] The only direct oxidation to the metal(II) oxidation state that has been reported[111] is the reaction between $Mo(CO)_2(dpe)_2$ and nitrosonium hexafluorophosphate in nitromethane, which yields the dicationic complex, *cis*-$[Mo(CO)_2(dpe)_2](PF_6)_2$.

(ii) Electrochemistry

Electrochemical oxidation and reduction would, in general, be considered to be substantially more specific than chemical processes and can provide kinetic and thermodynamic information. Furthermore, the possibility of synthesizing complexes in new oxidation states or in new isomeric forms may result from electrochemical investigations.

Because of the diversity of products formed in chemical oxidations, a comprehensive electrochemical investigation[113] was undertaken on these complexes (see attached paper) utilizing the techniques of dc and ac polarography (dropping mercury electrode), ac and cyclic voltammetry (platinum electrode) and low temperature electrochemistry. A variety of solvents were used including acetone, dichloromethane and nitromethane.

The electrochemistry of *cis*-$M(CO)_2(dpe)_2$ (M = Mo, W) can be summarized by the following scheme:

$$\begin{tikzcd}
cis\text{-}M(CO)_2(dpe)_2 \arrow[r, shift left, "-e"] & cis\text{-}[M(CO)_2(dpe)_2]^+ \arrow[l, shift left, "+e"] \arrow[d, "\text{very fast}"] & \text{rearrangement and/or decomposition products} \\
trans\text{-}M(CO)_2(dpe)_2 \arrow[u, "\text{slow}"'] \arrow[r, shift left, "-e"] & trans\text{-}[M(CO)_2(dpe)_2]^+ \arrow[l, shift left, "+e"] \arrow[r, shift left, "-e"] & trans\text{-}[M(CO)_2(dpe)_2]^{2+} \arrow[l, shift left, "+e"] \arrow[u]
\end{tikzcd}$$

Oxidation of *cis*-$M(CO)_2(dpe)_2$ produced the cation *cis*-$[M(CO)_2(dpe)_2]^+$. However, the cation is unstable and isomerizes very rapidly to the known *trans*-isomer, which is the product of chemical oxidations. Reduction of *trans*-$[M(CO)_2(dpe)_2]^+$ produced the previously unknown complex, *trans*-$M(CO)_2(dpe)_2$, which isomerizes slowly to the *cis*-isomer. The kinetics of isomerization have been measured.[114] The neutral *trans*-isomer can be prepared by low temperature reduction of the *trans*-cation[113] and was also observed as an intermediate in the reaction of *trans*-$Mo(N_2)_2(dpe)_2$ with carbon monoxide.[115] The *trans*-monovalent cation was oxidized at positive potentials to yield *trans*-$[M(CO)_2(dpe)_2]^{2+}$ which underwent a rapid rearrangement. It was not possible to determine the nature of the rearrangement products from the electrochemistry. Voltammetric data for $Mo(CO)_2(dpe)_2$ has been reported by other workers.[115,116]

Electrochemistry showed that the solid state synthesis of $Cr(CO)_2(dpe)_2$ resulted in the formation of a mixture of *cis*- and *trans*- isomers. The electrode processes for the *trans*-isomer are described by the following equations:

$$trans\text{-}[Cr(CO)_2(dpe)_2] \underset{+e}{\overset{-e}{\rightleftharpoons}} trans\text{-}[Cr(CO)_2(dpe)_2]^+$$

$$trans\text{-}[Cr(CO)_2(dpe)_2]^+ \underset{+e}{\overset{-e}{\rightleftharpoons}} trans\text{-}[Cr(CO)_2(dpe)_2]^{2+}$$

The *trans*-dication, which has not been reported previously, is quite stable on the electrochemical time scale. The electrode processes for the oxidation of the *cis*-isomer are given by the equations:

$$cis\text{-}Cr(CO)_2(dpe)_2 \underset{+e}{\overset{-e}{\rightleftharpoons}} cis\text{-}[Cr(CO)_2(dpe)_2]^+ \xrightarrow[\text{fast}]{\text{very}} trans\text{-}[Cr(CO)_2(dpe)_2]^+$$

The final product is the *trans*-cation, which is consistent with the result obtained from chemical oxidation. The chromium complexes are easier to oxidize than their molybdenum and tungsten counterparts.

Although electrochemistry was successful in rationalizing the known synthetic chemistry of these complexes, it also suggested that it should be possible to prepare complexes in the metal(II) oxidation state by direct oxidation of the zerovalent complexes. One of the aims of this work was to investigate this possibility.

(II) $M(CO)_2L_2$ (L = dpm, dmpe)

While this work was in progress, the synthesis and oxidation reactions of $M(CO)_2(dpm)_2$ (M = Cr, Mo and W)[117] and $M(CO)_2(dmpe)_2$ (M = Mo, W)[118-120] were reported. In both types of complexes, the neutral *cis*-species are easily oxidized to the *trans*-monovalent cations, which can be oxidized further to form seven-coordinate metal(II) complexes. The type of complexes formed are discussed further in Chapter 3.

The electrochemistry of the dpm complexes has been investigated.[121] Cyclic voltammetry gave information about the relative stabilities of the *cis*- and *trans*- isomers in each oxidation state, as well as the half wave potentials for the interconversion of these isomers between different oxidation states. The results are summarized in the equations.

$$\begin{tikzcd}
 & & \text{products} \\
cis\text{-}[M(CO)_2(dpm)_2] \arrow[r, shift left, "-e"] & cis\text{-}[M(CO)_2(dpm)_2]^+ \arrow[l, shift left, "+e"] \arrow[r, shift left, "-e"] \arrow[d, "\text{fast}^*"] & cis\text{-}[M(CO)_2(dpm)_2]^{2+‡} \arrow[l, shift left, "+e"] \arrow[u] \\
trans\text{-}[M(CO)_2(dpm)_2] \arrow[u, "\text{slow}"'] \arrow[r, shift left, "-e"] & trans\text{-}[M(CO)_2(dpm)_2]^+ \arrow[l, shift left, "+e"] \arrow[r, shift left, "-e"] & trans\text{-}[M(CO)_2(dpm)_2]^{2+} \arrow[l, shift left, "+e"] \arrow[u] \arrow[d] \\
 & & \text{products}
\end{tikzcd}$$

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[*] Rate of isomerism is slow at -75°C.

[‡] Predominant process at -75°C, at 25°C both divalent cations are rapidly converted to products.

The dpm complexes are easier to oxidize than the dpe analogues as shown by the halfwave potentials and this has an effect on chemical oxidations. Furthermore, the chromium complex is more easily oxidized than the molybdenum and tungsten counterparts.

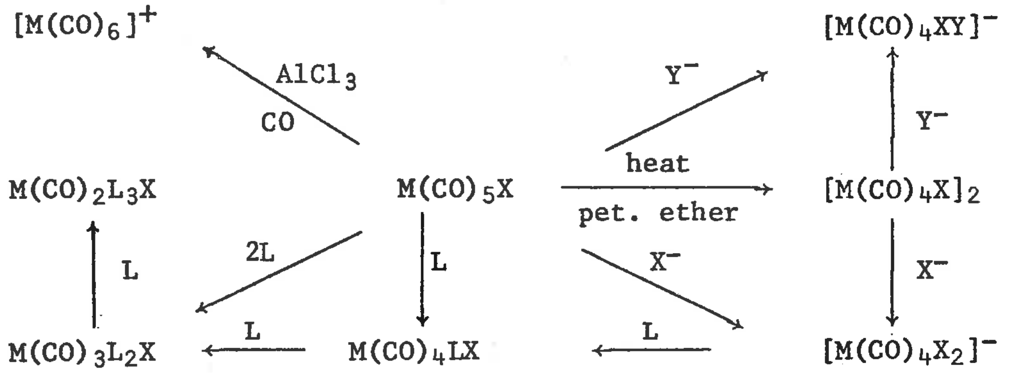
1.4 Chemistry of the Group VIIa Metal Carbonyls

The group VIIa metal carbonyls exist as the dimeric species $M_2(CO)_{10}$ (M = Mn, Tc, Re)[5,6] and this has a significant effect upon their chemistry. Direct reaction of the metal carbonyls with Lewis bases yields dimeric derivatives with retention of the metal-metal bond. These reactions have not been as comprehensively studied as those of the group VIa metal carbonyls. Monomeric species can be formed by either oxidative cleavage of the metal-metal bond, which results in the formation of metal(I) derivatives, or by reductive fission to form highly reactive metallate anions. The study of technetium chemistry is hindered by the fact that all isotopes are radioactive and their natural abundance is so low that the metal has to be prepared by nuclear fission reactions.[122] Rhenium carbonyl is very inert and drastic conditions are usually required to effect substitution. The organometallic chemistry of rhenium has been recently reviewed.[191]

(a) Substitution Reactions

Dimanganesedecacarbonyl reacts photochemically[123] with halide ions (X = Cl, Br, I) to yield the axially substituted ions $[Mn_2(CO)_9X]^-$ while thermal reaction[124] produces the diaxially substituted anions $[Mn_2(CO)_8X_2]^{=}$. However, the existence of the dianions has recently been questioned.[123] Manganese carbonyl reacts with monodentate phosphines and arsines to form complexes of the formula $[Mn_2(CO)_9L]$[125-127] which are usually axially substituted (L = PPh_3,[125] PF_3,[127] PMe_2Ph,[128,158] $AsMe_2Ph$[128,158]). The kinetics of the reaction have been investigated.[130] Moreover, $Re_2(CO)_{10}$ reacts with $PMePh_2$ to form *axial*-$Re_2(CO)_9(PMePh_2)$, whereas reaction with PMe_2Ph produces the equatorial isomer.[129] $Mn_2(CO)_{10}$ is also reported to react with RPh_3 (R = P, As, Sb) to form the monomeric paramagnetic complexes $[Mn(CO)_4RPh_3]$,[138,139] however, subsequent attempts to prepare these compounds were unsuccessful.[126] The reaction of $Mn_2(CO)_{10}$ (or $Mn_2(CO)_9L$[126,130]) with excess Lewis base either thermally[132,133] or photochemically[127,131,134] produced the disubstituted complexes $Mn_2(CO)_8L_2$, the majority of which are diaxially substituted (L = PPh_3, $P(OPh)_3$, PEt_3,[131] PF_3,[127] $PMePh_2$,[134,158] $AsPh_3$[131] etc.).[136] However, in $Mn_2(CO)_8L_2$ (L = $AsMe_2Ph$, $AsMe_3$, $AsEt_3$), the arsine ligands are attached equatorially.[134,158] Rhenium carbonyl reacts similarly to produce either diaxial (L = PPh_3)[135] or diequatorial (L = $PMePh_2$,[129] PMe_2Ph,[137] $AsMe_2Ph$[137]) complexes, as well as further substituted derivatives.[129,135,137] The reaction of $Mn_2(CO)_{10}$ with nitrogen donor Lewis bases (e.g. pyridine)[140] results in disproportionation to yield $[Mn^{II}(base)_6][Mn^{-I}(CO)_5]_2$.

The complexes $M_2(CO)_{10}$ (M = Mn,[147,148] Tc[149]) react with halogens to form the octahedral metal(I) pentacarbonylhalide complexes $M(CO)_5X$ (X = Cl, Br, I), which are isoelectronic with the group VIa pentacarbonylhalide anions. The rhenium complexes were prepared by high pressure carbonylation of rhenium halides.[150,151] The pentacarbonylhalides decompose on heating in an inert solvent to form the halogen bridged dimers $[M(CO)_4X]_2$ (M = Mn,[148] Tc,[149] Re[152]).[153] Reaction of the halopentacarbonyls with halide ion results in the formation of the dihalo complexes $[M(CO)_4X_2]^-$ (M = Mn,[124,154] Re;[155] X = Cl, Br, I). This method also enables mixed derivatives of the type $[M(CO)_4XY]^-$ (X and Y = halogen, X ≠ Y) to be prepared.[124,155] An alternative method for the preparation of both types of dihalotetracarbonylmanganate involves fission of the halogen bridge in the dimeric complexes $[Mn(CO)_4X]_2$.[124] At high temperature, interaction of $Re(CO)_5X$ with halides gave ions of the formula $[Re_2(CO)_7X_2Y]^-$ (X and Y = Cl, Br)[155], while reaction of $[Re(CO)_4I_2]^-$ with iodide yielded $[Re(CO)_3I_3]^{2-}$.[155] $Mn(CO)_5Cl$ reacts with carbon monoxide in the presence of aluminium chloride to produce the cation $[Mn(CO)_6]^+$[169], which is isoelectronic with $Cr(CO)_6$. The analogous hexacarbonyl of rhenium, $[Re(CO)_6]^+$, has been prepared in a similar manner.[170] The reactions of the pentacarbonyl halides are summarized in Scheme 1.1.

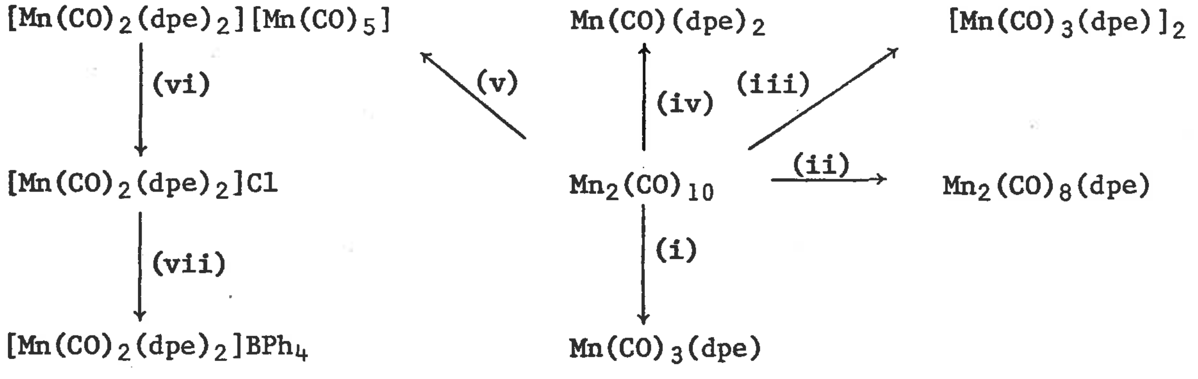


Scheme 1.1 Reactions of $M(CO)_5X$
($M = Mn, Re$; $X = Cl, Br, I$; Y = halide $\neq X$; $L = PPh_3, AsPh_3$, py, etc.)

The manganese pentacarbonylhalides react with Lewis bases ($L = RPh_3$ ($R = P, As, Sb$), $P(OPh)_3$ etc.) under mild conditions to form monosubstituted products of the type *cis*-$Mn(CO)_4LX$, ($X = Cl, Br, I$).[156] Rhenium pentacarbonylbromide reacts with PPh_3 under more vigorous conditions to form *cis*-$Re(CO)_4(PPh_3)Br$.[157] A second route to this type of complex involves fission of the dimers $[M(CO)_4L]_2$. Bromination of $[M(CO)_4(PPh_3)]_2$ ($M = Mn, Re$) and $[Mn(CO)_4L]_2$ ($L = PPh(OMe)_2, PPh_2(OMe)$) at 0°C produced a mixture of *cis*- and *trans*— $M(CO)_4(PPh_3)Br$[157] and *trans*-$Mn(CO)_4LBr$[158] respectively. $[Re_2(CO)_9(PMePh_2)]$ reacts with dry HCl gas to form *trans*-$Re(CO)_4(PMePh_2)Cl$ and $Re(CO)_5Cl$ while $[Re(CO)_4(PMePh_2)]_2$, under the same conditions, forms *cis*-$Re(CO)_4(PMePh_2)Cl$.[129] Complexes of the general formula, *cis*- and *trans*-$Re(CO)_4LX$ ($L = PMe_2Ph, AsMe_2Ph$; $X = Cl, Br, I$) were prepared by halogen fission of the dimers $[Re(CO)_4L]_2$.[137] Most of the aforementioned *trans*- complexes could be converted to the *cis*-isomers by heating in a suitable solvent.[137,157]

Reaction of $M(CO)_5X$ ($M = Mn, Re$; $X = Cl, Br, I$) with excess Lewis base in petroleum ether at 120°C produced the disubstituted derivatives *mer*-$M(CO)_3L_2X$, ($L = PPh_3, AsPh_3$) and *fac*-$M(CO)_3L_2X$, (L = py, bpy).[148] $Re(CO)_5I$ is reported to react with phosphines in refluxing benzene to give *fac*-$Re(CO)_3L_2I$ ($L = PPh_3, P(OPh)_3$).[162] When the reaction is carried out under mild conditions (37°C) using non-bulky ligands, the *fac*-isomers are formed, which isomerize to the *mer*-complexes on warming to 50-60°C; the kinetics of the process have been measured.[159] Attempts to prepare *fac*-$Mn(CO)_3(PPh_3)_2Br$ using this method resulted in the formation of $Mn(CO)_4(PPh_3)Br$, which, on warming, was converted to *mer*-$Mn(CO)_3(PPh_3)_2Br$.[159] $Mn(CO)_5Br$ reacts rapidly with two molar equivalents of ligand (L = PR_3 (R = Me, OMe, OEt), PMe_2Ph, $P(OMe)_2Ph$) in refluxing benzene to give initially *fac*-$Mn(CO)_3L_2Br$, which isomerizes to the *mer*-isomer. When an excess of ligand was used, the trisubstituted complexes *mer*-$Mn(CO)_2L_3Br$ were formed. Reaction of the tris(trimethylphosphite) complex with excess trimethylphosphite produced $Mn(CO)\{P(OMe)_3\}_4Br$.[160] $Re(CO)_5Br$ reacts similarly with these ligands in benzene/petroleum ether containing sodium borohydride to form both *fac*- and *mer*-$Re(CO)_3L_2Br$ and *mer-cis*-$Re(CO)_2L_3Br$.[161] Disubstituted rhenium complexes have also been prepared by fission of the dimers $[Re_2(CO)_7L_3]$.[129,137]

The reactions of manganese carbonyl with dpe have been investigated by several workers and the products obtained are shown in Scheme 1.2.



Scheme 1.2 Reactions of $Mn_2(CO)_{10}$ with dpe

(i) ref. 143, 144; (ii) ref. 142; (iii) ref. 144; (iv) ref. 143, 144; (v) - (vii) ref. 143.

Reimann and Singleton[144] studied the reactions of $Mn_2(CO)_{10}$ with dpm and isolated $Mn_2(CO)_8(dpm)$ and $[Mn(CO)_3(dpm)]_2$. Colton and Commons[145] reported that $Mn_2(CO)_{10}$ reacts with dpm and dam to yield $Mn_2(CO)_8L$ (L = dpm, dam), $Mn_2(CO)_6(dpm)_2$ and $Mn_2(CO)_5(dpm)_2$; the latter complex contains a novel bridging carbonyl group. The crystal structure of the pentacarbonyl complex has been determined.[146] The reaction between $Re_2(CO)_{10}$ and dpe in sealed tubes gave either a mixture of $[Re(CO)_3(dpe)]_2$ and $Re(CO)_3(dpe)$ or *cis*-$Re(CO)_2(dpe)_2$, depending on the conditions. Heating $Re(CO)_2(dpe)_2$ with dpe resulted in decarbonylation to give $Re(CO)(dpe)_2$.[135]

The product of the reaction of the manganese pentacarbonylhalides with dpe depends on the particular halide. $Mn(CO)_5Cl$ reacts to form only the ionic complex, *trans*-$[Mn(CO)_2(dpe)_2]Cl$.[164] The reaction of dpe (one mole or slight excess) with $Mn(CO)_5X$ (X = Br, I) yields *fac*-$Mn(CO)_3(dpe)X$[143,163] while reaction of $Mn(CO)_5Br$ with excess dpe produces *trans*-$[Mn(CO)_2(dpe)_2]Br$.[164] The reaction of $Re(CO)_5I$ with excess dpe in refluxing benzene yields *fac*-$Re(CO)_3(dpe)I$ which is converted to the ionic complex *cis*-$[Re(CO)_2(dpe)_2]I$ only under drastic conditions. The cation undergoes decarbonylation at high temperatures to form $[Re(CO)(dpe)_2I]$.[162] *Cis*-$[Re(CO)_2(dpe)_2]X$ is also obtained by treating *cis*-$Re(CO)_2(dpe)_2$ with acids (HX).[135] The potentially quadridentate ligand QP reacts with $Mn(CO)_5X$ (X = Cl, Br) to give $Mn(CO)_3(QP)X$, in which the ligand is bidentate.[165] The cation $[Mn(CO)_2(QP]^+$, which contains fully coordinated QP, was prepared by ultraviolet irradiation of $[Mn(CO)_3(QP)]^+$, which, in turn, was prepared by reacting $[(C_6H_6)Mn(CO)_3]^+$ with QP.[165]

An alternative route to mononuclear complexes involves reactions of the pentacarbonylmetallate anions, $[M(CO)_5]^-$ (M = Mn, Re). Various methods for the formation of these anions have been reported;[5,37] the simplest being direct cleavage of the metal carbonyls by metallic sodium in tetrahydrofuran.[37,171] The anions are very reactive and behave as nucleophiles in their reactions. The mixed carbonyl complex $(CO)_5MnRe(CO)_5$ was formed by reacting $[Mn(CO)_5]^-$ with $Re(CO)_5Cl$.[172] Complexes of the formula

$[R_3E\text{-}M(CO)_5]$ (R = H, Me, Ph, Cl, Br; E = Ge, Sn, Pb; M = Mn, Re) were prepared by reacting the anions $[M(CO)_5]^-$ with the appropriate group IVb halogen complex.[35,173,191] The metallate anions react with alkyl (RX) and acyl (RCOX) halides to form complexes of the type $[RM(CO)_5]$ and $[(RCO)M(CO)_5]$ respectively. The acyl derivatives undergo facile decarbonylation on heating to form the corresponding alkyl derivatives.[37] The phosphine-substituted manganese carbonyl anions $[Mn(CO)_4PR_3]^-$ (R = Ph, OPh) are obtained by sodium reduction of the dimers $[Mn(CO)_4PR_3]_2$[133] and they react in a similar fashion.

(b) Oxidation Reactions

Fac- and *mer*-$Mn(CO)_3L_2Br$ (L = PMe_3, $P(OMe)_3$, PMe_2Ph; L_2 = dpe, dpm) are oxidized by nitrosonium hexafluorophosphate to the manganese(II) salts *fac*-$[Mn(CO)_3L_2Br]PF_6$.[111,167] Similar treatment of *mer-cis*-$Mn(CO)_2L_3Br$ (L = PMe_3, $P(OMe)_3$, $P(OMe)_2Ph$, PMe_2Ph) with $NOPF_6$ gave *mer-trans*-$[Mn(CO)_2L_3Br]PF_6$ with the exception of the trimethylphosphine complex which gave *mer-cis*-$[Mn(CO)_2(PMe_3)_3Br]PF_6$.[167] The *mer-trans*-cations react with the ligand L in refluxing chloroform to give the cations *cis*-$[Mn(CO)_2L_4]^+$.[167] The reaction of *cis*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]^+$ with $NOPF_6$ produced the dipositive cation, *trans*-$[Mn(CO)_2\{P(OMe)_2Ph\}_4]^{2+}$.[167] The cation, *trans*-$[Mn(CO)_2(dpe)_2]^+$ is oxidized by concentrated nitric acid to the dication, *trans*-$[Mn(CO)_2(dpe)_2]^{2+}$.[166] The electrochemistry of $Mn(CO)_3(dpm)X$ (X = Cl, Br) and *trans*-$[Mn(CO)_2(dpe)_2]^+$ has been reported.[113,168] The electrochemistry of the *trans*-cation[113] is in accordance with the synthetic chemistry. However, the electrochemistry of *fac*-$Mn(CO)_3(dpm)X$[168] suggested that the cation, *fac*-$[Mn(CO)_3(dpm)X]^+$, is unstable and rapidly isomerizes to the *mer*-isomer. The *mer*-isomer was shown to be the product of chemical oxidations.[168] Attempts to oxidize $[Mn(CO)_2(QP)]^+$ were unsuccessful.[165]

1.5 Fluoro Complexes

Halocarbonyl complexes (halogen = Cl, Br, I) and their derivatives are known for virtually every transition metal.[174] On the other hand, the number of fluoro complexes is limited and successful synthetic routes have only been recently developed.

The method used to prepare the group VIa pentacarbonylhalide anions, which involves heating the metal carbonyl and tetraalkylammonium halide in diglyme, did not yield the fluorocarbonyl derivative.[175] A reaction took place, but no product could be isolated. Mild syntheses for the fluoro anions have now been reported. Douglas and Ruff[51] prepared $[Cr(CO)_5F]^-$ and $[W(CO)_5F]^-$ by reacting the dimeric anions $[M_2(CO)_{10}]^=$ (M = Cr, W) with silver fluoride and by ultraviolet irradiation of the hexacarbonyls in the presence of $(Ph_3P)_2NF$, as shown in the equations:

$$M(CO)_6 + F^- \xrightarrow[CH_2Cl_2]{h\nu} [M(CO)_5F]^- + CO$$

$$[M_2(CO)_{10}]^= + 2AgF \xrightarrow{THF} 2[M(CO)_5F]^- + 2Ag$$

No product could be isolated when the corresponding molybdenum derivatives were used. Cihonski and Levenson[50] used potassium fluoride, solubilized by the addition of dibenzo-18-crown-6, preparing the chromium and tungsten fluorocarbonyl anions by irradiation in tetrahydrofuran. The molybdenum analogue was not prepared. The fluorine-bridged anions $[(CO)_3MF_3M(CO)_3]^{3-}$ (M = Cr, Mo, W)* were prepared by reacting either $M(CO)_6$ or $(arene)M(CO)_3$ with tetraethylammonium fluoride.[176]

$Mo(CO)_4Cl_2$ reacts with liquid anhydrous hydrogen fluoride to form $Mo(CO)_4F_2$, which can be oxidized by xenon difluoride to give $Mo(CO)_3F_3$, which reacts further to form $Mo(CO)_3F_4$. Reaction of $Mo(CO)_3F_4$ with XeF_2 results in complete carbonyl loss to give MoF_6. Furthermore, $Mo(CO)_3F_4$ dispropor-

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* The reaction also proceeded with the other halide ions and with pseudohalides

tionates on standing in the presence of hydrogen fluoride to yield $Mo(CO)_3F_3$ and MoF_6.[177] $W(CO)_4Cl_2$ reacts similarly with hydrogen fluoride to form $W(CO)_4F_2$. Reaction with XeF_2 produced a mixture of $W(CO)_6$ and WF_6. Tungsten hexacarbonyl itself reacts with XeF_2 to give WF_5.[177] The polymeric complex $Mo(CO)_2F_4$ has been prepared by reacting $Mo(CO)_6$ with MoF_6. The carbonyl groups are labile and addition of triphenylphosphine gave $Mo(PPh_3)_2F_4$.[178]

All attempts to prepare manganese pentacarbonylfluoride have been unsuccessful. The only two known carbonyl fluorides of manganese are $Mn(CO)_3F_3$ and the dimer $[Mn(CO)_4F]_2$, which presumably contains fluoride bridges. Both complexes were prepared by treating $Mn(CO)_5Br$ with silver fluoride in dichloromethane.[179] Fluoropentacarbonylrhenium was prepared by a metathetical reaction between $Re(CO)_5Cl$ and anhydrous hydrogen fluoride[180,182] and by oxidizing $Re_2(CO)_{10}$ with xenon difluoride.[180] O'Donnell and co-workers reported[180,181] that the reaction of $Re_2(CO)_{10}$ with ReF_6 produced a mixture of $Re(CO)_5F$, $Re(CO)_3F_3$ and ReF_5. Pure $Re(CO)_3F_3$ was obtained by oxidizing $Re(CO)_5F$ with xenon difluoride.[180] On the other hand, Bruce and co-workers reported[182] that the reaction between $Re_2(CO)_{10}$ and XeF_2 in 1,1,2-trichlorotrifluoroethane produced $[Re(CO)_5F\cdot ReF_5]$ and that the reaction of $Re_2(CO)_{10}$ with ReF_6 in anhydrous hydrogen fluoride gave a mixture of $[Re(CO)_5F\cdot ReF_5]$ and $[Re(CO)_6]^+[Re_2F_{11}]^-$.[183] The crystal structure of $[Re(CO)_5F\cdot ReF_5]$ shows that the two rhenium atoms are joined by a fluorine bridge.[183]

Carbonyl fluorides of ruthenium have been prepared by reacting $Ru_3(CO)_{12}$ with xenon difluoride in inert solvents (anhydrous HF, 1,1,2-trichlorotrifluoroethane).[184] $Ru_3(CO)_{12}$ reacted with three moles of XeF_2 to produce the tetramer $[Ru(CO)_3F_2]_4$ and with 4.5 moles to give the monomer $Ru(CO)_3F_3$. When excess XeF_2 was used or RuF_5 was reacted with carbon monoxide at 200°C, the product was the tetrameric complex $[Ru(CO)_3F_2\cdot RuF_5]_2$.

The crystal structure of $[Ru(CO)_3F_2]_4$ has been determined.[185]

Fluoro complexes of the type *trans*-$[MF(CO)(PPh_3)_2]$ (M = Ir, Rh) were prepared by boiling the chloro analogues with ammonium fluoride and silver carbonate in methanol.[186,187] The iridium complex was also prepared by fluoride substitution of $[Ir(CO)(MeCN)(PPh_3)_2]^+$[188] and the rhodium complex by metathesis of $[RhCl(CO)(PPh_3)_2]$ with silver fluoride in acetone.[189] The fluoro ligand is labile and a large number of complexes containing oxygen donor ligands were prepared by substitution reactions.[186] High pressure carbonylation was used to prepare $Pt(CO)_2F_8$ from platinum(IV)fluoride and $[Rh(CO)_2F_3]_2$ from rhodium(IV)fluoride.[190]

1.6 Carbonyl Complexes Containing Oxyanion Ligands

Organic oxygen donors such as ketones and ethers react with metal carbonyls[34,192], but these types of complexes will not be discussed.

Complexes containing coordinated nitrate are fairly common in coordination chemistry. The first metal carbonyl derivative to contain coordinated nitrate was $Mn(CO)_5(ONO_2)$,[193] which was prepared by the reaction of $Mn_2(CO)_{10}$ with nitrogen dioxide. Rhenium carbonyl reacts similarly with nitrogen dioxide to form $Re(CO)_5(ONO_2)$ in high yield.[196] The nitrato group is retained during reactions of $Mn(CO)_5(ONO_2)$ with Lewis bases (L = py, PPh_3, $AsPh_3$; L_2 = bpy) to give complexes of the type $Mn(CO)_{5-n}L_n(ONO_2)$ (n = 1, 2).[194,195] $Mo(CO)_2(dmpe)_2$ reacts with silver nitrate to give the seven-coordinate molybdenum(II) adduct $[Mo(CO)_2(dmpe)_2(ONO_2)]NO_3$.[118] The analogous reaction with silver sulphate gave $[Mo(CO)_2(dmpe)_2(OSO_3)]$ which was converted to the bidentate sulphato complex $[Mo(CO)(dmpe)_2(SO_4)]$ by normal laboratory light.[120] The reaction of $Ir(CO)(PPh_3)_2Cl$ with silver nitrate in acetone yields $Ir(CO)(PPh_3)_2(ONO_2)$ when a slight excess of the silver salt is used and $[Ir(CO)(PPh_3)_2(NO_3)_2Ag]$ when a large excess is added.[209] Iron complexes of the formula $(Cp)Fe(CO)_2X$ ($X = NO_3$, CF_3CO_2, $PhCO_2$, *p*-Me-$C_6H_4SO_3$, $OP(O)(OPh)_2$) were prepared by oxidative fission of the dimer $[(Cp)Fe(CO)_2]_2$ with the corresponding silver salt.[197]

The perchlorate ion is generally considered to be non-coordinating and inert. However, under the appropriate circumstances, the ion will form complexes containing the classic ligands, particularly with nickel and copper.[272] The only metal carbonyl complexes presently known to contain coordinated perchlorate are $M(CO)(PPh_3)_2(OClO_3)$ (M = Ir, Rh)[198,199] and $Co(CO)_2(PPh_3)_2(OClO_3)$.[198] A number of organometallic derivatives have been isolated including $(C_6Cl_5)Ni(PMe_2Ph)_2(OClO_3)$,[200] which was only prepared *in situ*, $(C_6F_5)Pt(PEt_3)_2(OClO_3)$[201] and $Me_3Pt(OClO_3)$;[202] the latter complex is very unstable. Perchlorato ligands are labile and are easily substituted by a variety of ligands including water and this method has been used to prepare aquo complexes.[200,201]

Carboxylato derivatives of metal carbonyls appear to be very stable and are easily prepared. The perfluorocarboxylato complexes $[M(CO)_5(O_2CR_f)]$ $(M = Mn, Re; R_f = CF_3, C_2F_5, C_3F_7)$ were prepared by reacting $M(CO)_5Br$ with the silver perfluorocarboxylate salt. This metathesis has general synthetic utility and a large number of derivatives were isolated for the metals iron, molybdenum, cobalt, titanium and zirconium.[203] Pentacarbonyl-σ-allylmanganese reacts with trifluoroacetic acid with propene evolution to give $Mn(CO)_5(O_2CCF_3)$.[204] The allylic group is also displaced[204] by strong acids (HNO_3, H_2SO_4) to yield $Mn(CO)_5(ONO_2)$ and the bisulphato complex $Mn(CO)_5(OSO_3H)$. Reaction with perchloric acid did not produce the perchlorato complex. $Re(CO)_5(O_2CCF_3)$ has been prepared by treating $CH_3Re(CO)_5$ with trifluoroacetic acid.[205] The trifluoroacetato group is retained in reactions of $Mn(CO)_5(O_2CCF_3)$ with Lewis bases to give $Mn(CO)_3L_2(O_2CCF_3)$ (L = py, PPh_3, $P(OPh)_3$; L_2 = bpy, phen, dpe),[206,207] $Mn(CO)_2\{P(OMe)_3\}_3(O_2CCF_3)$[207] and $Mn(CO)(dmpe)_2(O_2CCF_3)$.[207] Carboxylato derivatives of the group VIa metals, $[M(CO)_5(O_2CR)]^-$ (M = Cr, Mo, W; R = alkyl, perfluoroalkyl), have been prepared by several methods. These involve (a) thermal substitution of the metal carbonyl,[208,210] (b) reaction of the pentacarbonylhalide ions with thallium(I)carboxylate[208] or (c) treatment of the dianions $[M_2(CO)_{10}]^{2-}$ with mercury or silver carboxylate.[210]

The hydroxo complexes $[M(CO)_5(OH)]^-$ (M = Cr, W) were prepared by irradiating a mixture of $M(CO)_6$, potassium hydroxide and dibenzo-18-crown-6 in dichloromethane.[50] Treatment of (arene)$M(CO)_3$ (M = Cr, Mo, W; arene = toluene, mesitylene) with tetramethylammonium hydroxide produced the hydroxy-bridged dimers $[(CO)_3M(OH)_3M(CO)_3]^{3-}$; these complexes are particularly unstable and decompose on exposure to air.[176] Hydroxy-bridged dimers were also obtained when the metal carbonyls were heated with potassium hydroxide in alcohols. In ethanol, $Cr(CO)_6$ reacts to form $K_2[(CO)_3Cr(OH)_3Cr(CO)_3H]$[47] and $Mo(CO)_6$ reacts to form $K_3[(CO)_3Mo(OH)_3Mo(CO)_3]$, which on acidification yields the free acid $[Mo_2(CO)_6(OH)_3H_3]$.[48] $W(CO)_6$ also yields the hydroxy-bridged dimer,[48] however, treatment with mineral acids produced trimeric complexes.[49] The same reactions in methanol resulted in the formation of dimers containing both hydroxy and methoxy bridges.[47,48]

Aquo and hydroxy complexes have been prepared by a miscellany of methods. Johnson and Winterton[211] reported that $[Mn(CO)_5(H_2O)]^+$ is one of the products of acidic hydrolysis of the 3- and 4-pyridiomethylmanganese-pentacarbonyl ions in aqueous solution. They did not isolate or characterize the complex. $Re(CO)_3(H_2O)_2X$ (X = Cl, Br) was prepared by refluxing $Re(CO)_5X$ in a formic acid-hydrochloric acid mixture and evaporating to dryness.[212] $Cs_2[Rh(CO)_2(H_2O)Cl_3]$ was produced by the reaction of $[Rh(CO)_2Cl_2]^-$ with cesium chloride.[213] The hydroxy complexes $[M(OH)(CO)(PPh_3)_2]$ (M = Ir, Rh) have been prepared by several methods.[186,188,214]

The other aim of this work was to systematically investigate the preparation of metal carbonyl, and in particular manganese, complexes containing coordinated inorganic anions and to ascertain whether these derivatives could be used to prepare fluoro complexes. In particular, it was proposed to concentrate on the preparation of the as yet unsynthesized complex $Mn(CO)_5F$.

CHAPTER 2

REACTIONS OF $M(CO)_2(DPE)_2$ (M = Cr, Mo, W) WITH NITROSONIUM HEXAFLUOROPHOSPHATE

2.1 Introduction

Nitrosonium hexafluorophosphate ($NOPF_6$) can behave as either a powerful one-electron oxidant or as a nitrosylating agent, as illustrated by the following examples. Ferrocene and complexes such as *fac*-$Mn(CO)_3(PMe_3)_2Br$ are oxidized to the ferricinium and *fac*-$[Mn(CO)_3(PMe_3)_2Br]^+$ cations respectively.[216] The tetracarbonyl complexes $M(CO)_4$(dpe) (M = Mo, W) react with nitrosonium hexafluorophosphate in polar solvents to form the cationic carbonyl nitrosyls $[M(CO)_3(NO)(dpe)]PF_6$, whereas $Cr(CO)_4$(dpe) is oxidised in methanol/toluene to $[Cr(CO)_4(dpe)]PF_6$.[112]

Reimann and Singleton[111] reported in a preliminary communication that *cis*-$Mo(CO)_2(dpe)_2$ reacted with nitrosonium hexafluorophosphate in dichloromethane to form *trans*-$[Mo(CO)_2(dpe)_2]PF_6$ (red), which isomerized after a period of time to give yellow *cis*-$[Mo(CO)_2(dpe)_2]PF_6$. When *trans*-$[Mo(CO)_2(dpe)_2]PF_6$ was treated with nitrosonium hexafluorophosphate in nitromethane, the dipositive complex *cis*-$[Mo(CO)_2(dpe)_2](PF_6)_2$ was formed. Johnson *et al.*[112] reported in a preliminary communication that nitrosonium hexafluorophosphate oxidation of $M(CO)_2(dpe)_2$ (M = Cr, Mo, W) in methanol/toluene mixtures leads exclusively to the *trans*-$[M(CO)_2(dpe)_2]^+$ cations, whereas the *cis*-monocations are the sole products in acetonitrile. However, no details of the preparations were given in either of the above communications.

2.1.1 Preparation of $M(CO)_2(dpe)_2$

Several methods have been reported[58,60(a),109] for the preparation of $M(CO)_2(dpe)_2$ (M = Cr, Mo, W); these are summarized in Appendix 2. The complexes were prepared by refluxing $M(CO)_6$ with excess dpe in diglyme (see Appendix 1), which produced the *cis*-isomers in very high yield.[109] The *trans*-isomer of $Cr(CO)_2(dpe)_2$ was prepared by the solid-state reaction of (mesitylene)$Cr(CO)_3$ with dpe.[58]

2.2 Oxidation of $Mo(CO)_2(dpe)_2$ in Dichloromethane (Preparation of $[Mo(CO)_2(dpe)_2F]PF_6$)

When *cis*-$Mo(CO)_2(dpe)_2$ was mixed with two equivalents of nitrosonium hexafluorophosphate in dichloromethane, the neutral complex dissolved rapidly with evolution of nitric oxide to give a red solution of the known cation, *trans*-$[Mo(CO)_2(dpe)_2]^+$ (ν_{CO} 1878 (vs) cm^{-1}). Over a period of 10 - 15 minutes the colour changed to yellow and finally to green. The infrared spectrum, in the carbonyl stretching region, of the reaction mixture (Fig. 2.1a) showed a weak band at 1980 cm^{-1}, two very strong bands at 1945 and 1889 cm^{-1} and a number of medium-weak bands due to decomposition products.

The reaction mixture separated into three bands on an alumina column; these were bright yellow, brown and green respectively. The yellow band was eluted with dichloromethane. The compound was found to be extremely soluble in this solvent. The addition of light petroleum or diethyl ether produced oils or powders. Canary yellow crystals were obtained when methanol was added to the concentrated eluate. Two very strong bands were present in the infrared spectrum (Fig. 2.1b) at 1945 and 1889 cm^{-1}; these are in good agreement with the values reported by Reimann and Singleton (1948 and 1892 cm^{-1}). No nitrosyl absorptions were observed. The brown band was eluted with polar solvents such as acetone or methanol. The infrared spectrum showed a broad band of medium intensity between 1600 and 1700 cm^{-1} plus a number of weak bands, which corresponded to those observed for the reaction mixture. The green band was difficult to elute and is probably a high oxidation-state molybdenum complex. If excess nitrosonium hexafluorophosphate was used, extensive decomposition occurred.

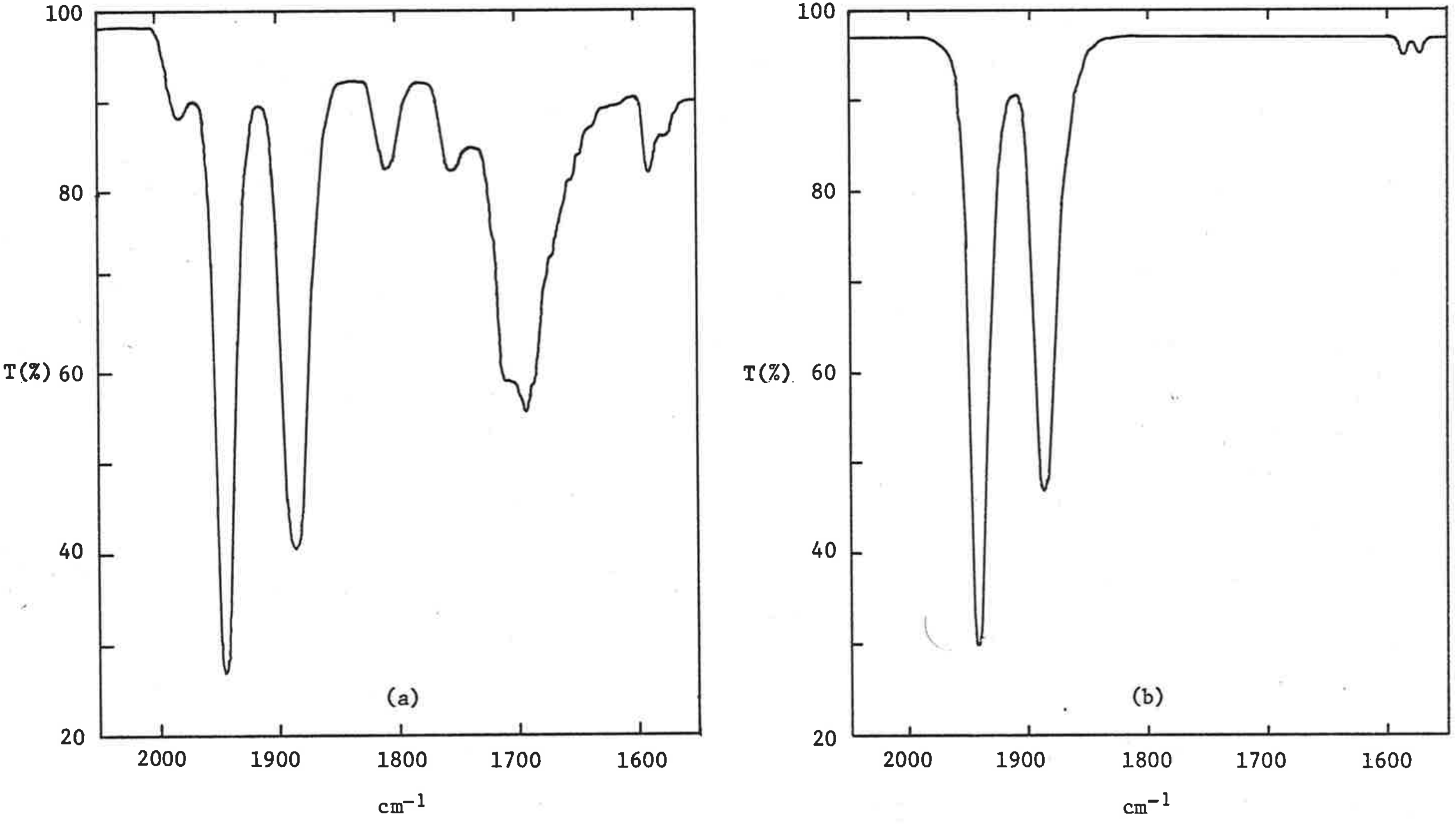


Fig. 2.1 Infrared Spectrum of $[Mo(CO)_2(dpe)_2F]PF_6$

(a) Reaction Mixture. (b) Eluate from an Alumina Column.

2.2.1 Characterization and Properties of $[Mo(CO)_2(dpe)_2F]PF_6$

The electrochemistry of the $M(CO)_2(dpe)_2$ (M = Cr, Mo or W) system was previously investigated (see attached paper).[113] It was shown that the cation, *cis*-$[Mo(CO)_2(dpe)_2]^+$, prepared electrochemically from *cis*-$Mo(CO)_2(dpe)_2$ and therefore isostructural with it, was unstable and isomerized extremely rapidly to the well characterized *trans*-isomer. The electrochemistry of the $NOPF_6$ oxidation product is completely different; no reduction waves were observed at the platinum electrode in acetone, dichloromethane and nitromethane. In nitromethane an oxidation wave was observed at 1.10V. At 25°C, a cyclic voltammogram in this solvent gave an oxidation peak at 1.17V and a reduction peak at 1.0V. The ratio of anodic to cathodic peak heights was 3.7:1. A quasireversible charge transfer with a follow up chemical reaction is indicated. Oxidation in dichloromethane was even more difficult and occurred close to the limit of the accessable positive potential range with an $E_{\frac{1}{2}}$ value of approximately 1.6V. No reversibility was found at 25°C, however, at -70°C a reversible oxidation was found as indicated by cyclic voltammetry. No wave was found in acetone. Thus, the compound is extremely stable with respect to both reduction and oxidation, but shows considerable solvent effect towards oxidation and is definitely not iso-structural with the species formed initially when *cis*-$Mo(CO)_2(dpe)_2$ is oxidized.

From a consideration of its properties, the compound was formulated as the seven-coordinate molybdenum(II) fluoro complex, $[Mo(CO)_2(dpe)_2F]PF_6$. The compound was found to be diamagnetic in solution at 30°C as determined by the Evan's method.[217] All known seven-coordinate metal(II) complexes, such as $[M(CO)_2(L)_2X]X$ (M = Cr, Mo, W; L = bpy, phen, diars; X = Br, I)[90,92,93,96] and $M(CO)_3LX_2$ (L = bpy, dpe, diars; X = Cl, Br)[77,89,90,92], are diamagnetic. The limited number of known six-coordinate metal(II) complexes are paramagnetic, e.g. $Mo(CO)_2(diars)I_2$ μ_{eff} 1.98 B.M.,[92] $[Cr(CO)_2(\nu\text{-triars})I]BPh_4$ μ_{eff} 2.83 B.M.,[94] $Mo(CO)_2(py)_2X_2$ (X = Cl, Br) μ_{eff} 2.7-2.8 B.M.[42] Furthermore, octahedral molybdenum(I) compounds must be paramagnetic, since they have a d^5 electronic configuration. The ion, *trans*-$[Mo(CO)_2(dpe)_2]^+$, has a magnetic moment of 1.6 B.M., which is consistent with one unpaired electron.[89]

The two carbonyl stretching bands (Table 2.1) are in the region expected for a molybdenum(II) compound. The metal(II) cations, $[M(CO)_2(diars)_2X]^+$ (M = Cr, Mo, W; X = Br, I), show two strong carbonyl bands in the infrared in the regions 1960 - 1923 cm^{-1} and 1890 - 1852 cm^{-1} respectively.[90,92,93] These spectra were, however, only recorded as nujol mulls.

The ^{19}F NMR spectrum of $[Mo(CO)_2(dpe)_2F]PF_6$, recorded in CD_2Cl_2 at 301°K, showed a doublet ($J_{P,F}$ = 710.5 Hz) due to the hexafluorophosphate ion at -5.32 ppm (relative to CF_3CO_2H, external) and a quintet ($J_{P,F}$ = 27.8 Hz), with relative intensities 1:4:6:4:1, due to the fluorine atom coordinated to the molybdenum at +189.5 ppm. The integration ratio was 6:1. The ^{31}P NMR spectrum, also recorded at 301°K, showed a doublet ($J_{P,F}$ = 27.2 Hz) due to the dpe ligands at -47.5 ppm (w.r.t. 85% H_3PO_4, external) and a septet ($J_{P,F}$ = 710.2 Hz) due to the hexafluorophosphate ion at +144.0 ppm; the integration ratio was 4:1. No change was observed in the ^{31}P NMR spectrum on cooling the solution to 191°K, apart from a slight amount of line broadening which may be due solely to changes in viscosity. This suggests that the cation is non-fluxional.

In the ^{19}F NMR spectra[218] of the cations $[MF(PEt_3)_2(PR_3)]^+$ (M = Pt, Pd; R = Et, Ph) and of *trans*-$Ir(CO)F(PPh_3)_2$, the *cis* phosphorous-fluorine coupling constant is of the order of 28-32 Hz., while the *trans* coupling constant varies between 140 and 160 Hz. The NMR data for $[Mo(CO)_2(dpe)_2F]PF_6$ indicate that the fluorine atom coordinated to the metal is equally coupled to the four symmetrically equivalent phosphorous atoms, while the low value of the phosphorous-fluorine coupling constant suggests a *cis* arrangement between the fluorine and the phosphines; this is consistent with a tetragonally capped trigonal prismatic structure. The proposed structure is shown in Figure 2.2.

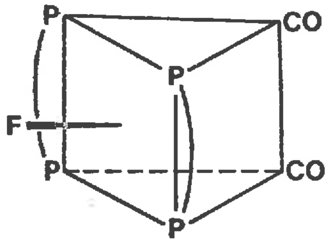


Fig. 2.2 Proposed Structure for $[Mo(CO)_2(dpe)_2F]^+$

This structure has been found for $[Mo(CO)_2(diars)_2Cl]I_3$[219] and for $[W(CO)_2(dmpe)_2I]I$.[91]

The relative energy levels of the d orbitals in the various isomers possible for seven-coordinate complexes have been determined.[221] The energy level diagram for a capped trigonal prismatic complex is shown in Figure 2.3.

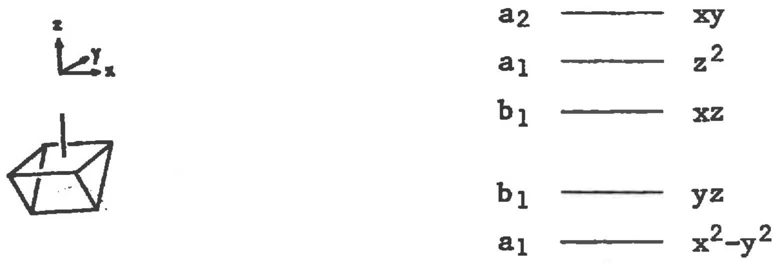


Fig. 2.3 Energy Level Diagram for a Capped Trigonal Prism.

It follows that d^4 molybdenum(II) complexes having this structure will be diamagnetic. The same conclusion follows for the other possible structures (pentagonal bipyramid, capped octahedron) and this explains the observed diamagnetism of seven-coordinate metal(II) carbonyl complexes (metal = Cr, Mo, W) in general.

The bond angle between the carbonyl groups (2θ) in a dicarbonyl complex can be calculated from the relative intensities of the two carbonyl stretching bands by using the equation[220(a)]

$$I_{sym}/I_{asy} = \cot an^2 \theta$$

where I is the intensity of the symmetric and asymmetric vibrations respectively. The band at higher frequency can be assigned to the symmetric mode.[220(b)] When this model was tested with complexes of known structure, the spectroscopically derived angles were in excellent agreement with those obtained from the crystal structure determinations.[247] The intensity ratio for $[Mo(CO)_2(dpe)_2F]PF_6$, measured in dichloromethane solution, is 1.57:1, which gives a bond angle of 77 degrees. The only direct comparison that can be made is with $[Mo(CO)_2(diars)_2Cl]I_3$, in which the bond angle, obtained from the crystal structure determination, is 67.7°.[219]

$[Mo(CO)_2(dpe)_2F]PF_6$ is very stable in the dark, but develops a brown colour on exposure to light. This is accompanied by the appearance of a broad band in the infrared spectrum between 1600 and 1700 cm^{-1}. The complex is very soluble in dichloromethane, soluble in nitromethane and acetonitrile, slightly soluble in acetone and insoluble in chloroform and methanol. The molar conductance of a 1.03×10^{-3} M solution of $[Mo(CO)_2(dpe)_2F]PF_6$ in nitromethane was 77.6 S cm^2, which is typical of a 1:1 electrolyte.[222]

The perchlorate and tetraphenylborate salts of the cation were prepared by metathetical reactions. No significant changes were observed in the carbonyl stretching frequencies as a result of these metatheses (see Table 2.1). The infrared spectra of the salts were recorded in the solid state (see Table 2.2). The spectra consisted mainly of medium intensity absorptions due to skeletal vibrations of dpe. Only two of the three possible[19,21] M-C-O bending modes could be assigned with certainty, while the M-C stretching modes could not be assigned with any degree of confidence. It is believed that one of the ν_{M-C} modes occurs below 400 cm^{-1}. These modes of vibration are at lower frequency relative to *cis*-$Mo(CO)_2(dpe)_2$,[19,21] which is consistent with decreased metal-carbonyl backbonding. The metal-

TABLE 2.1

Properties of the Fluoro Complexes

Compound	Colour	ν_{CO} $(cm^{-1})^{A}$	Λ_M $(S\ cm^2)^{B}$	Bond Angle[C] (deg.)
$[Mo(CO)_2(dpe)_2F]PF_6$	canary yellow	1945, 1889	77.6	77
$[Mo(CO)_2(dpe)_2F]ClO_4$	canary yellow	1944, 1889	-	77
$[Mo(CO)_2(dpe)_2F]BPh_4$	canary yellow	1944, 1888	-	77
$[\{Mo(CO)_2(dpe)_2\}_2F](PF_6)_3$	pale yellow	1964, 1904	227	76
$[W(CO)_2(dpe)_2F]PF_6$	canary yellow	1935, 1875	77.7	79

[A] In dichloromethane. All bands are very strong.

[B] All concentrations *c.* 1.0 × 10^{-3} M in nitromethane at 25°C.

[C] Angle between the carbonyl groups (2θ). Calculated from the equation

$\frac{I_{sym}}{I_{asy}} = \text{cotan}^2\,\theta$, where I is the band intensity. The values are believed to be accurate to ± 2°.

TABLE 2.2

Vibrational Spectra of $[Mo(CO)_2(dpe)_2F]X$ (nujol)

	Frequency (cm^{-1})		
Assignment	$X = PF_6^-$	$X = ClO_4^-$	$X = BPh_4^-$
ν_{sym} (CO)	1936 vs	1937 vs	1937 vs
ν_{as} (CO)	1886 vs	1882 vs	1879 vs
Aromatic ring	1585 w	1585 w	1575 m
vibrations	1573 w	1572 w	–
Perchlorate ν_{as} (Cl-O)	–	1100 vs, br	–
$\nu_{P-C(aromatic)}$	1100 ms	–	1100 m
Hexafluorophosphate ν_{as} (P-F)	845 vs	–	–
C-H out of plane	748 s	747 s	748 s, 739 s
def.	701 s	700 s	710 sh, 699 s
Perchlorate δ_{as} (OClO)	–	629 m	–
δ (MCO)	578 mw	582 mw	580 w
δ (MCO)	540 s	536 s	535 s
Hexafluorophosphate δ (FPF)	565 s	–	–
Other prominent	880 m, 818 m	882 m, 815 m	875 m, 819 m
bands	526 ms, 515 m	525 m, 515 ms	526 sh, 515 m
	487 w, 418 m	490 m, 418 m	488 m, 418 m

phosphorous and the metal-fluorine stretching modes could not be assigned with any certainty. The metal-fluorine stretching absorption in $NO[MoO_2F_3]$ occurs at 640 cm^{-1}.[226]

2.3 Oxidation of $Mo(CO)_2(dpe)_2$ in Nitro Solvents (Preparation of $[\{Mo(CO)_2(dpe)_2\}_2F](PF_6)_3$)

$Mo(CO)_2(dpe)_2$ reacted rapidly with nitrosonium hexafluorophosphate in nitromethane to afford a bright yellow solution with evolution of nitric oxide. The infrared spectrum showed that the solution contained a mixture of what will be called product A (80%) and $[Mo(CO)_2(dpe)_2F]PF_6$ (product B) (20%). The addition of excess nitrosonium hexafluorophosphate produced a green solution. Bands were now present in the spectrum at 1795 (mw) and 1680 (m,br) cm^{-1}. This decomposition parallels that observed in dichloromethane. In nitroethane the predominant product (80%) was B together with a small amount (20%) of A, while in nitrobenzene B was the sole product. Only a small amount of decomposition was observed in the two latter solvents.

Product A is very soluble in nitromethane and was isolated as a pale yellow powder by filtering the solution into ether. The carbonyl stretching frequencies (Table 2.1) are in reasonable agreement with the values reported by Reimann and Singleton (1969 and 1907 cm^{-1})[111] and the complete infrared spectrum is virtually the same as that for $[Mo(CO)_2(dpe)_2F]PF_6$. If, as Reimann and Singleton have postulated, product A is the di-cation, *cis*-$[Mo(CO)_2(dpe)_2](PF_6)_2$, then the complex will have an effective atomic number of only sixteen and should therefore, be very reactive with respect to coordination with any suitable electron-pair donor. It was found that product A is not a dication, but is best formulated as a dimeric fluoro-bridged species, $[\{Mo(CO)_2(dpe)_2\}_2F](PF_6)_3$.

The molar conductance in nitromethane (6.60×10^{-4} molar) is 227 S cm^2, if the complex is assumed to be dimeric. Geary[222] states that the molar conductance of a 3:1 electrolyte is in the region 220 - 260 S cm^2. If the formulation of the complex as *cis*-$[Mo(CO)_2(dpe)_2](PF_6)_2$ is assumed to be correct, the conductance of the solution (1.26×10^{-3} M) is 120 S cm^2 mol^{-1}, which is midway between a 1:1 ($\Lambda = 75 - 95$ S cm^2 mol^{-1}) and a 2:1 ($\Lambda = 150 - 180$ S cm^2 mol^{-1}) electrolyte.[222]

The ^1H NMR spectrum, recorded in $CDCl_3$, showed a resonance at δ 7.33 due to the phenyl protons and a broad resonance at δ 2.73 due to the methylene protons of the dpe, in the ratio 5:1. The compound slowly decomposed in this solvent, since the solution darkened to a brown-yellow colour and a brown precipitate formed in the tube on standing. The ^{19}F NMR spectrum, recorded in $CDCl_3$, showed, in addition to the hexafluorophosphate doublet (J = 713 Hz) at -5.3 ppm, a broad non-Gaussian resonance without fine structure at +62.4 ppm (relative to CF_3CO_2H, ext.) due to the bridging fluorine atom; the integration ratio was approximately 18:1. This resonance is at a higher frequency relative to that observed for the mononuclear complex, $[Mo(CO)_2(dpe)_2F]^+$, and this is consistent with the further deshielding of the fluorine in a bridged complex. No phosphorous-fluorine coupling was present in the ^{31}P NMR spectrum; the singlet due to the phosphorus atoms of the dpe was observed at -56.5 ppm (relative to 85% H_3PO_4), shifted slightly downfield relative to $[Mo(CO)_2(dpe)_2F]^+$.

It would be reasonable to assume that in $[\{Mo(CO)_2(dpe)_2\}_2F](PF_6)_3$ each molybdenum moiety has a capped trigonal prismatic structure. A molecular model of the complex, assuming that the fluorine atom is bonded to the face containing the phosphines, showed that the atomic radius of fluorine was too small to enable it to bridge the two molybdenum centres, because of the steric interactions between the phenyl groups. The incorporation of bridging dpe ligands into the molecule, as shown in Figure 2.4(a), significantly reduces these repulsions. An alternative structure, in which the fluorine is bonded to one of the faces containing the carbonyl groups, is shown in Figure 2.4(b). The interactions between the phenyl groups are at a minimum in the staggered conformation, which is the one shown in the Figure.

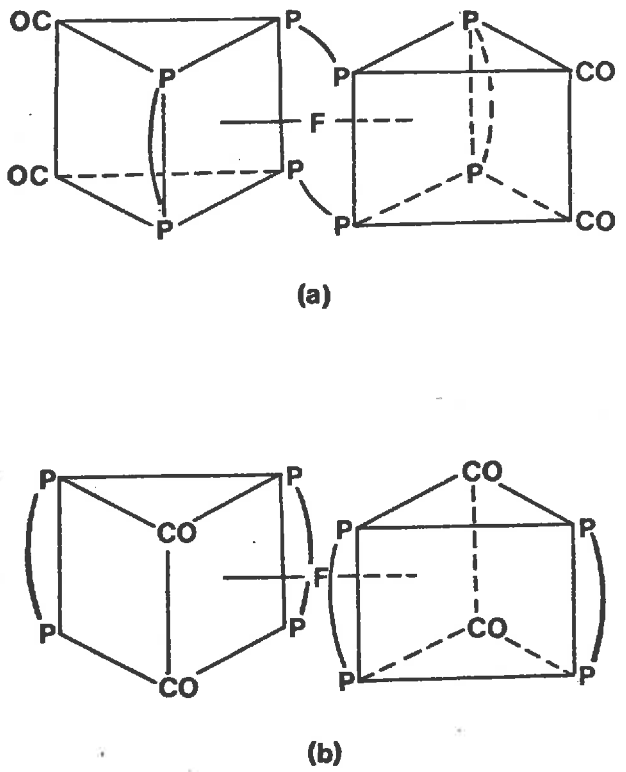


Fig. 2.4 Possible Structures for $[\{Mo(CO)_2(dpe)_2\}_2F]^{3+}$

The stability and reactions of the complex, as described in the next section, appear to favour the bridged formulation.

Bridging dpe ligands are not unusual. For example, $(C_7H_8)Mo(CO)_3$ reacts with dpe in refluxing benzene to form $Mo_2(CO)_6(dpe)_3$, however, the available data did not allow the workers to decide between one or three bridging ligands.[109] Derivatives of $(Cp)M(CO)_3X$ ($M = Mo, W$; $X = Cl, I, COCH_3$) containing bridging dpe have been prepared by several workers[223-225] mainly by reflux reactions.

2.4 Reactions of $[\{Mo(CO)_2(dpe)_2\}_2F](PF_6)_3$

$[\{Mo(CO)_2(dpe)_2\}_2F](PF_6)_3$ is very soluble in polar organic solvents. On standing in dichloromethane at room temperature the complex changed over a period of approximately 18 – 20 hours into the monofluoro cation, $[Mo(CO)_2(dpe)_2F]^+$. A small amount of decomposition also occurred and the reaction was accompanied by a colour change from pale yellow to deep yellow-brown. The progress of the reaction was followed by both infrared and ^{19}F NMR spectroscopy. The same reaction occurred in methanol. After 24 hours $[Mo(CO)_2(dpe)_2F]PF_6$ had precipitated as bright yellow crystals and the pale yellow mother liquor showed no carbonyl absorptions in the infrared. The carbonyl stretching frequencies of the product were identical to those in Table 2.1. The addition of excess tetraethylammonium fluoride to a solution of the fluoro-dimer in dichloromethane/methanol (3:1) increased the rate of formation of $[Mo(CO)_2(dpe)_2F]^+$ and only 4 – 5 hours were necessary for the reaction to proceed to completion. Furthermore, decomposition was negligible during this period of time.

The reaction of the fluoro-bridged dimer with chloride and bromide followed a completely different course. When excess tetraethylammonium bromide was added to a solution of $[\{Mo(CO)_2(dpe)_2\}_2F](PF_6)_3$ in nitromethane, a deep yellow precipitate of the dimeric complex $[Mo(CO)_2(dpe)_{1.5}Br_2]_2$ was formed, in moderate yield, after several hours stirring at room temperature. Carbon monoxide was evolved in the initial stages of the reaction, which indicates that bromide substitution of the carbonyl groups also occurs, and this explains the moderate yield of the dimeric product. The deep yellow-brown filtrate showed no carbonyl absorptions in the infrared spectrum. A yellow powder was obtained upon the addition of diethylether. However, no attempt was made to purify or characterize this solid.

$[Mo(CO)_2(dpe)_{1.5}Br_2]_2$ is soluble in dichloromethane and acetone,but insoluble in the highly polar organic solvents. The infrared spectrum of the complex in dichloromethane solution showed two very strong carbonyl stretching bands at 1939 and 1860 cm^{-1} respectively. The intensity ratio of the bands is 1.21:1, measured in dichloromethane solution, and this gives a bond angle of 85 degrees. The low frequency spectrum of the complex as a nujol mull showed absorptions at 570 (ms) and 536 (s) cm^{-1}, which are assigned as δ_{m-c-o} modes. The complex is a non-electrolyte. This is indicated by its insolubility in nitromethane and other highly polar solvents and by a molar conductance in nitrobenzene (8.55×10^{-4} M) of 0.57 S cm^2. The ^{31}P N.M.R. spectrum of the complex, recorded in $CDCl_3$, showed two resonances at -32.0 and -26.9 ppm respectively (relative to 85% H_3PO_4), with an integration ratio of 2:1.

The reaction of the cation $[\{Mo(CO)_2(dpe)_2\}_2F]^{3+}$ with excess tetraphenylarsonium chloride in nitromethane yielded the analogous chloro complex $[Mo(CO)_2(dpe)_{1.5}Cl_2]_2$ in low yield. The carbonyl stretching frequencies, recorded in dichloromethane, are 1940 (vs) and 1859 (vs) cm^{-1} respectively and the molar conductance in nitrobenzene (7.70×10^{-4} M) is 0.64 S cm^2. The deep yellow filtrate showed carbonyl absorptions at 1942 (ms) and 1876 (m) cm^{-1}, which suggests that some $[Mo(CO)_2(dpe)_2Cl]^+$ has also been formed. The preparation and characterization of this complex is described in Chapter 3. The other by-product of the reaction was a bright yellow carbonyl free solid, which was not characterized. The reaction with iodide was very slow and was not studied.

The proposed structure for the halo dimers is shown in Fig. 2.5; the two $[Mo(CO)_2(dpe)X_2]$ (X = Cl, Br) moieties are bridged by a dpe molecule.

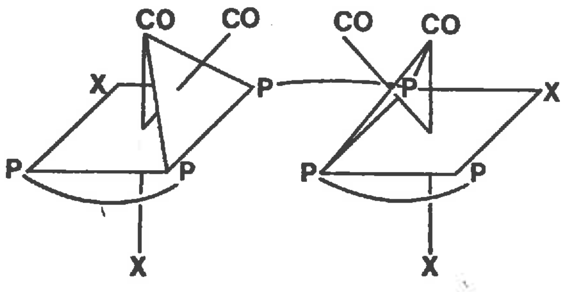


Fig. 2.5 Proposed Structure for $[Mo(CO)_2(dpe)_{1.5}X_2]_2$ (X = Cl, Br)

The stereochemistry about each molybdenum atom may be either a capped trigonal prism, a capped octahedron or, more likely, a distorted structure intermediate between the two idealized geometries. The increase in the carbonyl-carbonyl bond angle relative to $[Mo(CO)_2(dpe)_2F]PF_6$ and related complexes (see Chapter 3) is consistent with less steric hindrance about the metal and may be indicative of a change in geometry.

The structure of the seven-coordinate complex, $[Mo(CO)_2(dam)_2Cl_2]$, which contains both chelating and monodentate dam, is a relatively undistorted capped octahedron with a carbonyl group in the capping position.[248] The structures of the analogous complexes, $[Mo(CO)_2(dam)_2Br_2]$ and $[Mo(CO)_2(dpm)_2Cl_2]$, have been described as distortions from both capped octahedral[248,249] and capped trigonal prismatic geometry.[248-250] $Mo(CO)_2(PMe_2Ph)_3Br_2$ has a capped octahedral structure,[251] whereas the chlorine analogue is distorted; the molecule having approximate C_s symmetry.[252] Ligand-ligand repulsion energy calculations by Dewan *et al.*[250] for molecules of the type M(bidentate)(monodentate)$_5$ containing a bidentate ligand with a "normalized bite"[250] equal to that of dpe, calculated to be 1.3 from the data of Uchida *et al.*[253], yielded four different possible stereochemistries. The four structures are of comparable energy and the potential barriers between them are low.

The other possible formulation for the products obtained by reacting $[\{Mo(CO)_2(dpe)_2\}_2F]^{3+}$ with excess halide is the seven-coordinate species $Mo(CO)_2(dpe)_2X_2$, which contains both monodentate and chelated dpe. However, this formulation can be rejected because it is inconsistent with the NMR data. The ^{31}P NMR spectrum of this complex would show, in addition to the resonances assignable to the coordinated phosphines, a resonance due to the uncoordinated phosphine at a chemical shift comparable to that of free dpe, i.e. at approximately +13 ppm. This differentiation between bound and unbound phosphorus atoms belonging to the same ligand has been observed in the

^{31}P NMR spectra of *fac*- and *mer*-$Mo(CO)_3(dpm)_2$.[228]

2.5 Oxidation of $Mo(CO)_2(dpe)_2$ in Cyano Solvents (Preparation of Organonitrile Complexes)

A suspension of $Mo(CO)_2(dpe)_2$ in acetonitrile reacted rapidly with nitrosonium hexafluorophosphate to yield a lemon-yellow solution of the acetonitrile complex $[Mo(CO)_2(dpe)_2(MeCN)](PF_6)_2$. The addition of excess nitrosonium hexafluorophosphate produced a green solution due to decomposition to the molybdenum(III) oxidation state. This was accompanied by the appearance of decomposition bands in the infrared spectrum. The acetonitrile complex was isolated as a pale yellow powder by filtering the reaction mixture into diethylether. The complex is very soluble in dichloromethane, chloroform, acetone and acetonitrile. $[Mo(CO)_2(dpe)_2(MeCN)](BPh_4)_2$ was prepared by filtering the reaction mixture into a methanolic solution of sodium tetraphenylborate and was isolated as a pale yellow powder. The salt could not be obtained pure and always contained a small amount of hexafluorophosphate as evidenced by the elemental analyses and by the weak band in the infrared spectrum at 850 cm^{-1}. The compound is very soluble in dichloromethane, acetone and acetonitrile, insoluble in methanol and forms a gum in chloroform. $Mo(CO)_2(dpe)_2$ reacts in an identical manner with nitrosonium hexafluorophosphate in benzonitrile to yield the benzonitrile complex, $[Mo(CO)_2(dpe)_2(PhCN)](PF_6)_2$. The solubility properties are similar to those of the acetonitrile complex.

Both complexes show two very strong carbonyl stretching bands in the infrared spectrum (Table 2.3). The frequencies are identical to those observed for the cation, $[\{Mo(CO)_2(dpe)_2\}_2F]^{3+}$, within the limits of experimental error. The intensity ratios of the bands are larger than those obtained for the fluoro complexes; this suggests a slight decrease in the carbonyl-carbonyl bond angle.

The infrared spectrum of the acetonitrile cation showed a weak carbon-nitrogen stretching band, which was shifted to slightly higher frequency relative to free acetonitrile (Table 2.3). The absolute value of ν_{CN} was dependent on both the anion and the solvent used to record the spectrum. The intense carbon-nitrogen stretching absorption for neat acetonitrile occurs at 2254 cm^{-1}.[229,230] The acetonitrile spectrum also contains a strong band at 2293 cm^{-1}, which arises from the combination of the symmetric CH_3 deformation at 1374 cm^{-1} and the carbon-carbon stretching mode at 919 cm^{-1}.[229] The band derives its intensity from proximity to the carbon-nitrogen stretching band. The infrared spectrum of a very concentrated solution of $[Mo(CO)_2(dpe)_2(MeCN)](PF_6)_2$ in chloroform showed a weak absorption at 2310 cm^{-1}, which is assigned as the aforementioned combination mode. This combination band was observed in the infrared spectra of the complexes, $[MX_4(MeCN)_2]$ (M = Ti, Zr; X = Cl, Br), as an absorption of medium intensity at 2310 ± 10 cm^{-1}; the weak ν_{CN} band was present at 2285 ± 5 cm^{-1}. The carbon-nitrogen stretching absorption for the benzonitrile complex (Table 2.3) is also shifted to higher frequency relative to neat benzonitrile (2231 cm^{-1}[230]). The observed frequency is solvent dependent and the magnitude of the shift is smaller than that observed for coordination of acetonitrile. The carbon-nitrogen stretching frequencies for a series of ruthenium(II) nitrile complexes were also found to be affected by the anion and the spectral medium.[230,236]

In almost all cases, coordination of an alkyl cyanide to a transition metal results in an increase in the carbon-nitrogen stretching frequency.[232] This increase is diagnostic of complex formation via the lone pair of electrons on the nitrogen atom; i.e. acetonitrile behaves solely as a σ donor and backbonding from the metal into the π^* orbitals of the cyano group occurs only to a minimal extent. It was concluded from studies on the reaction of tungsten hexacarbonyl with acetonitrile that acetonitrile was a better σ donor and a poorer charge acceptor than carbon monoxide.[192] Moreover, it has been deduced from Mössbauer studies on iron(II) complexes that acetonitrile and benzonitrile are considerably poorer σ donors and/or π acceptors than isocyanides and carbon monoxide.[233] This is precisely the type of ligand that is required for the stabilization of the molybdenum(II) cation formed in the oxidation of $Mo(CO)_2(dpe)_2$. Benzonitrile is expected to behave in the same manner as acetonitrile. Although the phenyl ring enables the molecule to accept charge from metal ions via $d_\pi - p_\pi$ back-bonding, this is not expected to occur to any significant extent in $[Mo(CO)_2(dpe)_2(PhCN)](PF_6)_2$. Significant π-backbonding has been claimed in ruthenium(II) pentammine-nitrile complexes, where ν_{CN} decreases on coordination, but the opposite trend is observed in the ruthenium(III) analogues.[230] The increase in ν_{CN} upon coordination has been explained in terms of two perturbations: (1) a kinematic coupling of the carbon-nitrogen and the metal-nitrogen stretching vibrations[234] and (2) an increase in the CN bond force constant resulting from hybridization changes in the coordinated RCN molecule.[235] The size of $\Delta\nu_{CN}$ (change in ν_{CN} on coordination) ranges up to +105 cm^{-1} for $PhCNBF_3$,[232] while typical shifts for transition metal complexes are of the order of 30 - 40 cm^{-1}.

The molar conductivity data for both the acetonitrile and benzonitrile cations are in agreement with the formulation of the complexes as 2:1 electrolytes. The molar conductance of $[Mo(CO)_2(dpe)_2(MeCN)](PF_6)_2$ (1.00×10^{-3} M) was 185 S cm^2 in acetone and 230 S cm^2 in acetonitrile. The conductance of $[Mo(CO)_2(dpe)_2(PhCN)](PF_6)_2$ in acetone (1.00×10^{-3} M) was 183 S cm^2 mol^{-1}. All these values are well within the ranges expected for a 2:1 electrolyte.[222] The tetraphenylborate salt, $[Mo(CO)_2(dpe)_2(MeCN)](BPh_4)_2$, gave consistently low conductances of the order of 144 S cm^2 mol^{-1} in acetone and 178 S cm^2 mol^{-1} in acetonitrile. According to Geary,[222] these low values are due to the low ionic mobility of the tetraphenylborate ion.

The ^1H NMR spectrum of $[Mo(CO)_2(dpe)_2(MeCN)](PF_6)_2$ in $CDCl_3$ showed the phenyl resonance at δ 7.37, the methylene protons as a broad resonance at δ 2.68 and the acetonitrile protons at δ 1.97, which is slightly upfield from free acetonitrile (δ 2.00). The integration ratio is 40:8:3. NMR data for nitrile complexes are not reported as frequently as the infrared data, perhaps due to solubility problems. The general trend for acetonitrile complexes appears to be a shift to high field for the methyl protons relative to the free ligand.[236,237] Chatt and co-workers found no correlation between the carbon-nitrogen stretching frequency and the chemical shift of the methyl group.[236] The ^1H NMR spectrum of $[Mo(CO)_2(dpe)_2(PhCN)](PF_6)_2$, recorded in $CDCl_3$, showed the phenyl protons as a single resonance at δ 7.30 and the methylene protons as a broad resonance at δ 2.90 in the ratio of 45:8 or 5.6:1. Both complexes slowly decomposed in $CDCl_3$; the solutions developed a brown colour and a small amount of brown gelatinous precipitate formed in the NMR tube while spectra were being recorded.

2.6 Oxidation of $W(CO)_2(dpe)_2$ in Dichloromethane

Nitrosonium hexafluorophosphate reacted with a suspension of $W(CO)_2(dpe)_2$ in dichloromethane to yield initially an orange solution of *trans*-$[W(CO)_2(dpe)_2]^+$ (ν_{CO} 1860 cm^{-1}) and nitric oxide. The cation reacted further to produce a bright yellow solution containing a mixture of tungsten(I compounds. The infrared spectrum of this solution (Fig. 2.6) showed strong carbonyl bands at 1960, 1935 and 1876 cm^{-1} and a broad band at 1678 (m) cm^{-1} due to decomposition products. The two carbonyl containing complexes could be easily separated. $[W(CO)_2(dpe)_2F]PF_6$, which is almost totally insoluble in methanol, was isolated in moderate yield (35 - 40%) as bright yellow crystals upon the addition of methanol to the concentrated reaction mixture. The other major product, which gives rise to the intense carbonyl

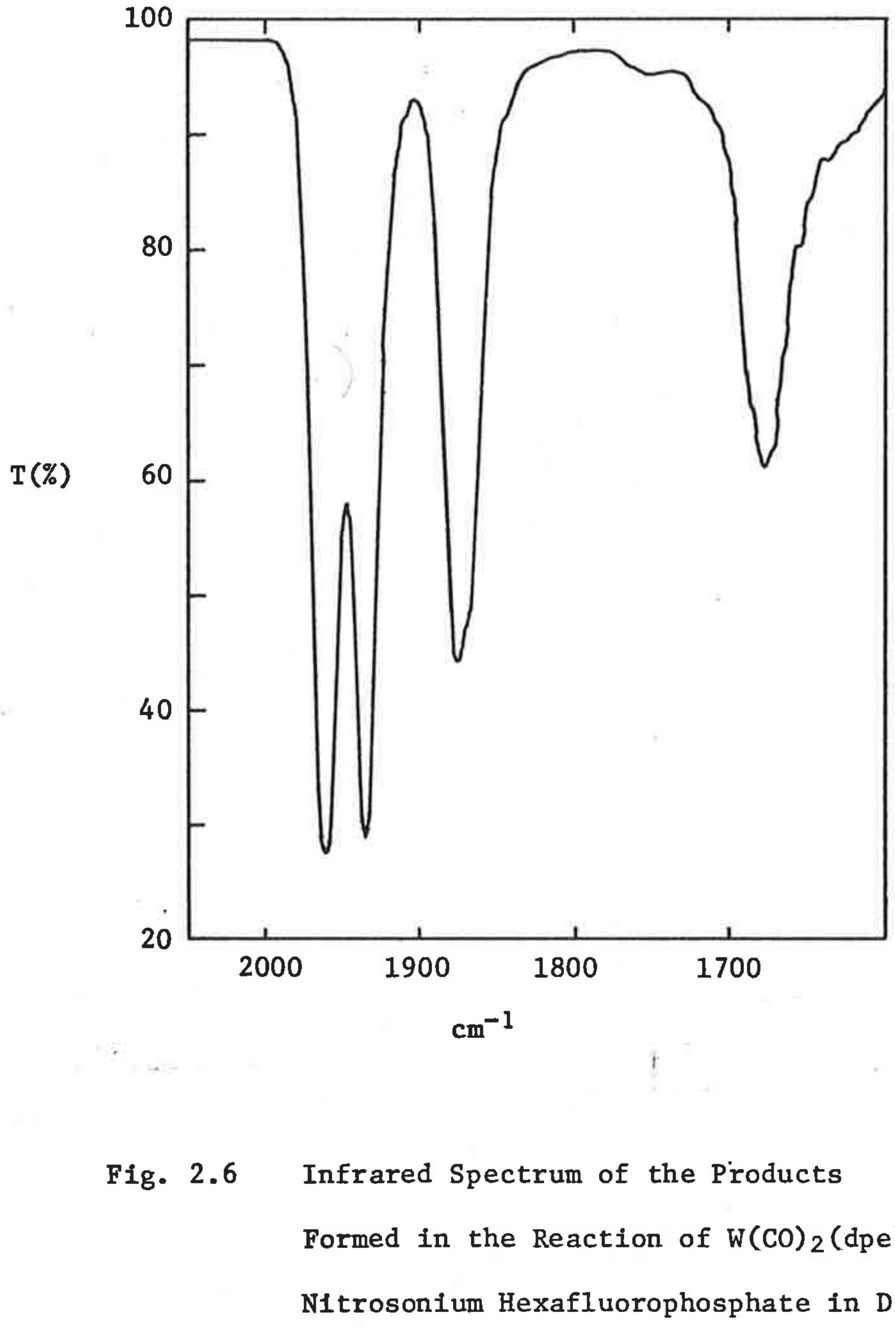


Fig. 2.6 Infrared Spectrum of the Products Formed in the Reaction of $W(CO)_2(dpe)_2$ with Nitrosonium Hexafluorophosphate in Dichloromethane.

TABLE 2.3

Properties of the Nitrile Complexes

Compound	Colour	$\nu_{CO}^{A,B}$ (cm^{-1})	ν_{CN} (cm^{-1})	R^C	Bond Angle^D (deg.)	Λ_M^E ($S\ cm^2$)
$[Mo(CO)_2(dpe)_2(MeCN)](PF_6)_2$	pale yellow	1965, 1905	2276 (w)^F	1.62	76	185
$[Mo(CO)_2(dpe)_2(MeCN)](BPh_4)_2$	pale yellow	1966, 1905	2275 (w)^A 2273 (w)^G	1.71	75	144
$[Mo(CO)_2(dpe)_2(PhCN)](PF_6)_2$	pale yellow	1964, 1905	2239 (m)^A 2234 (m)^F	1.80	73	182
$[W(CO)_2(dpe)_2(MeCN)](PF_6)_2$	pale yellow	1955^H, 1891	2271 (w)^G	-	-	-

A. In dichloromethane

B. All bands are very strong

C. $R = I_{sym}/I_{asy}$

D. Angle between the carbonyl bonds

E. Acetone solution, concentrations *c.* 10^{-3} M

F. In chloroform

G. In acetone

H. Estimated value

absorption observed at 1960 cm^{-1}, is extremely soluble in methanol and remains in solution, giving the filtrate a bright yellow colour. However, the decomposition products are also highly soluble in methanol. The carbonyl containing by-product could not be separated from the decomposition products and the complex was not characterized. Infrared monitoring of the reaction mixture showed that the by-product is already present in high concentration before the formation of $[W(CO)_2(dpe)_2F]^+$ begins. This complex is also formed in minor amounts during the preparation of $[Mo(CO)_2(dpe)_2F]PF_6$, as shown by the weak band at 1980 cm^{-1} in the infrared spectrum of the reaction mixture.

The presence of one carbonyl band in the IR spectrum is consistent with either a monocarbonyl or a *trans*-dicarbonyl complex. The latter formulation is favoured because of the inertness of tungsten carbonyl derivatives towards further substitution. The unique value of the carbonyl stretching frequency does not permit an unequivocal determination of the oxidation state. Molybdenum(II) and tungsten(II) dicarbonyl complexes generally show two bands in the infrared in the regions 1960 - 1925 cm^{-1} and 1890 - 1850 cm^{-1} respectively, e.g. $[W(CO)_2(diars)_2I]I_3$, 1925, 1852 cm^{-1}; $[Mo(CO)_2(diars)I_2]$, 1942, 1887 cm^{-1}. The carbonyl stretching frequencies of the tungsten complexes are always lower than their molybdenum analogues. A limited number of molybdenum(II) complexes containing *trans*-dicarbonyl groups of the formula $[Mo(CO)_2(dpm)_2X]X_3$ (X = Br, I) have been prepared and they show one carbonyl absorption in the infrared at 1905 cm^{-1}.[117] An increase in the carbonyl stretching frequencies is observed for trivalent complexes, e.g. $[Mo(CO)_2(diars)I_3]$ 1960, 1905 cm^{-1}. It is not known where monocarbonyl complexes in these oxidation states absorb in the infrared, since no complexes of this type have been synthezised.

The solubility properties of $[W(CO)_2(dpe)_2F]PF_6$ are similar to those of the molybdenum analogue. Two carbonyl stretching bands are present in the infrared spectrum (see Table 2.1) at frequencies slightly lower than those of $[Mo(CO)_2(dpe)_2F]PF_6$. The ratio of the band intensities is 1.47:1, which gives a carbonyl-carbonyl bond angle of 79 degrees. The complete infrared spectrum is presented in Table 2.4. The low frequency bands, apart from the δ_{MCO} modes, could not be assigned with any certainty. The molar conductance of the complex in nitromethane (1.02×10^{-3} M) is 77.7 S cm^2, which is consistent with the formulation of the complex as a 1:1 electrolyte.

2.7 Oxidation of $W(CO)_2(dpe)_2$ in Nitromethane

A suspension of $W(CO)_2(dpe)_2$ in nitromethane reacted rapidly with nitrosonium hexafluorophosphate to give a yellow solution. The infrared spectrum of the solution (Fig. 2.7) indicated that a mixture of products had been formed, since carbonyl bands were present at 1960 (vs), 1934 (s), 1890 (ms) and 1876 (ms) cm^{-1} respectively. The addition of excess nitrosonium hexafluorophosphate resulted in decomposition, producing a green solution. A pale yellow powder was isolated by filtering the reaction mixture into diethylether. The infrared spectrum of the powder, recorded in dichloromethane solution, was similar to that of the reaction mixture.

The carbonyl stretching bands at 1934 and 1875 cm^{-1} indicate that $[W(CO)_2(dpe)_2F]PF_6$ is one of the minor products of the reaction. The ratio of the intensities of the bands at 1960 and 1890 cm^{-1} is 3.5:1, whereas the corresponding ratios for $[M(CO)_2(dpe)_2F]^+$ (M = Mo, W) and $[\{Mo(CO)_2(dpe)_2\}_2F]^{3+}$ are approximately 1.5:1. This suggests that the two bands are not due to a single complex. The band at 1890 cm^{-1} implies that the other minor product is the fluoro-bridged dimer, $[\{W(CO)_2(dpe)_2\}_2F]^{3+}$. The other band for this cation is estimated to be at approximately 1955 cm^{-1} and is, of course, buried beneath the absorption at 1960 cm^{-1}. The major product of the reaction is the compound which gives rise to the intense carbonyl absorption at 1960 cm^{-1}. It is believed that this complex is identical to the one formed as a by-product in the preparation of $[W(CO)_2(dpe)_2F]PF_6$. The

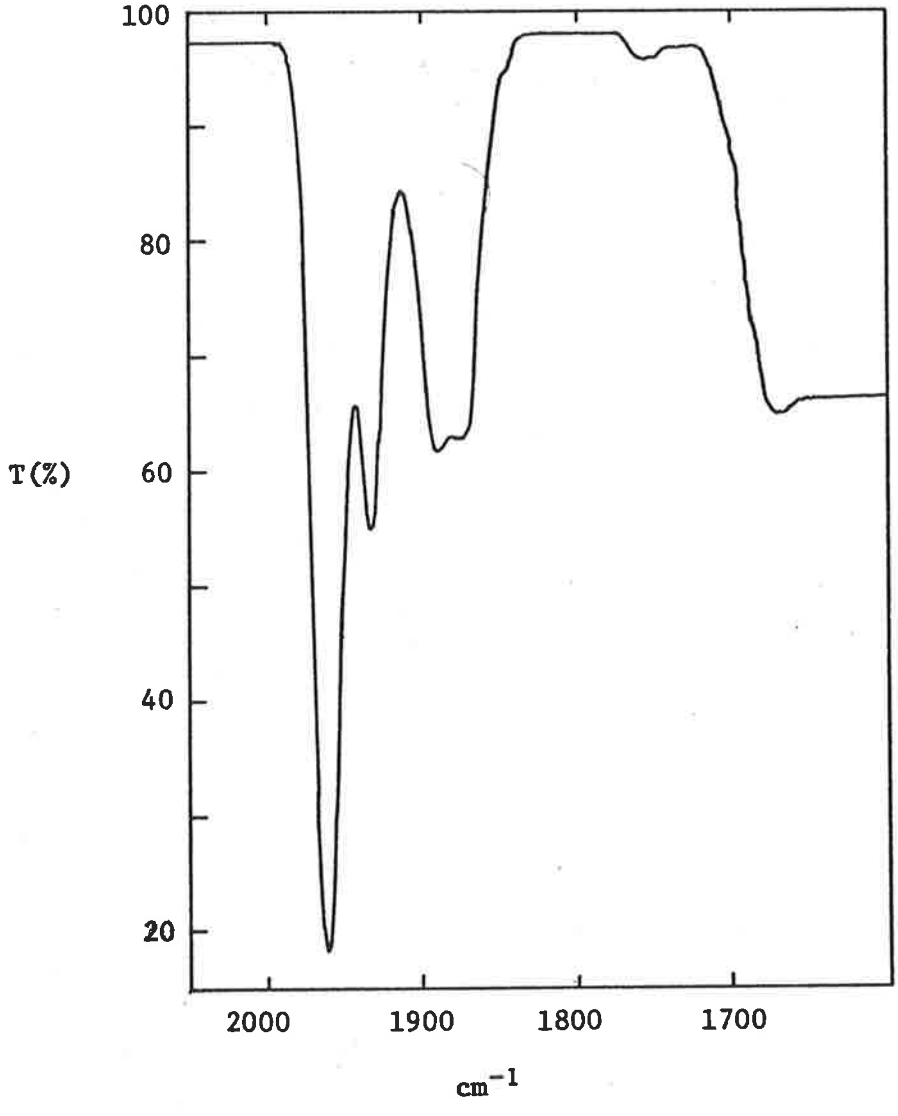


Fig. 2.7 Infrared Spectrum of the Products Formed in the Reaction of $W(CO)_2(dpe)_2$ with Nitrosonium Hexafluorophosphate in Nitromethane.

TABLE 2.4

Vibrational Spectrum of $[W(CO)_2(dpe)_2F]PF_6$ (nujol)

Assignment	Frequency (cm^{-1})
ν_{sym} (CO)	1930 vs
ν_{as} (CO)	1876 vs
Aromatic ring vibrations	1587 vw 1574 vw
$\nu_{P-C(aromatic)}$	1100 mw
Hexafluorophosphate ν_{as} (P-F)	844 vs
C-H out of plane def.	747 s 700 s
Hexafluorophosphate δ (FPF)	565 s
δ (MCO)	570 sh
δ (MCO)	542 s
Other prominent bands	880 m, 819 m 526 m, 518 m 505 m, 498 m 418 m

reaction products could not be separated, because they all have high solubilities in organic solvents.

The elemental microanalyses of the yellow powder, as could be expected, did not fit the calculated values for either $[W(CO)_2(dpe)_2F]PF_6$ or $[\{W(CO)_2(dpe)_2\}_2F](PF_6)_3$. The analyses did, however, indicate that there is only one hexafluorophosphate ion per formula unit, which implies a single positive charge per tungsten moiety. Furthermore, the analyses suggest that the major reaction product does not contain coordinated fluorine. The molar conductance of the complex in nitromethane (*c*. 1.0×10^{-3}M) assuming a molecular weight of 1200, is approximately 77 S cm^2, which is consistent with a singly charged cation.

No change was observed in the infrared spectrum when a dichloromethane solution of the yellow powder was allowed to stand at room temperature for 10 hours, or when an excess of tetraethylammonium bromide was added to the solution. The complex did, however, react with fluoride, but the product was not the fluoro-cation $[W(CO)_2(dpe)_2F]^+$. Broad carbonyl bands were present at 1903 and 1817 cm^{-1}.

2.8 Oxidation of $W(CO)_2(dpe)_2$ in Acetonitrile

$W(CO)_2(dpe)_2$ reacts rapidly with nitrosonium hexafluorophosphate in acetonitrile to yield a bright yellow solution. The infrared spectrum of the solution showed carbonyl bands at 1959 (vs) and 1891 (s) cm^{-1} in the ratio of 2.4:1. A pale yellow powder was isolated by filtering the reaction mixture into diethylether. The carbonyl stretching frequencies of the powder together with the relative band intensities, measured in dichloromethane, were identical to those for the reaction mixture.

The argument presented in the previous section suggests that a mixture of two complexes has been formed. The minor product can be identified as $[W(CO)_2(dpe)_2(MeCN)](PF_6)_2$ and the infrared absorption at 1891 cm^{-1} is due to this complex. The frequency of the other band is estimated to be 1955 cm^{-1}. Further evidence for the formation of this complex is provided by the weak C-N stretching absorption at 2271 cm^{-1} (acetone solution). The major product of the reaction is the complex which gives rise to the intense absorption at 1959 cm^{-1} and it is thought that this complex is identical to those formed in nitromethane and dichloromethane which show the identical carbonyl absorption.

The elemental analyses of the powder indicate a mixture of complexes; the major component being monocationic and the minor component being dicationic. The molar conductance of the product in acetone (*c*. 9.6×10^{-4} M), assuming that it consists solely of the acetonitrile complex, was approximately 130 S cm^2, which is in the range expected for a 1:1 electrolyte.[222] This result confirms the conclusions deduced above. The powder is insoluble in chloroform and the ^{1}H NMR spectrum was not recorded. The two products could not be separated due to similar solubilities in organic solvents.

2.9 Oxidation of $Cr(CO)_2(dpe)_2$

It was concluded from an electrochemical investigation that *trans*-$[Cr(CO)_2(dpe)_2]^+$ could be reversibly oxidized to the dication, *trans*-$[Cr(CO)_2(dpe)_2]^{2+}$ and that the dication is stable on the electrochemical time scale.[113] $Cr(CO)_2(dpe)_2$ (*cis* or *trans*) reacted rapidly with nitrosonium hexafluorophosphate in dichloromethane with evolution of nitric oxide to form a yellow solution of the known cation, *trans*-$[Cr(CO)_2(dpe)_2]^+$ (ν_{CO} 1850 (vs) cm^{-1}). The cation was oxidized further with the concomitant loss of carbon monoxide to produce a green solution containing chromium(III) species. The only change observed in the infrared spectrum was the disappearance of the band at 1850 cm^{-1}; there was no evidence for the formation of any chromium(II) compounds in significant concentrations. The addition of excess nitrosonium hexafluorophosphate resulted in decomposition of the green solution to a purplish-black colour. A similar reaction was observed in acetonitrile. There was no infrared evidence for the formation of an acetonitrile complex. $Cr(CO)_4(dpe)$ is oxidized by nitrosonium hexafluorophosphate in methanol/toluene to $[Cr(CO)_4(dpe)]PF_6$. In acetonitrile complete loss of carbon monoxide occurs to give $[Cr(NO)_2(MeCN)_4](PF_6)_2$.[112]

When nitromethane was used as the solvent, the neutral chromium complex was oxidized extremely rapidly (in the order of a few seconds) to a green solution, which quickly changed to yellow and finally to red. Since the green colour can be attributed to the chromium(III) oxidation state, the chromium(I) and (II) carbonyl complexes have only a transient existence in this solvent under strongly oxidizing conditions. Even the chromium(III) state has only slight stability and is readily oxidized further; the final oxidation state probably being +6. The infrared spectrum of the red solution showed a strong broad band at 1850 cm^{-1}. Cooling the reaction mixture did not significantly alter the rate of the reaction.

The cation, *trans*-$[Cr(CO)_2(dpe)_2]^+$, is easier to oxidize than the molybdenum or tungsten analogues.[113] On the other hand, the molybdenum and tungsten dications are able to accept another ligand into their coordination sphere, which the chromium(II) cation appears to be unable to do, possibly because of the smaller atomic radius of chromium and the resultant increase in steric hindrance of the phenyl groups. A major consequence of this is that the seven-coordinate molybdenum(II) and tungsten(II) complexes are reasonably resistant to further oxidation, as shown by the electrochemistry of $[Mo(CO)_2(dpe)_2F]PF_6$, while the six-coordinate chromium(II) cation is not stabilized in this manner. The oxidation to chromium(III) is reasonably facile, since the standard electrode potential for the equation:

$$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$$

in aqueous solution is -0.41V[246(a)] and thus, in the absence of any stabilizing influence, the chromium(II) cation will be further oxidized.

2.10 Discussion

The oxidation of $M(CO)_2(dpe)_2$ (M = Mo or W) by nitrosonium hexafluorophosphate in non-donor solvents has resulted in the formation of the first examples of phosphine-substituted fluorocarbonyl complexes of the group VIa metal carbonyls. Fluorocarbonyl complexes, both substituted and unsubstituted, are a relatively rare class of compound. The parent group VIa fluorocarbonyl anions, $[M(CO)_5F]^-$ (M = Cr, W), have only been recently prepared.[50,51] The only examples of substituted complexes that were found in the literature are the analogues of Vaska's compound, $MF(CO)(PPh_3)_2$ (M = Ir or Rh).[186-189] This dearth may be due to either instability of the products or a lack of convenient synthetic routes.

The source of fluoride is undoubtedly the hexafluorophosphate ion and probably involves the following equation:

$$PF_6^- \longrightarrow PF_5 + F^-$$

However, the rate of this reaction is extremely slow. The hexafluorophosphate ion is very stable in both alkaline and neutral solution and many salts are known.[238] The ion is slowly hydrolyzed in acidic media to form the orthophosphate ion.[238,239] A dissociative mechanism has been postulated with the rate determining step being the initial dissociation of one of the phosphorous-fluorine bonds.[239] The aquation is accelerated by alkali metal ions[240] and metal ion catalysis has been observed for Be(II), Al(III), Zr(IV) and Th(IV).[241] The six-coordinate metal(II) cation, $[M(CO)_2(dpe)_2]^{2+}$, that is initially formed in the oxidation of $M(CO)_2(dpe)_2$ (M = Mo, W) by nitrosonium hexafluorophospate must, therefore, abstract fluorine from the hexafluorophosphate ion. The initial step appears to involve capture of the hexafluorophosphate ion by the dication to give a transient $[M(CO)_2(dpe)_2F\text{-}PF_5]^+$ species from which PF_5 is rapidly eliminated.[254] Fluoride abstraction occurred in the reaction of $(Cp)Mo(CO)_3MCl_3$ (M = Si, Ge) with silver hexafluorophosphate to give $(Cp)Mo(CO)_3MF_3$.[242]

Nitrosonium hexafluorophosphate is an extremely versatile reagent in organometallic syntheses [243] and its reactions have been recently reviewed.[244] The usual mode of reaction of the nitrosonium ion is ligand substitution to form nitrosyl complexes. This type of reaction is generally observed for relatively unsubstituted metal carbonyl complexes,as shown by the following examples:[112,245]

$$M(CO)_4(dpe) \xrightarrow[MECN]{NOPF_6} [M(CO)_3(NO)(dpe)]PF_6 \quad (M = Mo, W)$$

$$Fe(CO)_3(PPh_3)_2 \xrightarrow[MeOH/C_6H_6]{NOPF_6} [Fe(CO)_2(NO)(PPh_3)_2]PF_6 .$$

In protic solvents the ion can behave as a proton source, according to the equation:

$$NOPF_6 + MeOH \rightleftarrows MeONO + HPF_6$$

and this may result in the formation of hydrido complexes.[243,245] In weakly coordinating solvents, such as dichloromethane or benzene, the nitrosonium ion can behave as a powerful one-electron oxidizing agent.[111,112,167,243] Thus, species of the type *fac*-$Mn(CO)_3L_2Br$ ($L = PMe_3$, $P(OMe)_3$ etc.) are oxidized to the corresponding cations, *fac*-$[Mn(CO)_3L_2Br]^+$.[167]

As the degree of substitution of a metal carbonyl by phosphine ligands increases, the electron density on the metal also increases, which results in a strengthening of the metal-carbon bond. The remaining carbonyl groups, therefore, become increasingly more difficult to substitute. Chatt and Watson[58] found that it was impossible to displace carbon monoxide from $Mo(CO)_2(dpe)_2$ by heating the complex with excess phosphine. It follows from the above reasoning that substitution of the carbonyl groups in $M(CO)_2(dpe)_2$ ($M = Cr, Mo, W$) by the nitrosonium ion is an unfavourable process and thus, the alternative mode of reaction, namely oxidation, proceeds exclusively. The resultant metal(II) cations ($M = Mo, W$), which are 16 electron systems, are stabilized by the acceptance of a σ donor ligand into the coordination sphere. On the other hand, the coordination of nitrosyl to these cations would have a destabilizing effect, since the nitrosyl group, in addition to being a σ donor, is also an excellent π acceptor and bonds to metal ions in a manner analogous to carbon monoxide.

2.11 Experimental

General

All preparations and reactions except metatheses were carried out in an atmosphere of high-purity dry nitrogen. Nitrosonium hexafluorophosphate was manipulated in a nitrogen-filled dry box. Solvents were of analytical grade purity and were dried over Linde 4A molecular sieves before use. All compounds were stored in the dark as they turned either brown or green when exposed to light for a few hours. The light petroleum used in the experiments had b.p. < 40°. The preparations of the starting materials are described in Appendices 1 and 2. The instruments used for the physical measurements are described in Appendix 1. Carbonyl stretching frequencies were usually recorded in dichloromethane solution and complete spectra as nujol mulls between potassium bromide plates.

$[Mo(CO)_2(dpe)_2F]PF_6$

$Mo(CO)_2(dpe)_2$ (427 mg, 0.450 mmol) and $NOPF_6$ (162 mg, 0.923 mmol, i.e. 2.05:1) were mixed within a dry box. Dichloromethane (6 ml) was added and the mixture was rapidly stirred for 10 - 15 min. until the solid had completely dissolved to a green solution. The reaction mixture was eluted through a short (5 cm) column of alumina with dichloromethane. The bright yellow eluate was concentrated to a few millilitres, methanol (*c.* 10 ml) was added and canary yellow crystals of $[Mo(CO)_2(dpe)_2F]PF_6$ (260 mg) separated on cooling. These were filtered, washed with methanol and dried in a vacuum.

(Found: C, 58.3; H, 4.4; F, 12.1; P, 13.8.
$C_{54}H_{48}F_7MoO_2P_5$ requires: C, 58.3; H, 4.4; F, 12.0; P, 13.9%).

$[Mo(CO)_2(dpe)_2F]X$ $(X = BPh_4, ClO_4)$

A very concentrated solution of $NaBPh_4$ in methanol was added dropwise with shaking to a solution of $[Mo(CO)_2(dpe)_2F]PF_6$ (97 mg) in dichloromethane (0.4 ml) until precipitation commenced. The canary yellow crystals of $[Mo(CO)_2(dpe)_2F]BPh_4$ (103 mg, 93%) were washed liberally with methanol and light petroleum, and dried in a vacuum.

(Found:	C, 70.7; H, 5.3; F, 1.7; P, 9.6.
$C_{78}H_{68}BFMoO_2P_4$ requires:	C, 72.8; H, 5.3; F, 1.5; P, 9.6%).

For the perchlorate salt a concentrated solution of $LiClO_4$ in methanol was added to a dichloromethane or acetone solution of $[Mo(CO)_2(dpe)_2F]PF_6$. The canary yellow crystals were treated as above.

$[\{Mo(CO)_2(dpe)_2\}_2F](PF_6)_3$

This fluoro-bridged complex was prepared by slowly adding $NOPF_6$ to a vigorously stirred suspension of $Mo(CO)_2(dpe)_2$ (100 mg) in nitromethane (2.0 ml) until the solution was bright yellow. The solution was filtered with stirring into diethyl ether (60 ml). The pale yellow powder (90 mg) was filtered, washed with light petroleum and dried in a vacuum. The complex always contained a small amount of $[Mo(CO)_2(dpe)_2F]PF_6$.

(Found:	C, 51.5; H, 4.2; F, 17.3; P, 13.9.
$C_{108}H_{96}F_{19}Mo_2O_4P_{11}$ requires:	C, 55.2; H, 4.1; F, 15.4; P, 14.5%).

Reaction of $[\{Mo(CO)_2(dpe)_2\}_2F](PF_6)_3$ with Halide

(i) Bromide: Excess solid Et_4NBr was added to a solution of the complex prepared as above from $Mo(CO)_2(dpe)_2$ (100 mg) in nitromethane (1.30 ml). The mixture was stirred for 2.5 - 3 hrs. The deep yellow precipitate of $[Mo(CO)_2(dpe)_{1.5}Br_2]_2$ (45 mg) was filtered, washed with nitromethane, and light petroleum, and dried in a vacuum.

(Found:	C, 55.3; H, 4.0; Br, 16.1; P, 10.5.

$C_{82}H_{72}Br_4Mo_2O_4P_6$ requires: C, 54.2; H, 4.0; Br, 17.6; P, 10.2%).

(ii) Chloride: Similarly solid Ph_4AsCl was used to yield $[Mo(CO)_2(dpe)_{1.5}Cl_2]_2$ (30 mg).

(Found: C, 58.9; H, 4.5; Cl, 8.7; P, 10.8.

$C_{82}H_{72}Cl_4Mo_2O_4P_6$ requires: C, 60.0; H, 4.4; Cl, 8.7; P, 11.3%).

(iii) Fluoride: Solid Et_4NF was added to a solution of the bridged fluoro complex in dichloromethane/methanol (3:1). On standing for 4-5 hrs. at room temperature, the infrared solution spectrum showed complete conversion to $[Mo(CO)_2(dpe)_2F]^+$.

$[Mo(CO)_2(dpe)_2(MeCN)](PF_6)_2$

In a dry box, $NOPF_6$ was added slowly and with vigorous stirring to a suspension of $Mo(CO)_2(dpe)_2$ (110 mg) in acetonitrile (2.0 ml) until the solution was bright yellow (excess $NOPF_6$ causes the solution to turn green and should be added very carefully when the colour of the solution is orange). The solution was filtered dropwise into stirred diethyl ether (60 ml). The pale yellow powder (110 mg) was filtered, washed free of acetonitrile with diethyl ether and dried in a vacuum.

(Found: C, 51.5; H, 4.2; F, 17.3; P, 13.9.

$C_{56}H_{51}F_{12}MoNO_2P_6$ requires: C, 52.6; H, 4.0; F, 17.8; P, 14.5%).

$[Mo(CO)_2(dpe)_2(MeCN)](BPh_4)_2$

The solution of $[Mo(CO)_2(dpe)_2(MeCN)](PF_6)_2$ in acetonitrile was filtered with stirring into a solution of $NaBPh_4$ (350 mg) in methanol (30 ml). The yellow precipitate (110 mg) was filtered, washed with methanol and light petroleum, and dried in a vacuum. The salt could not be obtained free of hexafluorophosphate.

(Found: C, 73.4; H, 5.6; F, 3.1; P, 8.3.

$C_{104}H_{91}BMoNO_2P_4$ requires: C, 76.7; H, 5.6; F, 0; P, 7.6%).

$[Mo(CO)_2(dpe)_2(PhCN)](PF_6)_2$

The method is identical to that for the acetonitrile complex, except that $Mo(CO)_2(dpe)_2$ forms a solution; yield 110 mg.

(Found: C, 53.3; H, 4.1; F, 17.0; P, 13.2

$C_{61}H_{53}F_{12}MoNO_4P_6$ requires: C, 54.7; H, 4.0; F, 17.0; P, 13.9%).

$[W(CO)_2(dpe)_2F]PF_6$

$NOPF_6$ was added slowly and with vigorous stirring to a suspension of $W(CO)_2(dpe)_2$ (100 mg) in dichloromethane (2.5 ml) until the solution was bright yellow. The solution was filtered, concentrated to a minimum volume and methanol (*c.* 10 ml) was added. On standing, $[W(CO)_2(dpe)_2F]PF_6$ precipitated as bright yellow crystals (27 mg), which were filtered, washed with methanol and dried in a vacuum. A second crop of crystals (18 mg) was obtained by concentrating the filtrate to approximately 2 mls.

(Found: C, 54.0; H, 4.3; F, 11.5; P, 11.5

$C_{54}H_{48}F_7O_2P_5W$ requires: C, 54.0; H, 4.0; F, 11.1; P, 12.9%).

The bright yellow mother liquor showed an intense absorption in the infrared spectrum at 1960 cm^{-1} as well as a strong band at 1670 (br) cm^{-1}.

Reaction of $W(CO)_2(dpe)_2$ with $NOPF_6$ in Polar Solvents

(i) Nitromethane

A suspension of $W(CO)_2(dpe)_2$ (100 mg) in nitromethane (2.0 ml) was treated with $NOPF_6$ with rapid stirring until the solution was bright yellow. The solution was filtered dropwise with stirring into diethyl ether (60 ml). The pale yellow powder (80 mg) was filtered, washed free of nitromethane with ether and dried in a vacuum.

(Found: C, 49.5; H, 4.2; F, 9.4; P, 11.6%).

(ii) Acetonitrile

An identical procedure was used to yield a pale yellow powder (100 mg).

(Found: C, 48.4; H, 3.8; F, 11.9; P, 12.3%).

CHAPTER 3

OXIDATION OF $M(CO)_2(DPE)_2$ (M = Cr, Mo or W)

3.1 Introduction

Complexes of the formula $M(CO)_2(dpe)_2$ (M = Cr, Mo or W) have been prepared by several methods, which are summarized in Appendix 2. The molybdenum and tungsten complexes are isolated solely as the *cis*-isomers, whereas both the *cis*- and *trans*-isomers of $Cr(CO)_2(dpe)_2$ can be prepared.

Cis-$M(CO)_2(dpe)_2$ (M = Mo, W) is oxidized by iodine (1.5 moles) to the cation, *trans*-$[M(CO)_2(dpe)_2]^+$, which was isolated as the triiodide salt.[89] Treatment with silver perchlorate resulted, not in oxidation, but in metathesis to give *trans*-$[M(CO)_2(dpe)_2]ClO_4$.[89] The molybdenum(0) and tungsten(0) complexes are also oxidized by atmospheric oxygen in mildly acidic tetrahydrofuran to form the *trans*- metal(I) cation;[110,255] the anion in this case depends on the nature of the acid.[110] The reaction is reversible and addition of dilute alkali to a solution of the cation regenerates the neutral complexes quantitatively.[110] The complex *trans*-$Cr(CO)_2(dpe)_2$, in dichloromethane solution, undergoes a facile oxidation on exposure to air to form the cation, *trans*-$[Cr(CO)_2(dpe)_2]^+$.[110]

The hydride complex $[Mo(CO)_2(dpe)_2H]^+[(CF_3CO_2)_2H]^-$ has been prepared by the addition of a large excess of trifluoroacetic acid to *cis*-$Mo(CO)_2(dpe)_2$ in dichloromethane.[256] The complex has also been prepared using fluorosulphonic acid.[227] Treatment of $M(CO)_2(dpe)_2$ (M = Mo, W) with mercuric halide gave adducts of the formula $[M(CO)_2(dpe)_2HgX]HgX_3$ (X = Cl, Br, I). Attempted recrystallization resulted in dissociation to reform the neutral dicarbonyl complexes.[257]

In this chapter, direct oxidations to the metal(II) oxidation state by a variety of oxidants including nitrosyl chloride, bromine and iodine are described, together with the reactions of the products. The results are summarized in the scheme following page 114.

3.2 Preparation of $[Mo(CO)_2(dpe)_2X]^+$ (X = Cl, Br or I)

(a) $[Mo(CO)_2(dpe)_2Cl]^+$

When nitrosyl chloride, diluted with dry nitrogen, was bubbled into a suspension of $Mo(CO)_2(dpe)_2$ in dichloromethane, the neutral complex dissolved to form a bright red solution of the known cation, *trans*-$[Mo(CO)_2(dpe)_2]^+$. The cation reacted further to afford a bright yellow solution of the seven-coordinate molybdenum(II) complex $[Mo(CO)_2(dpe)_2Cl]Cl$, which was isolated as a bright yellow microcrystalline solid upon the addition of carbon tetrachloride. An attempted precipitation with light petroleum produced an oil. The compound is very soluble in the common polar organic solvents. The tetraphenylborate salt was prepared as bright yellow crystals by metathesis with sodium tetraphenylborate in dichloromethane-methanol. The sodium chloride produced in the reaction could not be completely removed, even though the crystals were washed with water. The compound is soluble in dichloromethane and nitrobenzene and slightly soluble in acetone, nitromethane and acetonitrile.

The colour changes mentioned above were observed when phosphorous pentachloride was added to a suspension of $Mo(CO)_2(dpe)_2$ in dichloromethane. The infrared spectrum of the resultant bright yellow solution indicated that oxidation to $[Mo(CO)_2(dpe)_2Cl]^+$ had occurred. The complex was not isolated. Chloro complexes have been prepared by oxidation with antimony pentachloride. Thus, treatment of $W(CO)_3(\nu\text{-triars})$ and $W(CO)_2(QP)$ gave $[W(CO)_3(\nu\text{-triars})Cl]SbCl_6$[95] and $[W(CO)_2(QP)Cl]SbCl_6$[68] respectively.

Two very strong carbonyl stretching bands (Table 3.1) are present in the infrared spectra of $[Mo(CO)_2(dpe)_2Cl]X$ (X = Cl, BPh_4). The relative intensities of the bands indicate a carbonyl-carbonyl bond angle of 77°. The complete infrared spectra are presented in Table 3.2. The molar conductance of the chloride salt in acetone (1.15×10^{-3} M) was 111 S cm^2, which is typical of a 1:1 electrolyte.[222] The conductance of the tetraphenylborate salt was consistently low; the value in acetone (8.00×10^{-4} M) being 78 S cm^2 mol^{-1}.

The usual mode of reaction of nitrosyl chloride is as a nitrosylating agent, as shown by the following equations:[244]

$$M(CO)_{6-x}(PPh_3)_x \xrightarrow{NOCl} M(NO)Cl_3(OPPh_3)_x \qquad M = Mo, W;\ x = 2, 3$$

$$M(CO)_6 \xrightarrow{NOCl} [M(NO)_2Cl_2]_n \qquad M = Mo, W$$

Under certain circumstances the halide does not coordinate and, formally, NO$^+$ has been added to replace one CO; for example:

$$Fe(CO)_3L_2 \xrightarrow{NOCl} [Fe(NO)(CO)_2L_2]^+$$

$$[CpM(CO)_3]^- \xrightarrow{NOCl} CpM(CO)_2(NO) \qquad M = Cr, Mo, W$$

In the reaction of nitrosyl chloride with $Mo(CO)_2(dpe)_2$, the nitrosyl halide behaves solely as a one-electron oxidant producing the molybdenum(II) cation, which is stabilized by the coordination of chloride. The nitric oxide produced in the reaction does not coordinate to the metal. The reaction is thus analogous to that observed for nitrosonium hexafluorophosphate. Oxidation was observed in the reactions of nitrosyl chloride with the anions $[Re(CO)_5]^-$ and $[CpFe(CO)_2]^-$ producing $Re_2(CO)_{10}$ and $[CpFe(CO)_2]_2$ respectively.[244]

As was explained in Chapter 2.10, the carbonyl groups in $Mo(CO)_2(dpe)_2$ are harder to displace than those in relatively unsubstituted complexes, so that the most facile mode of reaction is oxidation. The molybdenum(II) cation, initially formed in the reaction, appears to be preferentially stabilized by the coordination of a negatively charged ligand.

A similar reaction is expected for the other nitrosyl halides, but, as will be discussed below, more convenient synthetic routes to these complexes are available.

(b) $[Mo(CO)_2(dpe)_2Br]^+$

The bromo complex was prepared by treating a suspension of

$Mo(CO)_2(dpe)_2$ in dichloromethane with a solution of bromine (2.2 - 2.3 equivalents) in carbon tetrachloride. The reaction proceeded smoothly producing initially an orange solution, which changed to bright yellow. The product was isolated as the tribromide salt, $[Mo(CO)_2(dpe)_2Br]Br_3$, $1.5CCl_4$, in the form of bright yellow microcrystals upon the addition of carbon tetrachloride. The reaction must be carried out briskly with the product being isolated after a period of approximately eight minutes, otherwise the complex begins to react with the tribromide ion, as described in section 4.

The presence of carbon tetrachloride of crystallization was confirmed by the elemental microanalyses and by the bands in the infrared spectrum (Table 3.3). The solvent of crystallization could be removed by stirring the solid with diethylether for approximately 90 minutes. When the solid was heated in a vacuum, decomposition of the complex began before the solvent of crystallization was completely removed. $Mo(CO)_2(dpe)_2$ was treated with one equivalent of bromine in an attempt to prepare the bromo complex as the mono-bromide salt. An orange non-crystalline powder was isolated from the bright orange reaction mixture. The infrared and UV/visible spectra both showed that the solid was a mixture of $[Mo(CO)_2(dpe)_2Br]Br$ and *trans*-$[Mo(CO)_2(dpe)_2]Br$.

The salts, $[Mo(CO)_2(dpe)_2Br]X$ ($X = ClO_4^-$, BPh_4^-, PF_6^-), were prepared by adding a methanolic solution of NaX to a dichloromethane solution of $[Mo(CO)_2(dpe)_2Br]Br_3,1.5CCl_4$. All three compounds were isolated as bright yellow crystals. The perchlorate salt crystallized with one molecule of dichloromethane of crystallization, while the other two were solvent free. The other product of the metathesis was sodium bromide, but this was easily removed by washing the solids with water. The tribromide salt is very soluble in the common organic solvents; the perchlorate, hexafluorophosphate and tetraphenylborate salts are soluble in acetone and dichloromethane, insoluble or slightly soluble in methanol and insoluble in chloroform.

Two strong carbonyl stretching bands are present in the infrared spectra of the bromo compounds and these are recorded in Table 3.1 together with the carbonyl-carbonyl bond angles. The complete infrared spectra of the various salts are presented in Table 3.3. The molar conductances in nitromethane (Table 3.1) are typical of 1:1 electrolytes.[222] The molar conductance of a freshly prepared solution of the tribromide salt in acetone ($M = 1.04 \times 10^{-3}$) was 100 S cm^2. The conductance of the solution decreased fairly rapidly with time and the yellow solution developed an orange colour. The conductance of this salt in nitromethane also decreased with time, but at a much slower rate. The reason for this change is fully discussed in section 4.

(c) $[Mo(CO)_2(dpe)_2I]^+$

$Mo(CO)_2(dpe)_2$ is known to react with iodine (1.5 equivalents) in dichloromethane to form the molybdenum(I) complex *trans*-$[Mo(CO)_2(dpe)_2]I_3$.[89] When a dichloromethane solution of this complex, prepared *in situ* as above, was stirred with a large excess of iodine (approximately 12 equivalents), further oxidation occurred to yield the molybdenum(II) iodo complex $[Mo(CO)_2(dpe)_2I]I_3$, which was isolated as brown crystals upon the addition of methanol to the reaction mixture. The iodine which also crystallized under these conditions was removed by washing the product with ethanol. The reaction must be carried out fairly rapidly (i.e. over a period of approximately 8 minutes), because the iodo complex reacts further with iodine as discussed in section 4.

$[Mo(CO)_2(dpe)_2I]I_3$ is soluble in dichloromethane, chloroform, acetone and slightly soluble in nitromethane and acetonitrile. When sulphur dioxide was bubbled through solutions of the complex in dichloromethane, acetone or nitromethane containing a drop of water, the tri-iodide ion was rapidly reduced to give a bright yellow solution of $[Mo(CO)_2(dpe)_2I]I$. No reaction occurred in the absence of water. The tetraphenylborate salt, $[Mo(CO)_2(dpe)_2I]BPh_4$, was obtained as bright yellow crystals by metathesis in dichloromethane-methanol. The compound is soluble in dichloromethane, slightly soluble in the polar organic solvents (except methanol) and insoluble in chloroform. Attempts to prepare the perchlorate salt by adding a very concentrated solution of lithium perchlorate to a solution of $[Mo(CO)_2(dpe)_2I]I_3$ in dichloromethane were unsuccessful.

Two strong carbonyl stretching bands were observed in the infrared spectra of $[Mo(CO)_2(dpe)_2I]X$ ($X^- = I_3, BPh_4$), (see Table 3.1). The complete infrared spectrum of the tetraphenylborate salt is recorded in Table 3.4. The molar conductance of $[Mo(CO)_2(dpe)_2I]I_3$ in acetone (see Table 3.1) is consistent with the formulation of the complex as a 1:1 electrolyte.

$[Mo(CO)_2(dpe)_2I]I$ has been prepared by Colton and co-workers[263] by refluxing $Mo(CO)_4I_2$ with an excess of dpe in chloroform. The reported carbonyl stretching frequencies (Table 3.1) of the yellow product are slightly higher than those observed in this work. The molar conductance of the complex is in good agreement with the value obtained for $[Mo(CO)_2(dpe)_2I]I_3$.

(d) Preparations Involving Nitrosonium Hexafluorophosphate

The molybdenum(II) chloro and bromo complexes could also be prepared by using nitrosonium hexafluorophosphate in the presence of the appropriate halide; the preparation of the iodo complex was not studied. When nitrosonium hexafluorophosphate was added to a mixture of $Mo(CO)_2(dpe)_2$ and an excess (approximately 2.5 equivalents) of either tetraphenylarsonium chloride or tetraethylammonium bromide in dichloromethane, the molybdenum complex dissolved rapidly to give a red solution of *trans*-$[Mo(CO)_2(dpe)_2]^+$, which reacted further to form a bright yellow solution of $[Mo(CO)_2(dpe)_2X]^+$

(X = Cl, Br). The carbonyl stretching frequencies of the products are identical to those recorded in Table 3.1.

However, while the solution was still red, a strong carbonyl absorption was present in the infrared spectrum at 1975 cm^{-1}. The intensity of the band decreased as more nitrosonium hexafluorophosphate was added and this species could not be isolated. When the reaction mixture was bright yellow, this band was of only weak intensity. In the reaction of $Mo(CO)_2(dpe)_2$ with nitrosonium hexafluorophosphate in the absence of halide (Chapter 2.2), the absorption observed at 1980 cm^{-1}, which is assumed to be due to the same side reaction, is always of weak intensity. This is consistent with rapid decomposition of the by-product or it may be that only a small amount of the by-product is actually formed. The fact that $[Mo(CO)_2(dpe)_2F]PF_6$ is formed in approximately 50% yield suggests that a side reaction to form products, which do not contain carbonyl groups, is occurring. It is believed that the un-isolatable by-product formed in these reactions is identical to one of the products formed in the nitrosonium hexafluorophosphate oxidation of $W(CO)_2(dpe)_2$ (see Chapter 2.6 - 2.8).

The method described above appears to be a general route to seven-coordinate molybdenum(II) complexes; the only limitation being the solubility of the coordinating anion. The addition of excess nitrosonium hexafluorophosphate results in decomposition, as noted in Chapter 2.

3.2.1 Properties of the Halo Complexes

In the complexes discussed in the previous section only one halide ion is coordinated to the metal, since the complexes are all 1:1 electrolytes and the tetraphenylborate and other salts were prepared by metatheses. The X-ray powder patterns of the chloro, bromo and iodo complexes as the tetraphenylborate salts are identical, which indicates that the complexes are isomorphous; the powder pattern for the fluoro complex is different.

The carbonyl stretching frequencies of the halo complexes (X = F, Cl, Br, I) are similar (see Table 3.1); a slight decrease is observed for the bromo and iodo complexes relative to the fluoro complex. The chloro complex does not fit into this sequence and its carbonyl stretching frequencies are lower than those for the other complexes; the reason for this is not, at present, known. Nyholm and co-workers[94] found, for a series of complexes of the formula $[M(CO)_3LX]Y$ (M = Mo, W; L = ν-triars, *l*-triars; X = Br, I; Y = Br, I, ClO_4, BPh_4), an absence of any significant trend in the physical properties with respect to changing the halogen and the central metal. The carbonyl stretching frequencies are in many cases virtually identical, but the variations that do exist are apparently random.

The bond angles between the carbonyl groups (Table 3.1), calculated from the relative intensities of the carbonyl stretching bands as described in Chapter 2.2.1, increase slightly in the order I < Br < Cl < F, which is inversely correlated with the decrease in the atomic radius of the halogen. In a series of tantalum complexes of the formula $Ta(CO)_2(dmpe)_2X$ (X = Cl, Br, CN, CH_3), the intensity ratio of 1.61:1 was found to be largely invariant. From this data, the workers computed a bond angle of 74 ± 2°.[258] In comparison, the bond angle in $[Mo(CO)_2(diars)_2Cl]I_3$ is 67.7°.[219] The complete infrared spectra of the cations $[Mo(CO)_2(dpe)_2X]^+$ (X = F, Cl, Br, I) (Tables 3.2 - 3.4 and 2.2) are virtually identical. Furthermore, no changes are observed during metathetical reactions, which indicates that the basic moiety remains unchanged.

It is proposed that the cations $[Mo(CO)_2(dpe)_2X]^+$ (X = Cl, Br, I) have the same structure in the solid state as the fluoro complex, $[Mo(CO)_2(dpe)_2F]^+$, i.e. a capped trigonal prism (Fig. 2.2). This appears to be the preferred stereochemistry for this type of complex, as shown by the X-ray molecular structure determinations of $[Mo(CO)_2(diars)_2Cl]I_3$[219] and $[W(CO)_2(dmpe)_2I]I$.[119] Furthermore, this geometry has been assigned to the tantalum complexes, $Ta(CO)_2(dmpe)_2X$ (X = Cl, Br, CN, CH_3), on the basis of the infrared and ^{31}P NMR spectral data.[258]

Colton and co-workers[263] suggested that the $[Mo(CO)_2(dpe)_2I]^+$ cation may be six-coordinate on the basis of its reaction with carbon monoxide. However, the physical properties of the iodo complex, in particular the X-ray powder pattern, are identical to those of the other halo complexes and there is no reason to suppose that this complex has a different structure.

TABLE 3.1

Properties of the Monohalo Molybdenum Complexes

Complex	Colour	ν_{CO} $(cm^{-1})^A$	R^B	Bond Angle^C (deg)	Λ_M^D $(S\ cm^2)$
$[Mo(CO)_2(dpe)_2F]PF_6$	canary yellow	1945, 1889	1.57	77	77.6^E
$[Mo(CO)_2(dpe)_2Cl]Cl$	pale yellow	1942, 1878	1.59	77	111^F
$[Mo(CO)_2(dpe)_2Cl]BPh_4$	yellow	1942, 1878	1.61	77	-
$[Mo(CO)_2(dpe)_2Br]Br_3$, $1.5CCl_4$	bright yellow	1945, 1880	1.68	75	$76.3^{E,G}$
$[Mo(CO)_2(dpe)_2Br]ClO_4$, CH_2Cl_2	bright yellow	1945, 1879	1.70	75	79.0^E
$[Mo(CO)_2(dpe)_2Br]BPh_4$	bright yellow	1944, 1880	1.69	75	-
$[Mo(CO)_2(dpe)_2Br]PF_6$	bright yellow	1944, 1879	-	-	-
$[Mo(CO)_2(dpe)_2I]I_3$	brown	1945, 1880	1.78	74	138^F
$[Mo(CO)_2(dpe)_2I]I^H$	yellow	1950, 1885	-	-	144^F
$[Mo(CO)_2(dpe)_2I]BPh_4$	bright yellow	1945, 1880	1.80	73	-

A. Measured in dichloromethane solution. All bands are very strong. B. $R = I_{sym}/I_{asy}$, where I is the band intensity; values of R are usually ± 0.04. C. Bond angle (2θ) between the carbonyl groups, obtained from the equation $R = \cot^2\theta$ (see ref. 247). The values are believed to be accurate to ± 2°. D. Measured at 25°C. All concentrations *c.* 1.0×10^{-3} M. The tetraphenylborate salts gave consistently low values (*c.* 80 - 90 $S\ cm^2$ in acetone). E. In nitromethane. F. In acetone. G. Λ_m in acetone *c.* 100 $S\ cm^2$, decreases with time. H. Anker, M.W., Colton, R., Rix, C.J. and Tomkins, I.B., *Aust.J.Chem.*, 22, 1341, (1969).

TABLE 3.2

Infrared Spectra of $[Mo(CO)_2(dpe)_2Cl]X$, ($X = Cl, BPh_4$) (nujol)

Assignment	Frequency (cm^{-1}) $X = Cl^-$	 $X = BPh_4^-$
$\nu_{sym}(CO)$	1933 vs	1941 vs
ν_{as} (CO)	1865 vs	1878 vs
Aromatic ring	1587 w	1580 mw
vibrations	1573 w	
$\nu_{P-C(aromatic)}$	1096 m	1096 m
C-H out of	746 s	747 sh, 741 s
plane def.	698 s	710 sh, 705 s
δ(MCO)	575 m	575 m
δ(MCO)	535 s	539 s
Other prominent	882 w	881 w
bands	830 w,br	828 w
	—	530 sh
	514 m	515 m
	490 m	487 m
	418 mw	418 mw

TABLE 3.3

Infrared Spectra of $[Mo(CO)_2(dpe)_2Br]X$, ($X = Br_3$, ClO_4, BPh_4, PF_6)^{A,B}

Assignment	Frequency (cm^{-1})			
	$X = Br_3^{-C}$	$X = ClO_4^{-D}$	$X = BPh_4^-$	$X = PF_6^-$
ν_{sym}(CO)	1940 vs	1937 vs	1942 vs	1940 vs
ν_{as} (CO)	1876 vs	1872 vs	1879 vs	1876 vs
Aromatic ring	1585 w	1586 w	1586 mw	1588 w
vibrations	1572 w	1573 w	-	1574 w
$\nu_{P-C(aromatic)}$	1094 m	obscured	1094 m	1094 ms
Carbon tetrachloride ν_{C-Cl}	793 s	-	-	-
Combination	767 sh	-	-	-
bands	758 sh	-	-	-
C-H out of	750 s	751 s	748 s^E	750 s
plane def.	700 s	695 s	704 s^E	698 s
δ(MCO)	568 m	568 ms	569 ms	570 sh
δ(MCO)	539 m	536 s	535 s	540 s
Other prominent	879 mw	879 m	880 m	880 sh
bands	834 mw	833 m	826 m	obscured
	528 m	526 s	529 sh	530 s
	510 m	512 s	512 ms	513 s
	490 m	490 sh	-	490 ms
	483 m	485 ms	485 ms,br	485 sh
	418 mw	418 mw	415 mw	419 mw

A. The bands due to the anions are not included in the Table; the relevant

Table 3.3 (Cont..)

frequencies are recorded in Table 2.2

B. Recorded as KBr discs.

C. The compound also contains 1.5 molecules of carbon tetrachloride of crystallization.

D. The compound contains one molecule of dichloromethane of crystallization.

E. The bands are split into doublets, the other absorptions are at 742 (s) and 710 (s) cm^{-1} respectively.

TABLE 3.4

Infrared Spectrum of $[Mo(CO)_2(dpe)_2I]BPh_4$ (nujol)

Assignment	Frequency (cm^{-1})
ν_{sym}(CO)	1946 vs
ν_{as} (CO)	1882 vs
Aromatic ring vibrations	1578 mw
$\nu_{P-C(aromatic)}$	1093 m
C-H out of plane def.	746 sh, 742 s 710 sh, 700 s
δ(MCO)	567 m
δ(MCO)	538 s
Other prominent bands	880 w 824 w 530 sh 515 ms 488 m 415 m

3.3 ^{31}P Nuclear Magnetic Resonance Spectra

(a) $M(CO)_2(L_2)_2$

The proton-decoupled ^{31}P NMR spectra of the dicarbonyl complexes, $M(CO)_2(L_2)_2$ (M = Cr, Mo; L_2 = dpe, dpm), recorded in $CDCl_3$, showed two resonances of equal intensity and this confirms the *cis*-configuration deduced from infrared spectroscopy.[58,121] A typical spectrum is illustrated in Figure 3.1 and the data are recorded in Table 3.5a. Each resonance is split into a doublet of doublets and this indicates that each phosphorus atom is coupled to two other non-equivalent phosphorus atoms. The infrared spectrum (see Appendix 3) of $Cr(CO)_2(dpe)_2$ in benzene showed that the complex exists as a mixture of *cis*-(40%) and *trans*-(60%) isomers in this solvent. When the spectrum of the complex in C_6D_6 was recorded, the two resonances due to the *cis*-isomer were readily observed, but there was no resonance due to the *trans*-isomer. The reason for this is presently unknown.

The dicarbonyl complexes have C_2 symmetry, as shown schematically in Figure 3.2 :

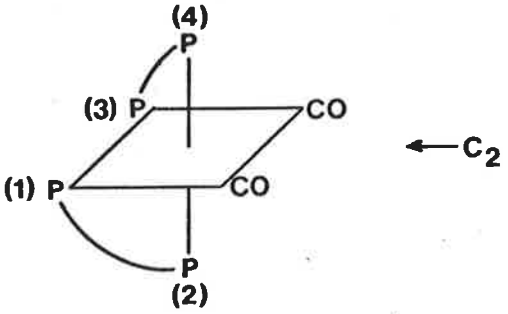


Fig. 3.2 Structure of the Complexes $M(CO)_2(L_2)_2$

P_1 and P_3 are symmetrically equivalent, as are P_2 and P_4; each pair of phosphines gives rise to a separate resonance. It appears that the nuclear resonance of a phosphine in a *trans* position relative to a carbonyl group occurs at higher field than that of a phosphine in a *trans* position relative to another phosphine[54,262] (e.g. *cis*-$Mo(CO)_4(PPh_2Bu)_2$ -25.8 ppm,

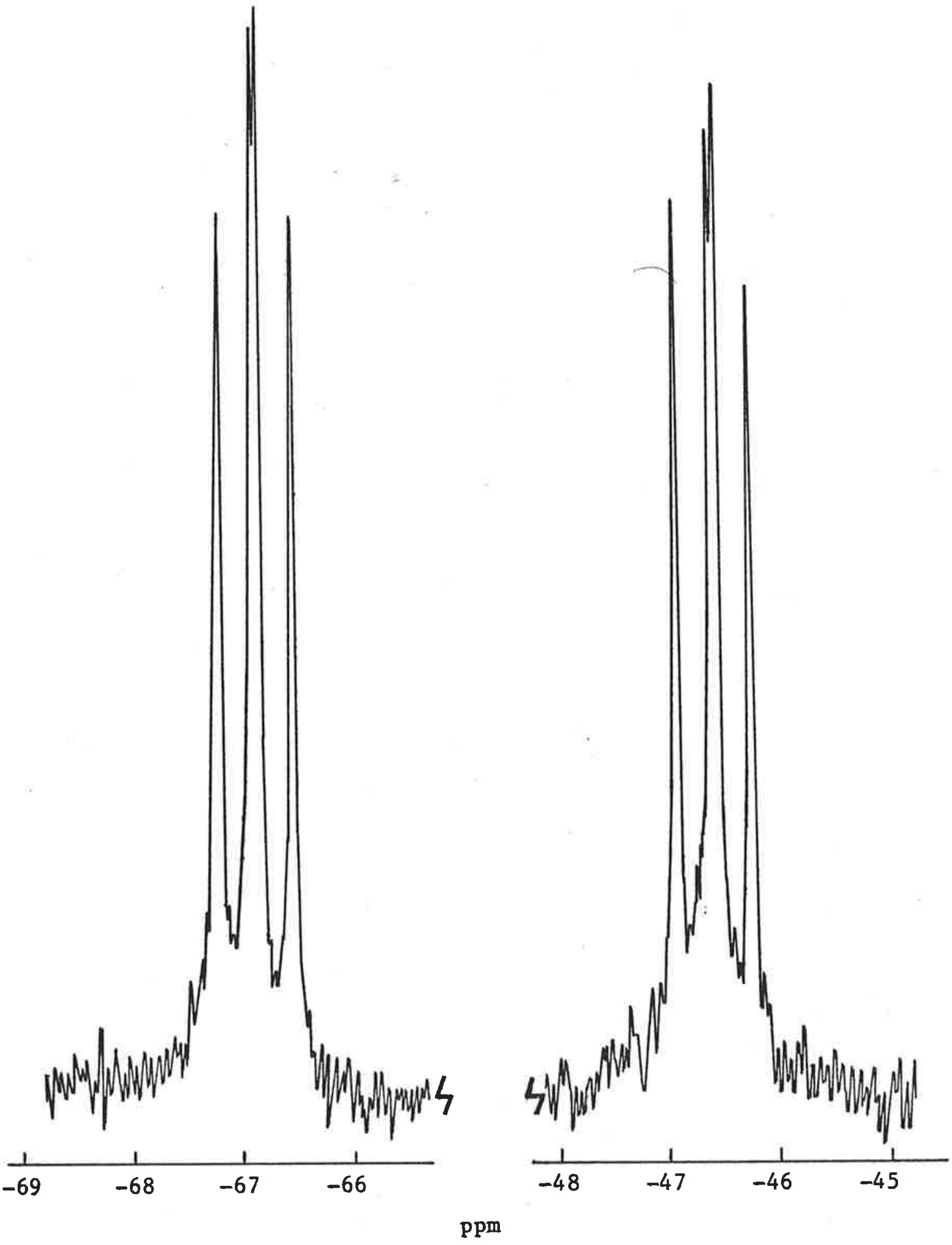


Fig. 3.1 ^{31}P NMR Spectrum of $Mo(CO)_2(dpe)_2$ in $CDCl_3$.

trans-$Mo(CO)_4(PPh_2Bu)_2$ -38.9 ppm, free ligand +17.1 ppm[262]). For this reason, the upfield resonance in the spectrum of *cis*-$M(CO)_2(L_2)_2$ is assigned to P_1 and P_3 and the resonance at lower field to P_2 and P_4.

Since symmetrically equivalent atoms are not spin-spin coupled, it follows that there is no *cis*-coupling between P_1 and P_3 and no *trans*-coupling between P_2 and P_4. The doublet of doublets must, therefore, be due to coupling of P_1 (and thus P_3) to P_2 and P_4, and vice-versa. Since P_1 and P_2 are linked by a hydrocarbon bridge, through which they can interact to some extent, $J_{P_1-P_2}$ should be different to $J_{P_1-P_4}$. The effect should be more dramatic in the case of dpm complexes, because the phosphorous atoms are separated by only a methylene bridge.

It appears to be a general phenomenon that the *trans*-coupling constants across a metal are larger than the *cis*-coupling constants. The effect is only observed in complexes containing two different types of phosphines. In a series of platinum complexes of the formula *cis*/*trans*-$[PtCl_2(Bu_3^nP)(R_3P)]$ (R = Ph, OPh, Et, etc.), the *cis*-phosphorous-phosphorous coupling constants were always small and of the order of 15 - 24 Hz, while the *trans*-coupling constants were very large (715 Hz, R = OPh; 474 Hz, R = Ph; 462 Hz, R = Et)[259]. King and Cloyd[72] have reported spectral data for a series of complexes containing unsymmetrical bi- and tri-dentate phosphine ligands. In $M(CO)_4(Me_2PCH_2CH_2PPh_2)$ (M = Cr, Mo), the coupling constants (*cis*) are 15 Hz (M = Cr) and 7 Hz (M = Mo) respectively, compared with 25 Hz for the free ligand. Similar results were obtained for complexes of the formula $\{PhP(CH_2CH_2PR_2)_2\}M(CO)_3$ (R = Me, Ph). In comparison, the coupling constant in *trans*-$Mo(CO)_4(PPh_3)(PBu_3)$ is 50 Hz.[260] The ^{31}P NMR spectra of both isomers of $Mo(CO)_3(dpm)_3$ have been reported.[228] The *fac*- isomer showed a *cis*-coupling constant of 24.4 Hz. In the *mer*-isomer, the *cis*-coupling constants were 24.4 and 25.6 Hz respectively, whereas the *trans*-coupling constant was 72.4 Hz. The above examples suggest that there is no *trans* coupling in the dicarbonyl complexes $M(CO)_2(L_2)_2$, as was deduced from symmetry arguments.

In this study, the chemical shifts were initially measured relative to dpe as an internal reference and dpe was then calibrated against 85% H_3PO_4 as the external standard. The chemical shift obtained for dpe was +13.1 ppm, compared with the reported value of +12.9 ppm.[261] Dpe and related ligands (e.g. dpm, PPh_3) resonate upfield from orthophosphoric acid and are assigned positive chemical shifts. A net deshielding effect is observed upon coordination to a metal ion[72] and the phosphine-substituted metal carbonyl complexes usually resonate downfield from the free ligands.[54,72,74,260] Some representative examples are shown in Table 3.5b. The coordination chemical shifts (absolute values) decrease in the order $Cr > Mo > W$.[54,74,260]

(b) $[Mo(CO)_2(dpe)_2X]^+$ (X = Cl, Br, I)

The proton-decoupled ^{31}P NMR spectra of the complexes $[Mo(CO)_2(dpe)_2X]^+$ (X = Cl, Br, I), recorded in either CD_2Cl_2 or $CDCl_3$, showed a single sharp resonance (Table 3.6a) at 301° K. The resonances are shifted downfield relative to free dpe and the chemical shifts increase in the order $I < Br < Cl$, which correlates with the increasing electronegativity of the halogen. The single resonance indicates that the phosphorous atoms are equivalent on the NMR time scale and this is consistent with a capped trigonal prismatic structure. Alternatively, the equivalence of the phosphines may be due to stereochemical non-rigidity.

The spectra of $[Mo(CO)_2(dpe)_2Br]ClO_4$ and $[Mo(CO)_2(dpe)_2I]BPh_4$ in CD_2Cl_2 were recorded at various temperatures, as illustrated in Figure 3.3. At 251° K, the spectra of the complexes were identical to those at 301° K. At 221° K, a slight amount of line broadening was observed. The extent of the broadening increased as the temperature was lowered further until, at 191° K, the signal had completely collapsed to give a very broad resonance.

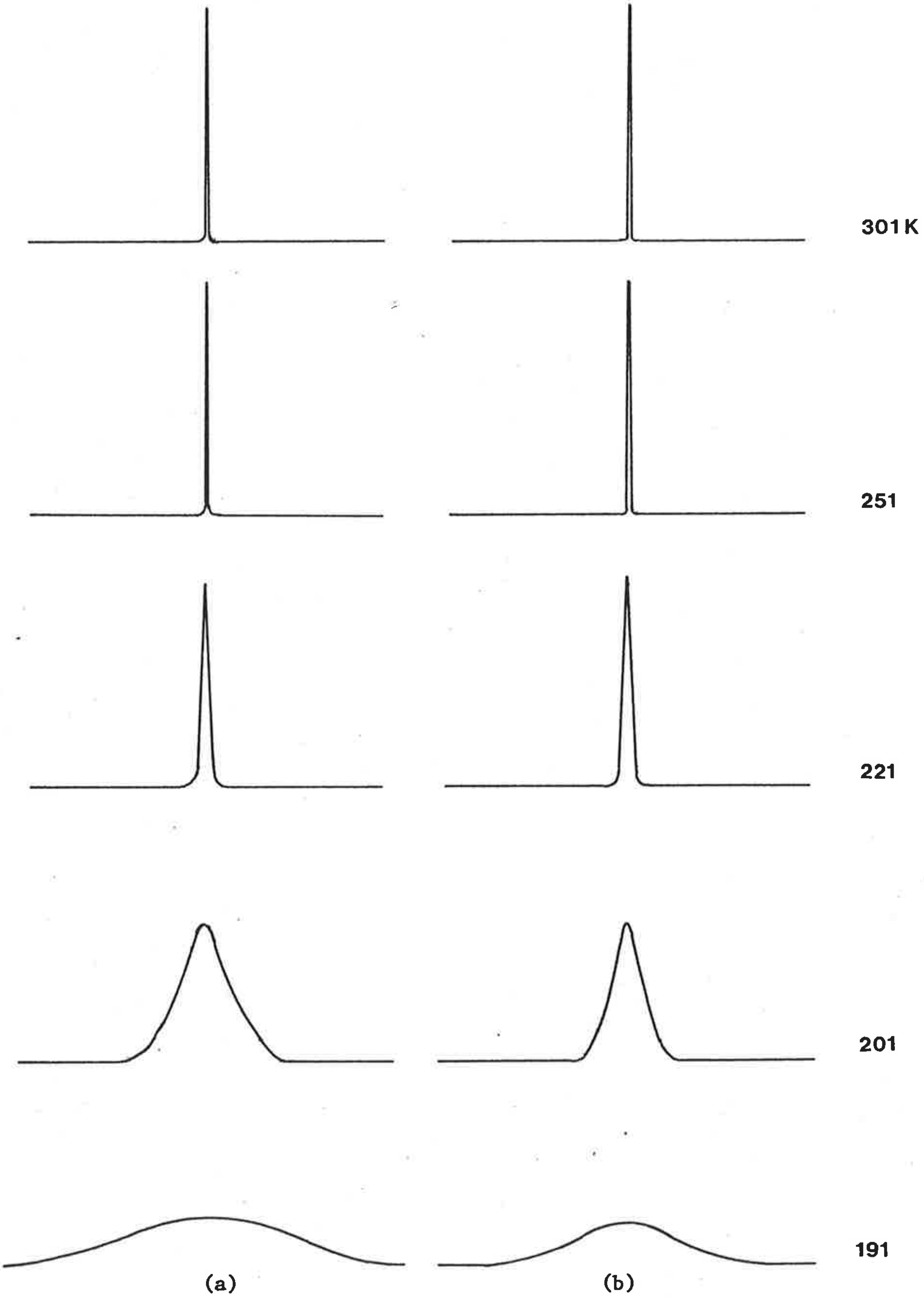


Fig. 3.3 Variation in the ^{31}P NMR Spectra of (a) $[Mo(CO)_2(dpe)_2Br]ClO_4$ and (b) $[Mo(CO)_2(dpe)_2I]BPh_4$ with Temperature.

It was not possible to significantly lower the temperature further without freezing the solution. Furthermore, viscosity broadening effects become very large near the freezing point of the solvent. The changes observed in the spectra were reversed on warming to 301° K. The halfwidths of the resonances at half height are recorded in Table 3.6b.

The bromo and iodo complexes appear to be fluxional; however, any conclusions that may be drawn are only tentative. If it is assumed that the "frozen" complex has a capped trigonal prismatic structure, the ^{31}P NMR signal will be split by the nuclear spin of both bromine ($I = 3/2$ for both isomers) and iodine ($I = 5/2$).[246(b)] The signal may be further broadened by the quadrupole moments of these atoms. The room temperature spectrum can be explained by a polytopal rearrangement, which leads to an averaging of the magnetic environments, thus destroying any coupling with the halogen atoms.

Proton NMR spectroscopy showed that the cations, $[M(CO)_2(dmpe)_2I]^+$ (M = Mo, W), were fluxional at room temperature and rigid at temperatures below 240° K. The low temperature spectra were interpreted in terms of a seven-coordinate capped trigonal prismatic structure. This conclusion is supported by the X-ray molecular structure determination of $[W(CO)_2(dmpe)_2I]I$, with which the molybdenum analogue is isomorphous.[119] The tantalum derivatives, $Ta(CO)_2(dmpe)_2X$ (X = Cl, Br, CN, CH_3), all show a single ^{31}P NMR resonance in the temperature range 363 to 193° K. On this basis, the workers concluded that these complexes also have capped trigonal prismatic structures.[258]

Stereochemical non-rigidity in solution at room temperature has been observed for complexes of the formula $M(CO)_3(fars)X_2$ (M = Mo, W; X = Br, I) and $Mo(CO)_2(fars)(L)Br_2$, (L = phosphine, phosphite). A rearrangement process involving the rapid scrambling of the carbonyl groups and the halogen atoms was postulated.[266] A similar rearrangement was used to rationalize the variable-temperature ^{1}H NMR spectra of *meso*- and *racemic*-[Mo(CO)$_3${*o*-C$_6$H$_4$(AsMePh)$_2$}I$_2$].[267]

TABLE 3.5a

^{31}P N.M.R. Spectra^{A,B} of *cis*-$M(CO)_2(L_2)_2$

Complex	J_{P-P} (Hz)	Shift (ppm) relative to dpe^C	Shift (ppm) relative to H_3PO_4 (85%)
$Cr(CO)_2(dpm)_2$	13.4, 23.2	-79.1	-66.0
		-54.7	-41.6
$Cr(CO)_2(dpe)_2$	8.6, 18.3	-104.9	-91.8
		-79.4	-66.3
$Mo(CO)_2(dpe)_2$	11.3, 12.8	-80.0	-66.9
		-59.7	-46.6

A. All spectra consisted of two resonances, each resonance is split into a doublet of doublets.

B. Recorded at 36.43 MHz in $CDCl_3$.

C. Used as an internal reference. Chemical shift of dpe relative to H_3PO_4 (85%) is +13.1 ppm.

TABLE 3.5b

^{31}P N.M.R. Chemical Shifts for some Group VIa Metal Carbonyl Complexes

Complex	Chemical Shift (ppm)^{A} Free Ligand	Chemical Shift (ppm)^{A} Complex	Reference
$Cr(CO)_5PPh_3$	+ 6.0	- 55.3	260
$Mo(CO)_5PPh_3$		- 37.5	260
$W(CO)_5PPh_3$		- 20.6	260
$Cr(CO)_4(dpm)$	+ 23.6	- 25.4	74
$Mo(CO)_4(dpm)$		0	74
$W(CO)_4(dpm)$		+ 23.6	74
$Cr(CO)_4(dpe)$	+ 12.9	- 79.4	74
$Mo(CO)_4(dpe)$		- 54.7	74
$W(CO)_4(dpe)$		- 40.1	74

A. w.r.t. H_3PO_4 (85%).

TABLE 3.6a

^{31}P N.M.R. Spectra^{A} of $[Mo(CO)_2(dpe)_2X]^+$

Compound	Shift (ppm) relative to dpe^{B}	 H_3PO_4 (85%)
dpe	-	+13.1
$[Mo(CO)_2(dpe)_2F]PF_6$^{C,D}	-60.8	-47.5
$[Mo(CO)_2(dpe)_2Cl]Cl$	-66.5	-53.4
$[Mo(CO)_2(dpe)_2Br]Br_3$	-65.1	-52.0
$[Mo(CO)_2(dpe)_2Br]ClO_4$^{C}	-64.8	-51.7
$[Mo(CO)_2(dpe)_2I]I_3$	-59.9	-46.8
$[Mo(CO)_2(dpe)_2I]BPh_4$^{C}	-61.2	-48.1

A. Recorded in $CDCl_3$ at 36.43 MHz.

B. Used as an internal reference.

C. Recorded in CD_2Cl_2.

D. J_{P-F} = 27.2 Hz, spectrum also contains septet (J_{P-F} = 710.2 Hz) at +130.8 ppm (relative to dpe) due to PF_6^-.

TABLE 3.6b

Variable Temperature ^{31}P N.M.R. Data^A for $[Mo(CO)_2(dpe)_2X]^+$

Temperature (°K)		$W_{\frac{1}{2}}$ (Hz)^B	
	$[Mo(CO)_2(dpe)_2F]PF_6$	$[Mo(CO)_2(dpe)_2Br]ClO_4$	$[Mo(CO)_2(dpe)_2I]BPh_4$
301	3	3	3
251	3	4	6
231	4	-	-
221	-	16	20
215	8	37	-
201	-	150	95
195	-	-	230
191	∿12	∿660	∿350

A. Recorded in CD_2Cl_2.

B. Halfwidth at half height, 0.5 Hz of this is due to artifical computer-generated line broadening.

3.4 Reactions of $[Mo(CO)_2(dpe)_2X]^+$

In the preparation of $[Mo(CO)_2(dpe)_2Br]Br_3$, the bromine must be added fairly briskly as described in section 3.2(b). If the complex was not isolated immediately, the colour of the reaction mixture changed to deep red and then, after a period of approximately 20 minutes, to orange due to further reaction of the monobromo complex. Infrared monitoring showed that the reaction had finished after 4 - 5 hours stirring, although some of the monobromo complex was still unreacted.

The turbid solution was filtered to collect an orange crystalline precipitate, which did not contain any carbonyl groups and was insoluble in all organic solvents. The lack of solubility suggests that the compound is polymeric and the formula $[Mo(dpe)_{1.5}Br_4]_n$ is proposed. The addition of light petroleum to the filtrate produced a second orange precipitate, which is also insoluble in all organic solvents. Two strong carbonyl stretching bands are present in the infrared spectrum (nujol mull) at 1936 and 1855 cm^{-1}. These frequencies are identical to those reported for the polymer $[Mo(CO)_2(dpe)_{1.5}Br_2]_n$ by Colton and co-workers.[263] It is thought that the orange complex has this formulation, but satisfactory elemental analyses could not be obtained.

Unreacted $[Mo(CO)_2(dpe)_2Br]^+$ was precipitated by concentrating the bright yellow filtrate and adding carbon tetrachloride. The sole species remaining in solution was the neutral seven-coordinate complex, $[Mo(CO)_2(dpe)_2Br_2]$, which was precipitated as a bright yellow powder by the addition of light petroleum. The carbonyl stretching frequencies are recorded in Table 3.7; the relative band intensities are 1.25:1. The addition of the bromide results in a ring opening so that the molecule contains both chelating and monodentate dpe. The molar conductance in acetone (8.22×10^{-4} M) was 22 S cm^2, which indicates that the product still contains a small amount (about 15%) of $[Mo(CO)_2(dpe)_2Br]^+$.

$[Mo(CO)_2(dpe)_2Br_2]$ is very soluble in dichloromethane, chloroform and acetone. However, in some preparations, when the precipitated complex was extracted with one of these solvents, an orange residue, insoluble in all organic solvents, remained. Two carbonyl bands are present in the infrared spectrum of this solid at 1940 (vs) and 1860 (vs) cm^{-1}. This suggests that $[Mo(CO)_2(dpe)_2Br_2]$, once formed, will react further to give polymeric species.

When $[Mo(CO)_2(dpe)_2Br]Br_3,1.5CCl_4$ was dissolved in nitromethane, the bright yellow solution rapidly darkened to a deep brown colour which, after a period of about 10 minutes, changed to orange. Infrared monitoring of the solution at room temperature showed that $[Mo(CO)_2(dpe)_2Br_2]$ was initially formed. The complex then slowly polymerized over a period of hours to give orange crystals of $[Mo(CO)_2(dpe)_{1.5}Br_2]_n$. Attempts to recrystallize $[Mo(CO)_2(dpe)_2Br]Br_3,1.5CCl_4$ from acetone-light petroleum resulted in partial or complete conversion to $[Mo(CO)_2(dpe)_2Br_2]$ plus polymeric products.

The main problem associated with the reaction between $[Mo(CO)_2(dpe)_2Br]^+$ and tribromide is that the tribromide ion, in solution, is in the following equilibrium:

$$Br_3^- \rightleftarrows Br^- + Br_2$$

and therefore, it is difficult to determine whether the reaction is due to bromine, bromide or both. Moreover, if the reaction is due solely to bromide, the presence of bromine may result in further oxidation. This problem can be overcome by the reaction of $[Mo(CO)_2(dpe)_2Br]X$ ($X = ClO_4^-$, BPh_4^-) with bromide.

The complexes $[Mo(CO)_2(dpe)_2Br]X$ ($X = ClO_4^-$, BPh_4^-) are very stable in dichloromethane solution and no change was observed in the infrared spectra after 24 hours. Both salts react completely with excess tetraethylammonium bromide (4-6 moles) at room temperature (23 - 25°C) over a period of 7 – 10 hours to form [$Mo(CO)_2(dpe)_2Br_2$]. The reaction was accompanied by a colour change from yellow to orange and the orange solution showed carbonyl absorptions at 1940 (vs) and 1859 (vs) cm^{-1}. The presence of excess bromide forces the reaction to completion. On standing for a further period of time, the dibromo complex polymerized with loss of dpe and orange crystals of [$Mo(CO)_2(dpe)_{1.5}Br_2$]$_n$ (ν_{CO} 1936 (vs), 1855 (vs) cm^{-1}) precipitated The polymerization reaction did not always take the same period of time and the rate constant probably has a high temperature dependence.

Repeated attempts to obtain a ^{31}P N.M.R. spectrum of [$Mo(CO)_2(dpe)_2Br_2$] were all unsuccessful. The spectrum of a CD_2Cl_2 solution of the complex, prepared *in situ* by allowing the above reactants to stand at room temperature for 4 – 5 hours, showed a resonance due to some unreacted monobromo complex, but no resonances due to the product. Furthermore, the higher probe temperature (28°C) accelerated the polymerization reaction and orange crystals were formed in the NMR tube while spectra were being recorded. This was accompanied by the appearance of a resonance due to free dpe. Attempts to monitor the progress of the reaction by placing a freshly prepared solution of the reactants in the spectrometer probe resulted in the rapid formation of the polymeric complex, [$Mo(CO)_2(dpe)_{1.5}Br_2$]$_n$. No signals due to the dibromo complex were observed. In this case the dibromo complex is functioning merely as an intermediate.

Two possible structures for [$Mo(CO)_2(dpe)_2Br_2$] are shown in Figure 3.4.

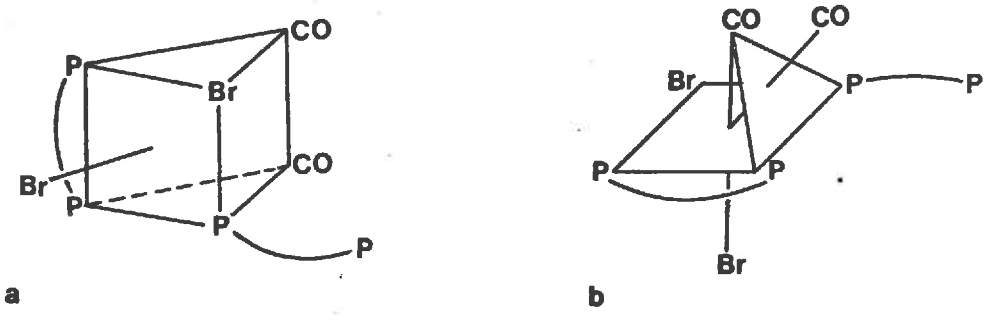


Fig. 3.4 Possible Structures for [$Mo(CO)_2(dpe)_2Br_2$]

Structure (a) is based on a capped trigonal prism, while structure (b) is a capped octahedron. The Figure shows the two extreme structures and their idealized geometries, whereas the actual structure may be distorted and intermediate between these two extremes. Capped trigonal prismatic geometry has been found for complexes of the type $[M(CO)_2(bidentate)_2X]^+$[91,219] and for *meso*- and *racemic*- $Mo(CO)_3\{o\text{-}C_6H_4(AsMePh)_2\}I_2$.[267] The structure of $[Mo(CO)_2(dam)_2Cl_2]$ was found to be a relatively undistorted capped octahedron with a carbonyl group in the unique capping position. The capped face of the octahedron contains the other carbonyl group and the two arsenic atoms from different arsine ligands. The uncapped face contains the two halogen atoms and one arsenic atom.[248] The geometries of $[Mo(CO)_2(dpm)_2Cl_2]$[248] and $[Mo(CO)_2(dam)_2Br_2]$[249] are similar, but more distorted.

The carbonyl stretching frequencies of $[Mo(CO)_2(dpe)_2Br_2]$, within the limits of experimental error, are identical to those for $[Mo(CO)_2(dpe)_{1.5}Br_2]_2$ (Chapter 2.4), which is to be expected, since the same basic moiety is common to both complexes. The decrease in ν_{CO} relative to $[Mo(CO)_2(dpe)_2Br]^+$ suggests that, in these types of complexes, the bromide ion has a greater electron-donating ability than dpe. This also explains the shift, to higher field, of the ^{31}P NMR signals of $[Mo(CO)_2(dpe)_{1.5}Br_2]_2$ relative to $[Mo(CO)_2(dpe)_2Br]^+$. The relative intensities of the carbonyl stretching bands in $[Mo(CO)_2(dpe)_2Br_2]$ and $[Mo(CO)_2(dpe)_{1.5}Br_2]_2$ are virtually identical and it is proposed that both complexes have the same geometry about the metal atom.

The chloro complex, $[Mo(CO)_2(dpe)_2Cl]^+$, is more stable with respect to addition of halide than the bromo complex. $[Mo(CO)_2(dpe)_2Cl]Cl$ can be recrystallized several times from dichloromethane-hexane without change. The complex isomerizes in dichloromethane solution over a period of 12 - 15 hours at room temperature to form $[Mo(CO)_2(dpe)_2Cl_2]$. The reaction does not proceed to completion and approximately 40% of the monochloro complex remains unreacted. The addition of an excess of tetraphenylarsonium chloride was necessary for complete conversion. On standing for a further period of time, the dichloro complex polymerizes to produce yellow-orange crystals of $[Mo(CO)_2(dpe)_{1.5}Cl_2]_n$. The carbonyl stretching frequencies of the complexes are recorded in Table 3.7. It is proposed that $[Mo(CO)_2(dpe)_2Cl_2]$ has a structure similar to that of the bromine analogue.

$[Mo(CO)_2(dpe)_2F]PF_6$ showed no tendency to react with tetraethylammonium fluoride in dichloromethane/methanol (1:1) even when a large excess was present.

The iodo complex reacts in a different manner. In the preparation of $[Mo(CO)_2(dpe)_2I]I_3$ the iodine must be added fairly rapidly and the complex isolated immediately, as described in Section 2(c). If, however, the reaction mixture is kept stirring, three strong carbonyl bands appear in the infrared spectrum at 2048, 1972 and 1916 cm^{-1} as the two bands due to the iodo cation disappear. The product was not isolated. The same reaction occurred, over a period of approximately 100 min., when a solution of $[Mo(CO)_2(dpe)_2I]I_3$ in dichloromethane was left in the infrared beam. Iodine was consumed in the reaction since the colour of the solution changed from deep red to bright yellow. The three carbonyl bands suggest that $Mo(CO)_3(dpe)I_2$ has been formed; the frequencies are in good agreement with the reported values.[89,263] In addition, bands of medium intensity were present at 1940 and 1860 cm^{-1}. These are identical to those for $[Mo(CO)_2(dpe)_2Br_2]$ and suggest that a small amount of the corresponding diiodo complex has been formed.

The proposed mechanism for the reaction is as follows. The iodide ion substitutes the mono-iodo complex in a process analogous to those described previously to form initially $[Mo(CO)_2(dpe)_2I_2]$. In fact, the mono-iodo complex should be more susceptible to this type of reaction than the other halo complexes due to the larger size of iodine. The steric repulsions arising from the coordination of two iodine atoms are so great that the dpe ligand, which is now monodentate, is completely expelled. The six-coordinate intermediate abstracts carbon monoxide from another molecule to form [Mo(CO)$_3$(dpe)I$_2$], while the free dpe molecule is oxidized by the iodine. A solution of dpe in dichloromethane does indeed react with iodine; the products of the reaction are unknown. The yield of [Mo(CO)$_3$(dpe)I$_2$] can at best be only 67% of the amount of mono-iodo complex; the other reaction product was not determined.

Colton and co-workers[263] have shown that the mono-iodo complex reacts with carbon monoxide under mild conditions according to the equation:

$$[Mo(CO)_2(dpe)_2I]I + CO \longrightarrow Mo(CO)_3(dpe)I_2 + dpe$$

The reaction is reversible according to the experimental conditions. The workers were unsure of the mechanism of the reaction, but suggested that the initial step is attack by carbon monoxide. However, by analogy with the systems described above, it can be seen that attack by iodide is also a viable mechanism.

$Mo(CO)_4X_2$ and $Mo(CO)_3(dpe)X_2$ (X = Cl, Br) react with an excess of dpe in refluxing chloroform to give complexes of the formula [Mo(CO)$_2$(dpe)$_2$X$_2$], which were isolated as yellow powders.[263] These complexes are identical to those produced in the reaction of [Mo(CO)$_2$(dpe)$_2$X]$^+$ with halide. Conductance measurements showed that they are non-electrolytes. The workers[263] postulated a seven-coordinate structure in which one dpe ligand is chelating and the other is monodentate. The complexes are very soluble in organic solvents, but they decompose, especially in concentrated solutions, to give polymeric products and dpe. This resulted in very poor proton NMR spectra. On the other hand, the proton NMR spectra of the dpm analogues showed unequivocally that these complexes contain both chelating and monodentate dpm.[43]

The dihalo complexes, $Mo(CO)_4X_2$ (X = Cl, Br), react at room temperature with excess dpe in either dichloromethane or acetone solution over a period of several hours to give orange crystalline precipitates, which are insoluble in all organic solvents. The empirical formula of these products is $Mo(CO)_2(dpe)_{1.5}X_2$ and the workers[263] postulated a dimeric dpe-bridged structure. The total insolubility of these compounds, however, suggests that they are not dimeric, but polymeric and the formula $[Mo(CO)_2(dpe)_{1.5}Br_2]_n$ is proposed. Furthermore, complexes, which were characterized as $[Mo(CO)_2(dpe)_{1.5}X_2]_2$ (X = Cl, Br), were obtained by the reaction of $[\{Mo(CO)_2(dpe)_2\}_2F]^{3+}$ with halide, as described in Chapter 2.4. These complexes are deep yellow and are reasonably soluble in organic solvents. The solubilities of the dihalo complexes decrease in the order $[Mo(CO)_2(dpe)_2X_2] > [Mo(CO)_2(dpe)_{1.5}X_2]_2 \gg [Mo(CO)_2(dpe)_{1.5}X_2]_n$.

Dihalo complexes of the type $Mo(CO)_2(triarsine)X_2$ (X = Cl, Br, I) have been prepared either by heating complexes of the formula $[Mo(CO)_3LX]X$ (L = *o*-triars, ν-triars, *l*-triars; X = Br, I) in an alcohol such as methanol or propanol,[65,94] or by refluxing $[Mo(CO)_3(\nu\text{-triars})Br]BPh_4$ with excess lithium halide (X = Cl, Br) in ethanol for a few minutes.[94] The tungsten analogues, except for the *o*-triars complexes, react similarly, but higher temperatures and longer reaction times are required.[65,94] When complexes of the formula $[W(CO)_2(QP)X]X$ (X = Br, I) are heated in a vacuum or the compounds $[W(CO)_2(QP)X]BPh_4$ (X = Cl, Br) are refluxed with an excess of the appropriate lithium halide salt in diglyme, substitution of one of the carbonyl groups occurs to give $[W(CO)(QP)X_2]$. The molybdenum analogues behave in a similar manner, but the products are less stable.[68]

TABLE 3.7

Properties of the Dihalo Complexes

Complex	Colour	ν_{CO} $(cm^{-1})^A$
$[Mo(CO)_2(dpe)_2Cl_2]$	yellow	$1940, 1856^B$
$[Mo(CO)_2(dpe)_{1\cdot5}Cl_2]_n$	yellow-orange	$1935, 1855^C$
$[Mo(CO)_2(dpe)_2Br_2]$	yellow	$1940, 1860^B$
$[Mo(CO)_2(dpe)_{1\cdot5}Br_2]_n$	orange	$1936, 1855^C$
$[W(CO)_2(dpe)_2Br_2]$	yellow	$1930, 1842^B$

A. All bands are very strong.

B. Dichloromethane solution.

C. Nujol mull.

3.5 Preparation and Reactions of $[W(CO)_2(dpe)_2X]^+$ (X = Br, I)

$W(CO)_2(dpe)_2$, suspended in dichloromethane, reacts smoothly with a solution of bromine (*c.* 2.3 equivalents) in carbon tetrachloride at room temperature to form initially a bright orange solution of the cation *trans*-$[W(CO)_2(dpe)_2]^+$, which reacts further to give a bright yellow solution of the tungsten(II) bromo complex, $[W(CO)_2(dpe)_2Br]^+$. Bright yellow crystals of the solvate, $[W(CO)_2(dpe)_2Br]Br_3,1.5CCl_4$, were obtained in high yield upon the addition of carbon tetrachloride to the reaction mixture. The presence of carbon tetrachloride of crystallization was confirmed by bands in the infrared spectrum in the region 800 - 750 cm^{-1} (see Table 3.9). The molar conductance (Table 3.8) of the complex in acetone (1.01×10^{-3} M) is typical of a 1:1 electrolyte. The tetraphenylborate salt was prepared by metathesis in dichloromethane-methanol and was isolated as bright yellow crystals. The carbonyl stretching frequencies of both salts are recorded in Table 3.8 and the complete infrared spectra are presented in Table 3.9.

The reaction of $W(CO)_2(dpe)_2$ with excess iodine (12 moles) in dichloromethane at room temperature is identical to that of the molybdenum analogue; $[W(CO)_2(dpe)_2I]I_3$ was isolated from the reaction mixture as brown crystals. The tetraphenylborate salt was prepared by metathesis. The crystals are a deeper yellow colour than the corresponding molybdenum complex. The carbonyl stretching frequencies of both salts are recorded in Table 3.8 and the complete infrared spectra are presented in Table 3.10. $[W(CO)_2(dpe)_2I]I$ has been prepared by refluxing $W(CO)_4I_2$ with an excess of dpe in chloroform.[263] The carbonyl stretching frequencies of the yellow product (Table 3.8) are in good agreement with those obtained in this work.

The solubility properties of the bromo and iodo complexes are similar to those of the molybdenum analogues. Both complexes show two strong carbonyl stretching bands in the infrared spectra, shifted to lower frequency relative to the analogous molybdenum complexes. There is no apparent trend in either the carbonyl stretching frequencies or in the relative band intensities. The X-ray powder patterns of the bromo and iodo complexes as the tetraphenylborate salt are identical, not only to each other, but also to the corresponding molybdenum complexes. The tungsten complexes are thus seven-coordinate and a capped trigonal prismatic structure is proposed. Furthermore, there is no reason to suppose that the iodo complex is in any way different to the other complexes, as was suggested by Colton *et al.*[263]

$[W(CO)_2(dpe)_2Br]^+$ reacts with bromide to form $[W(CO)_2(dpe)_2Br_2]$; the reaction is much slower than that observed for $[Mo(CO)_2(dpe)_2Br]^+$ and this is consistent with the increased inertness of tungsten complexes towards substitution. When a solution of $[W(CO)_2(dpe)_2Br]Br_3$ in dichloromethane was allowed to stand at room temperature, complete conversion to $[W(CO)_2(dpe)_2Br_2]$ occurred after 85 hours. The orange solution showed strong carbonyl absorptions in the infrared at 1930 and 1842 cm^{-1}. Furthermore, no polymeric or other decomposition products were formed during this period of time.

$[W(CO)_2(dpe)_2I]^+$ reacts slowly with triiodide at elevated temperatures to form $W(CO)_3(dpe)I_2$. When a solution of $[W(CO)_2(dpe)_2I]I_3$ was left in the infrared beam for 90 minutes, absorptions of medium intensity were present at 2043, 1959 and 1905 cm^{-1}, which are attributable to the tricarbonyl complex. An absorption was also present at 1845 (m) cm^{-1} and this suggests that a small amount of $[W(CO)_2(dpe)_2I_2]$ has been formed. The other band for this complex is estimated to be at 1930 cm^{-1}. However, the bands due to the monoiodo cation, although somewhat reduced in intensity, were still fairly strong.

TABLE 3.8

Properties of the Monohalo Tungsten Complexes

Complex	Colour	ν_{CO} $(cm^{-1})^{A}$	R^{B}	Bond Angle^{B} (deg)	$\Lambda_M{}^{C}$ $(S\ cm^2)$
$[W(CO)_2(dpe)_2F]PF_6$	canary yellow	1935, 1875	1.47	79	77.7^{D}
$[W(CO)_2(dpe)_2Br]Br_3$, $1.5CCl_4$	bright yellow	1935, 1865	1.66	76	113^{E}
$[W(CO)_2(dpe)_2Br]BPh_4$	bright yellow	1936, 1865	1.69	75	–
$[W(CO)_2(dpe)_2I]I_3$	brown	1937, 1868	1.71	75	–
$[W(CO)_2(dpe)_2I]BPh_4$	bright yellow	1937, 1868	1.69	75	–
$[W(CO)_2(dpe)_2I]I^{F}$	yellow	1935, 1865	–	–	–

A. Measured in dichloromethane solution. All bands are very strong. B. See Table 3.1. C. Measured at 25°C. All concentrations *c.* 1.0×10^{-3} M. D. In nitromethane. E. In acetone. F. Reference 263.

TABLE 3.9

Infrared Spectra[A] of $[W(CO)_2(dpe)_2Br]X$, ($X = Br_3$, BPh_4)

Assignment	Frequency (cm^{-1}) $X = Br_3^-$[B]	 $X = BPh_4^-$
ν_{sym}(CO)	1934 vs	1936 vs
ν_{as} (CO)	1864 vs	1868 vs
Aromatic ring	1586 w	1580 mw
vibrations	1575 w	
$\nu_{P-C(aromatic)}$	1093 m	1093 m
Carbon tetrachloride		
ν(C-Cl)	795 s	-
combination bands	768 sh	-
	760 sh	-
C-H out of	750 s	747 sh, 742 s
plane def.	700 s	711 sh, 705 s
δ(MCO)	569 m	569 m
δ(MCO)	540 s	540 s
Other prominent bands	880 mw	881 mw
	835 mw	826 mw
	530 m	530 sh
	514 ms	517 ms
	492 ms,br	492 sh
	-	490 ms
	420 ms	420 ms

A. Recorded as nujol mulls.

B. The compound contains 1.5 molecules of carbon tetrachloride of crystallization.

TABLE 3.10

Infrared Spectra[A] of $[W(CO)_2(dpe)_2I]X$, ($X = I_3$, BPh_4)

Assignment	Frequency (cm^{-1}) $X = I_3^-$	 $X = BPh_4^-$
$\nu_{sym}(CO)$	1932 vs	1939 vs
ν_{as} (CO)	1863 vs	1870 vs
Aromatic ring vibrations	1586 w	1580 mw
	1572 w	
$\nu_{P-C(aromatic)}$	1092 m	1092 m
C-H out of plane def.	747 s	746 sh, 742 s
	700 s	711 sh, 704 s
δ(MCO)	568 m	566 m
δ(MCO)	540 s	539 s
Other prominent bands	880 mw	880 mw
	823 mw	825 mw
	530 sh	530 sh
	514 ms	516 ms
	496 m	491 ms
	486 m	486 sh
	415 m	419 ms

A. Recorded as nujol mulls.

3.6 Oxidation of $Cr(CO)_2(dpe)_2$

It was shown electrochemically that *trans*-$[Cr(CO)_2(dpe)_2]^+$ could be reversibly oxidized to the dication, *trans*-$[Cr(CO)_2(dpe)_2]^{2+}$, and that the dication is stable on the electrochemical time scale. The half wave potential for the process in dichloromethane is +1.2V (*vs.* Ag/AgCl, (0.1 M LiCl; acetone)) compared with +1.3V for the oxidation of the analogous molybdenum and tungsten complexes.[113]

Treatment of a suspension of either *cis*- or *trans*-$Cr(CO)_2(dpe)_2$ in dichloromethane with a solution of bromine in the same solvent at room temperature produced initially a bright yellow solution of the known complex, *trans*-$[Cr(CO)_2(dpe)_2]^+$ (ν_{CO} 1848 cm^{-1}). The cation reacts further to give a green solution, which is indicative of the formation of a chromium(III) complex. The only change observed in the infrared spectrum was a decrease in the intensity of the band at 1848 cm^{-1}. This indicates that the chromium(II) complex, *trans*-$[Cr(CO)_2(dpe)_2]^{2+}$, is easily oxidized to the trivalent oxidation state with the concomitant loss of carbon monoxide. The most likely product of the reaction is $[Cr(dpe)_2Br_2]^+$ (see below).

$Cr(CO)_2(dpe)_2$ was treated with bromine (3 moles) in dichloromethane at -70°C and the products were isolated from the yellow solution by the addition of either carbon tetrachloride or a solution of sodium tetraphenylborate in methanol. The infrared spectrum (nujol mull) showed that the yellow solid consisted almost exclusively of *trans*-$[Cr(CO)_2(dpe)_2]^+$. A very weak absorption was also present at 1950 cm^{-1} and this may be due to the divalent chromium complex. However, despite repeated attempts, it was not possible to isolate this compound in any significant amount. The cation, *trans*-$[Cr(CO)_2(dpe)_2]^+$, was not oxidized by either iodine or silver perchlorate in dichloromethane, even when a very large excess of the reagent was added.

According to the Nernst equation, the standard electrode potential

(E°) for an oxidizing agent must be greater than E° (absolute value) for the complex being oxidized for complete reaction to occur. However, the half wave potentials for the $[M(CO)_2(dpe)_2]^+/[M(CO)_2(dpe)_2]^{2+}$ couples (M = Cr, Mo, W)[113] are larger than the E° values for bromine and iodine.[246(a)] One of the driving forces in the halogen oxidations of the molybdenum and tungsten complexes is that the six-coordinate metal(II) cations, initially produced in the reaction, accept a halide ion into their coordination sphere to give the seven-coordinate complexes that are finally isolated. This appears to be the principal reason for the formation of $[M(CO)_2(dpe)_2I]^+$ and, to a lesser extent, $[M(CO)_2(dpe)_2Br]^+$ (M = Mo, W). Moreover, the seven-coordinate complexes are resistant to further oxidation (see Chapter 2).

In the case of the chromium analogue, the metal(II) complex remains six-coordinate, and thus, the above process can not operate. Consequently, a powerful oxidant is required for the preparation of the divalent complex and this explains the failure of the reactions between *trans*-$[Cr(CO)_2(dpe)_2]^+$ and both iodine and silver(I). However, the chromium(II) complex, as explained in Chapter 2.9, is not stable with respect to oxidation and accordingly, further oxidation will occur under these conditions to give a chromium(III) complex.

Divalent chromium carbonyl complexes containing tertiary arsine ligands have been isolated. $Cr(CO)_2(diars)_2$ reacts with one mole of halogen (X = Br, I) at room temperature to give the seven-coordinate complexes $[Cr(CO)_2(diars)_2X]X$. Treatment with excess halogen at room temperature produced the trihalide salts without further oxidation of the metal.[93] Iodine oxidation of $Cr(CO)_3$(*o*-triars) in benzene at room temperature gave the stable complex $[Cr(CO)_3$(*o*-triars)$I]I_3$,[65] while a similar reaction with $Cr(CO)_3$(*l*-triars) at -70°C gave the cation $[Cr(CO)_3$(*l*-triars)$I]^+$, which was isolated as the tetraphenylborate salt. The complex decomposes rapidly at room temperature.[94] Under similar conditions $Cr(CO)_3$(ν-triars) yields the air stable derivative $[Cr(CO)_2(\nu\text{-triars})I]BPh_4$.[94] The neutral arsine-substituted complexes are easier to oxidize than $Cr(CO)_2(dpe)_2$, since complete conversion to products occurs with an equimolar quantity of the halogen and, furthermore, no chromium(I) derivatives have been isolated. This may be due to the fact that these complexes are less sterically hindered.

Halogen oxidation of substituted chromium carbonyl complexes usually results in the formation of chromium(III) complexes, which are generally dark green. Thus, treatment of $Cr(CO)_3(o\text{-triars})$ with bromine or iodine in chloroform gave $Cr(o\text{-triars})X_3$ (X = Br, I),[65] while similar reaction with $Cr(CO)_4(diars)$ yielded $[Cr(diars)X_3]_2$.[93] $Cr(CO)_2(QP)$ reacts with excess bromine to give $[Cr(QP)Br_3]$ and with excess iodine to yield $[Cr(QP)I_2]I_3$.[67] $Cr(CO)_2(diars)_2$ reacts with a large excess of iodine in refluxing carbon tetrachloride over a period of 18 hours to yield $[Cr(diars)_2I_2]I_3$.[93]

3.7 Oxidation of $Mo(CO)_2(dpe)_2$ with Nitric Acid and Nitrogen Dioxide

In the oxidations described previously in this Chapter, the oxidant was also a source of good electron-donor ligands, which coordinate to the metal and stabilize the product. If a non-coordinating oxidant was used, it may be possible to add ligands of choice and thus, synthesize complexes of the type $[M(CO)_2(bidentate)_2L]^+$ containing any desired ligand L. The oxidant must, of course, not react with the ligands themselves. As demonstrated in this Chapter [section 2(d)] and in Chapter 2, the nitrosonium ion may behave as a powerful, but inert, oxidant.

The reactions of $Mo(CO)_2(dpe)_2$ with nitric acid and nitrogen dioxide were examined to see whether these compounds could be used as general oxidants. Concentrated nitric acid oxidizes *trans*-$[Mn(CO)_2(dpe)_2]^+$ to *trans*-$[Mn(CO)_2(dpe)_2]^{2+}$. The dipositive cation is remarkably stable and dissolves in concentrated nitric acid without change.[166] When a suspension of $Mo(CO)_2(dpe)_2$ in nitromethane or acetone was treated with concentrated nitric acid, the complex dissolved with evolution of a gas to form a bright red solution, which rapidly changed to bright yellow. The infrared spectrum of the solution showed carbonyl absorptions at 1965 (s), 1900 (sh) and 1880 (s) cm^{-1} and this indicates that a mixture of complexes in oxidation states I and II has been formed. The addition of excess acid produced no change and attempts to isolate the products resulted in decomposition to give intractable precipitates.

When nitrogen dioxide, diluted with dry nitrogen, was bubbled through suspensions of $Mo(CO)_2(dpe)_2$ in a variety of solvents including dichloromethane, nitromethane, acetone and acetonitrile, the neutral complex dissolved to give a red solution, which changed to yellow. Infrared monitoring showed that the solutions still contained a large amount of *trans*-$[Mo(CO)_2(dpe)_2]^+$ (ν_{CO} 1878 (vs) cm^{-1}), which could not be completely oxidized even with a large excess of nitrogen dioxide. In the donor solvents, acetone and acetonitrile, strong carbonyl absorptions were present at 1965 and 1900 (sh) cm^{-1}. These indicate that a high concentration of a molybdenum(II) complex, possibly a solvento complex, has been formed. A considerable amount of decomposition always occurred, particularly if excess nitrogen dioxide was added. Similar results were obtained in dichloromethane and nitromethane, except that the bands due to the product were not as intense. In nitromethane a band was also present at 1975 (m) cm^{-1}. The products were not characterized.

Nitrogen dioxide reacts with a suspension of $Mo(CO)_2(dpe)_2$ in dichloromethane containing an excess (2 - 8 moles) of either tetraphenylarsonium chloride or tetraethylammonium bromide to form ultimately bright yellow solutions of $[Mo(CO)_2(dpe)_2X]^+$ (X = Cl, Br). However, while the solution was still red (and thus, the predominant species present was *trans*-$[Mo(CO)_2(dpe)_2]^+$), a very strong band was observed in the infrared spectrum at 1975 cm^{-1}. The complex was not resistant to further reaction and the intensity of the band rapidly decreased as more nitrogen dioxide was added. It is thought that this complex is similar to those formed in the oxidations with nitrosonium hexafluorophosphate [Chapters 2.6 - 2.8, 3.2(d)]. A moderate amount of decomposition had also occurred. In all the reactions mentioned above the amount of decomposition decreased when the solutions were cooled in an ice/ethanol bath.

Reimann and Singleton[270] reported that nitrogen dioxide behaves as a one-electron oxidant, oxidizing $Mo(CO)_2(dpe)_2$ instantaneously to *trans*-$[Mo(CO)_2(dpe)_2]^+$ in warm chloroform. They did not mention any further oxidation, which would undoubtedly have occurred under these conditions. On the whole, it must be concluded that, for these types of complexes, nitrogen dioxide is an unsatisfactory oxidant in the sense of producing clean oxidations and would appear to have only limited synthetic application.

3.8 Halide Abstraction Reactions

Halide abstractions are a general type of reaction. Because of the almost total insolubility of the silver halides (X = Cl, Br, I), the addition of a soluble silver salt to a wide variety of halide complexes in a large number of solvents almost invariably results in precipitation of the silver halide. In donor solvents the usual products of these reactions are solvento complexes, as illustrated by the following equations:[237,292]

$$\mathrm{Ir(CO)(PPh_3)_2Cl} \xrightarrow[\text{Solvent}]{\mathrm{Ag^+}} \mathrm{[Ir(CO)(solvent)(PPh_3)_2]^+ + AgCl}$$

$$\text{Solvent} = \mathrm{MeCN,\ PhCN,\ Me_2SO}$$

$$\mathrm{Mn(CO)_3L_2Br} \xrightarrow[\text{MeCN}]{\mathrm{Ag^+}} \mathrm{[Mn(CO)_3L_2(MeCN)]^+ + AgBr}$$

$$\mathrm{L = P(OMe)_3,\ PMe_2Ph}\ \text{etc.}$$

However, the silver ion can also behave as a strong oxidant and this may be the preferred mode of reaction with easily-oxidizable complexes.

The iodo complexes, $\mathrm{[Mo(CO)_2(dpe)_2I]X}$ ($\mathrm{X = I_3,\ BPh_4}$), react smoothly with silver perchlorate in acetonitrile and benzonitrile to produce the corresponding nitrile complexes, $\mathrm{[Mo(CO)_2(dpe)_2(RCN)]^{2+}}$ (R = Me, Ph), according to the equation:

$$\mathrm{[Mo(CO)_2(dpe)_2I]X} \xrightarrow[\text{RCN}]{\mathrm{AgClO_4}} \mathrm{[Mo(CO)_2(dpe)_2(RCN)](ClO_4)_2 + AgI\downarrow + AgX\downarrow}$$

Infrared monitoring showed that the anion could be completely precipitated before the halide abstraction reaction began. In the reaction of the triiodide salt, a suspension of the complex was used; the complex dissolved as the reaction proceeded yielding a bright yellow solution of the nitrile complex. No colour change occurred in the reaction of the tetraphenylborate salt. The infrared spectra of the solutions showed carbonyl absorptions, which were both sharp and intense, at 1962 and 1902 $\mathrm{cm^{-1}}$. These compare favourably with the frequencies recorded in Table 2.4, allowing for solvent effects. The nitrile complexes are stable with respect to heat and show no tendency to decompose in the presence of excess silver perchlorate.

Halide abstractions also occurred when the iodo complexes were treated with silver perchlorate in the nitro solvents RNO_2 (R = Me, Et, Ph). The resultant bright yellow solutions showed strong (and sharp) carbonyl absorptions in the infrared spectrum at 1965 and 1903 cm^{-1} (R = Me) and 1963 and 1903 cm^{-1} (R = Et, Ph). These suggest that the corresponding nitro complexes, $[Mo(CO)_2(dpe)_2(RNO_2)]^{2+}$, have been formed. Nitro solvents are generally considered to be poor ligands.[271] In the reaction of $Mo(CO)_2(dpe)_2$ with nitrosonium hexafluorophosphate in nitro solvents (Chapter 2.3), fluoride abstraction from the hexafluorophosphate ion occurs in preference to coordination of the solvent. However, the only other potential ligand is the perchlorate ion, which has an extremely poor electron-donating ability. In fact, perchlorato complexes can only be prepared by the strict exclusion of all other ligands (see Chapter 4). Although it is conceivable that a perchlorato complex may be formed as an intermediate in the aforementioned halide abstraction reactions, the perchlorato group will be rapidly substituted by the solvent, which is both a better ligand and is also present in large excess. It will be shown in Chapter 4 that perchlorato complexes react with polar solvents, including nitromethane, to give solvento complexes. In conclusion, it appears that organic nitro solvents will function as ligands in the absence of other suitable electron-pair donors.

The bromo complexes, $[Mo(CO)_2(dpe)_2Br]X$ ($X = Br_3, BPh_4, ClO_4$), react similarly with silver perchlorate in acetonitrile and benzonitrile to form bright yellow solutions of the corresponding nitrile complexes. When the nitro solvents RNO_2 (R = Me, Et) were used, the reaction mixtures showed carbonyl absorptions at 1962 and 1902 cm^{-1}, which were broad and less intense than those observed for the reactions of the iodo complex; sometimes well-defined shoulders were present at 1978 and 1908 cm^{-1}. This suggests that a rearrangement has occurred during the abstraction of the halide, thus, producing a mixture of solvento complexes. Furthermore, the infrared spectra showed bands at 1100 (s,br) and 630 (s) cm^{-1}, which indicates that the perchlorate ion is not coordinated.

Attempts to prepare a perchlorato adduct by stirring $[Mo(CO)_2(dpe)_2Br]ClO$ with silver perchlorate in dichloromethane resulted in decomposition. Although precipitation of silver bromide occurred, the only change observed in the infrared spectrum was a steady decrease in the intensity of the bands due to the bromo complex. This also indicates that dichloromethane has negligible electron-donating ability and behaves, to a good approximation, as an inert solvent.

When $[Mo(CO)_2(dpe)_2Cl]Cl$ was treated with silver perchlorate in acetonitrile, the ionic chloride was rapidly precipitated; however, the coordinated halide could not be abstracted even with an excess of the silver salt. The reaction with $[Mo(CO)_2(dpe)_2F]PF_6$ was not investigated since silver fluoride has solubility properties similar to those of silver perchlorate.

3.9 Oxidation of $M(CO)_2L_2$ (L = dpm, dmpe)

While this work was in progress, the redox reactions of the analogous systems, $M(CO)_2(dpm)_2$ (M = Cr, Mo, W)[117] and $M(CO)_2(dmpe)_2$ (M = Mo, W),[118-120] were reported. The former system has also been studied electrochemically[121] and the results are summarized in the introduction [Chapter 1.3(d)]. The half-wave potentials suggest that the dpm complexes are easier to oxidize than their dpe analogues; in particular, the divalent oxidation state should be more readily attained with dpm as the ligand. In both series of complexes, the chromium compounds are the easiest to oxidize. Cyclic voltammetry showed that the oxidation of *trans*-$[Cr(CO)_2(dpm)_2]^+$ was irreversible because the *trans*-divalent cation has no inherent stability. In contrast, the oxidation of *trans*-$[Cr(CO)_2(dpe)_2]^+$ is reversible and the dipositive cation is stable on the electrochemical time scale. It was shown in a voltammetric study[116] that $Mo(CO)_2(dmpe)_2$ is easier to oxidize than the dpe analogue.

Treatment of *cis*-$Cr(CO)_2(dpm)_2$ with excess iodine in dichloromethane gave the yellow-brown chromium(I) complex, *trans*-$[Cr(CO)_2(dpm)_2]I_3$. Similarly, reaction of the neutral complex with an equimolar amount of nitrosonium hexafluorophosphate produced yellow *trans*-$[Cr(CO)_2(dpm)_2]PF_6$. The addition of excess nitrosonium hexafluorophosphate resulted in further oxidation, but the products were not characterized. Silver perchlorate and both mercurous and mercuric halide (X = F, Cl, Br, I) oxidize $Cr(CO)_2(dpm)_2$ to the *trans*-cation in dichloromethane or acetone.

$Cr(CO)_2(dpm)_2$ reacts with concentrated perchloric acid in acetone to give the hydride, $[Cr(CO)_2(dpm)_2H]ClO_4$, as a pale yellow powder. The intense carbonyl stretching band in the infrared spectrum is shifted to higher wavenumber relative to the *trans*-cation. The diamagnetism of the complex, in both the solid state and in solution, indicates an oxidation state of II. The complex is electrochemically inactive; this appears to be a general property of seven-coordinate metal(II) complexes. The hydride, on standing in solution, is converted to *trans*-$[Cr(CO)_2(dpm)_2]^+$, while treatment with base yields *cis*-$Cr(CO)_2(dpm)_2$.

Oxidation of *cis*-$Mo(CO)_2(dpm)_2$ with an equimolar quantity of silver perchlorate in acetone or dichloromethane produced *trans*-$[Mo(CO)_2(dpm)_2]ClO_4$. Oxidation with iodine in dichloromethane gave the pale brown molybdenum(II) iodo complex, $[Mo(CO)_2(dpm)_2I]I_3$. The infrared spectrum showed that the *cis*-isomer (referring to the relative orientation of the carbonyl groups) had been formed. When the reaction was carried out in acetone, a mixture of *cis*- and *trans*- isomers was obtained. The pure *cis*-complex isomerized in acetone to give an equilibrium mixture of the two species. Oxidation with bromine in dichloromethane gave a mixture of *cis*- and *trans*-$[Mo(CO)_2(dpm)_2Br]Br_3$. Treatment of $Mo(CO)_2(dpm)_2$ with perchloric acid in acetone gave the pale green diamagnetic hydride, $[Mo(CO)_2(dpm)_2H]ClO_4$. The tungsten complex reacts in an analogous manner.

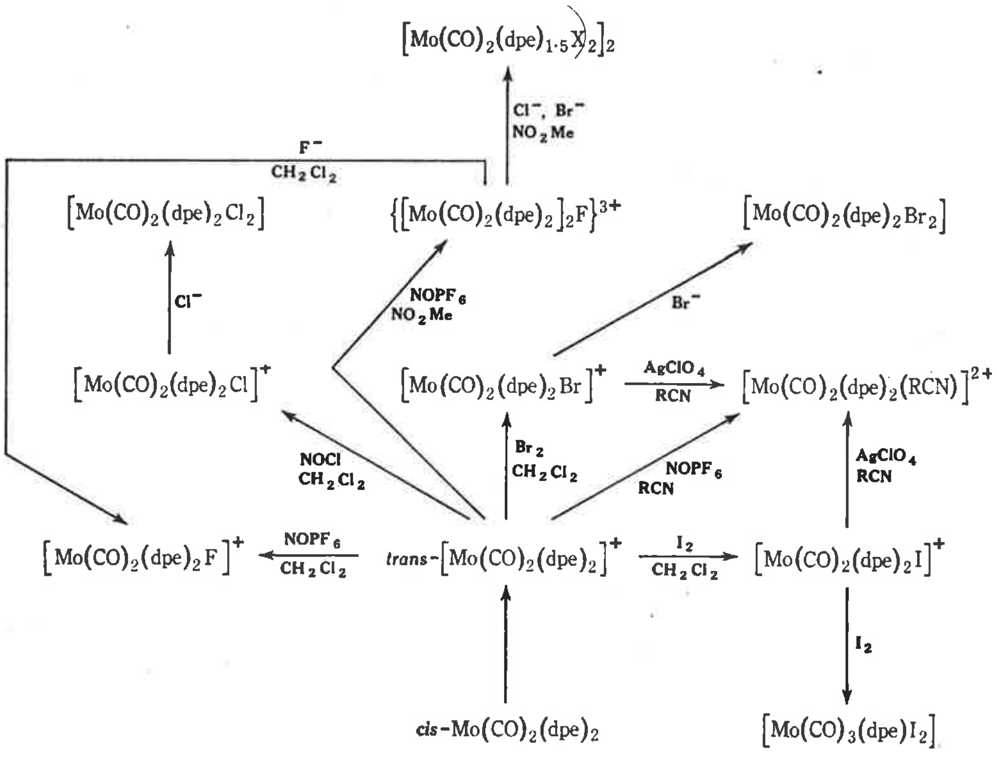
The reaction between equimolar quantities of *cis*-$Mo(CO)_2(dmpe)_2$ and AgX (X = NO_3, BF_4) in acetonitrile/dichloromethane resulted in oxidation to give *trans*-$[Mo(CO)_2(dmpe)_2]X$. The addition of a further mole of silver nitrate to a solution of *trans*-$[Mo(CO)_2(dmpe)_2]NO_3$ gave the yellow molybdenum(II) nitrato complex, $[Mo(CO)_2(dmpe)_2(ONO_2)]NO_3$. A similar reaction with silver sulphate yielded the sulphato complex, $[Mo(CO)_2(dmpe)_2(OSO_3)]$. The complex is neutral overall and must, therefore, be zwitterionic in the sense $[Mo^+-O-SO_3^-]$. In normal laboratory light this compound is converted to $[Mo(CO)(dmpe)_2(O_2SO_2)]$ containing bidentate sulphate with elimination of carbon monoxide.

Treatment of *cis*-$M(CO)_2(dmpe)_2$ (M = Mo, W) with iodine (one mole) in dichloromethane produced the yellow metal(II) complexes $[M(CO)_2(dmpe)_2I]I$. The molybdenum(II) complex has also been prepared by reacting $Mo(CO)_2(dmpe)_2$ with CF_3I. The addition of $PhCH_2Br$ to $Mo(CO)_2(dmpe)_2$ at room temperature gave $[Mo(CO)_2(dmpe)_2Br]Br$ and 1,2-diphenylethane quantitatively. A similar reaction with carbon tetrachloride at -80°C gave $[Mo(CO)_2(dmpe)_2Cl]Cl$ and C_2Cl_4 together with minor amounts of C_2Cl_6. The pale yellow hydride, $[Mo(CO)_2(dmpe)_2H]HCl_2$, was prepared by bubbling hydrogen chloride gas through a solution of $Mo(CO)_2(dmpe)_2$ in dichloromethane at room temperature. The relative stereochemistry of the carbonyl groups is *trans*, as shown by the presence of only one carbonyl stretching band in the infrared spectrum.

3.10 Discussion and Conclusions

It has been shown that complexes of the formula $M(CO)_2(dpe)_2$ (M = Mo, W) can be oxidized to the metal(II) oxidation state by a variety of oxidants with widely differing oxidizing abilities. The divalent species initially formed in solution is undoubtedly *trans*-$[M(CO)_2(dpe)_2]^{2+}$; however, this dication has only a transient existence since it will accept any suitable electron donor into its coordination sphere to form a seven-coordinate complex. This mechanism explains the reactions with mild oxidants such as iodine. The seven-coordinate complexes are reasonably resistant to further oxidation and this enables them to be isolated even in the presence of excess oxidant. If a suitable electron donor is not available or the metal(II) cation is structurally unable to accept another ligand as occurs in the chromium system, the cation decomposes usually by being oxidized further and with the loss of the carbonyl groups. The reactions of the molybdenum complexes are summarized in Scheme 3.1.

Three idealized geometries are usually considered for seven-coordinate complexes: the D_{5h} pentagonal bipyramid, the C_{3v} monocapped octahedron and the C_{2v} monocapped trigonal prism. Within these constraints the bulk of the available evidence suggests that tetraphosphine complexes of the formula $[M(CO)_2L_2X]^+$ (M = Mo, W; L = dpe, dmpe; X = Cl, Br, I) have capped trigonal prismatic structures. Furthermore, this is the only geometry consistent with the spectroscopic data for $[Ta(CO)_2(dmpe)_2X]$ (X = Cl, Br, CN, CH_3).[258] On the other hand, the data for the hydrido complexes $[M(CO)_2L_2H]^n$ (n = 0, +1; M = Cr, Mo, W; L = dpm, dmpe; M' = Ta; L = dmpe[264,265]) suggest that they all have capped octahedral structures. The difference in structures appears to be related to the size of the capping ligand rather than to electronic factors since, in the tantalum complexes, no discrimination on an electronic basis is observed at the capping site; i.e. halide (π donor), methyl (σ donor) and cyanide (π acceptor) all occupy the same site. However, the diamagnetic adducts,



Scheme 3.1 Oxidation of *cis*-$Mo(CO)_2(dpe)_2$

$[M(CO)_2(dpe)_2(HgX)]HgX_3$ (M = Mo, W; X = Cl, Br, I)[257] show only one carbonyl stretching band in the infrared spectrum and this is consistent with either a capped octahedral or, more likely, a pentagonal bipyramidal structure. The reason for this is, at present, uncertain.

The diversity of structures observed in the bidentate phosphine systems discussed previously is partly due to the flexibility of the $M(CO)_2L_2$ moiety. In contrast, the complexes *cis*-$M(CO)_2(QP)$ (M = Cr, Mo, W) have rigid structures due to the constraints imposed by the ligand. This is illustrated by the oxidation of the chromium complex to give *cis*-$[Cr(CO)_2(QP)]^+$.[67] Similarly, no rearrangement can occur in the oxidation of the molybdenum and tungsten analogues to the metal(II) complexes, $[M(CO)_2(QP)X]^+$ (M = Mo, W; X = Cl, Br, I),[68] and it is suggested that these complexes have capped octahedral structures. This lack of flexibility may also be responsible for the instability of the molybdenum derivatives.

The complexes $M(CO)_2L_2$ (M = Cr, Mo, W; L = dpm, dmpe) are easier to oxidize than the dpe analogues. It has been shown electrochemically[116] that there is no significant difference in the donor-acceptor properties of trimethylphosphine and triphenylphosphine and thus, dimethylphosphino- and diphenylphosphino-groups are expected to show similar electronic effects.[269] In an electrochemical study on a series of complexes of the formula $Cr(CO)_5L$ [L = NH_3, PR_3 (R = OMe, OPh, Me, Ph, etc)], there was no correlation between the halfwave potential for the oxidative one-electron-transfer process and the basicity of the Lewis base. The only explanation the workers could offer is that the halfwave potential is affected by the steric interactions between the ligands. This strongly suggests that the ease of oxidation of phosphine-substituted metal carbonyl complexes depends directly on the bulk of the complex or, more specifically, on the size of the substituent groups attached to the phosphines. It is proposed that the dpe complexes are more difficult to oxidize than their dmpe counterparts because the large phenyl rings in the former complexes protect the metal centre from attack by the oxidant more so than the methyl groups in the latter. Similarly, since dpe forms five-membered chelate rings and thus, has a larger bite* than dpm, which forms four-membered rings, it is more effective in protecting the metal from attack by the oxidant.

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* The bite (B)[250] of a ligand, in this case, is defined as

$$\frac{\text{distance between phosphorous atoms}}{\text{M-P bond length}}$$

B_{dpe} = 1.29 (calculated from the data in references 227, 253)

B_{dpm} = 1.05 (calculated from the data in reference 248)

3.11 Experimental

General

All preparations and reactions except metatheses were carried out in an atmosphere of high-purity dry nitrogen. Solvents were of analytical grade purity and were dried over Linde 4A molecular sieves before use. The light petroleum used in the experiments had b.p. < 40°. All compounds were stored in the dark as they developed either a brown or a green colour when exposed to the light for a few hours. The preparations of the starting materials are described in Appendices 1 and 2. Nitrosyl chloride was stored in glass ampules; these were broken inside a large flask and the nitrosyl chloride was transferred into the reaction flask using dry nitrogen as a carrier gas.

The instruments used for the physical measurements are described in Appendix 1. Carbonyl stretching frequencies were usually measured in dichloromethane solution while the complete infrared spectra were determined as nujol mulls between potassium bromide plates.

$[Mo(CO)_2(dpe)_2Cl]Cl$

NOCl diluted with dry N_2 was bubbled into a vigorously stirred suspension of $Mo(CO)_2(dpe)_2$ (120 mg) in dichloromethane (7.5 ml) until the solid had dissolved to give a bright red solution. Stirring was continued until the solution was orange. Carbon tetrachloride (20 ml) was added and the solution was concentrated to precipitate $[Mo(CO)_2(dpe)_2Cl]Cl$ as a pale yellow powder (70 - 80 mg, *c.* 62%). The solid was filtered, washed with carbon tetrachloride and light petroleum, and dried in a vacuum.

(Found:	C, 60.5; H, 4.9; Cl, 7.2; P, 12.0
$C_{54}H_{48}Cl_2MoO_2P_4$ requires:	C, 63.6; H, 4.8; Cl, 7.0; P, 12.2%).

$[Mo(CO)_2(dpe)_2Cl]BPh_4$

A concentrated solution of $NaBPh_4$ in methanol was added dropwise with shaking to a solution of $[Mo(CO)_2(dpe)_2Cl]Cl$ (100 mg) in dichloromethane (0.7 ml). The bright yellow crystals (96 mg, 75%) were washed with methanol, water, methanol and light petroleum, and dried in a vacuum. The compound still contained some sodium chloride.

(Found:	C, 69.9; H, 5.1; Cl, 4.7; P, 9.1
$C_{78}H_{68}BClMoO_2P_4$ requires:	C, 71.9; H, 5.3; Cl, 2.7; P, 9.5%).

$[Mo(CO)_2(dpe)_2Br]Br_3,1.5CCl_4$

Bromine (71 mg, 0.44 mmol; 2.2-2.3 equiv.) in carbon tetrachloride (8 ml) was added dropwise with magnetic stirring to a suspension of $Mo(CO)_2(dpe)_2$ (190 mg, 0.20 mmol) in dichloromethane (14 ml) over a period of about 8 min. The solid dissolved to an orange solution which turned yellow. Carbon tetrachloride (25-30 ml) was added slowly until turbidity was produced. A few extra millilitres were added and the mixture left in the refrigerator to complete the precipitation. The yellow solid was filtered, washed with carbon tetrachloride and light petroleum, and dried in a vacuum (240-250 mg, *c.* 85%).

(Found:	C, 44.5; H, 3.4; Br, 20.8; Cl, 15.0; P, 7.8
$C_{55}H_{48}Br_4Cl_6MoO_2P_4$ requires:	C, 44.5; H, 3.2; Br, 21.3; Cl, 14.2; P, 8.3%).

$[Mo(CO)_2(dpe)_2Br]BPh_4$

A concentrated solution of $NaBPh_4$ in methanol (*c.* 100 mg/ml) was added dropwise with shaking to a solution of $[Mo(CO)_2(dpe)_2Br]Br_3,1.5CCl_4$ (100 mg) in dichloromethane (0.75 ml). The solution turned cloudy, cleared and finally bright yellow crystals separated. These were filtered, washed with methanol, water, methanol and light petroleum, and dried in a vacuum (*c.* 70 mg, 75-80%).

(Found:	C, 68.1; H, 5.1; Br, 6.1; Cl, 0; P, 9.1
$C_{78}H_{68}BBrMoO_2P_4$ requires:	C, 69.5; H, 5.1; Br, 5.9; Cl, 0; P, 9.2%).

$[Mo(CO)_2(dpe)_2Br]ClO_4, CH_2Cl_2$

A concentrated solution of $LiClO_4$ in methanol was added slowly with shaking to a solution of the tribromide salt (100 mg) in dichloromethane (0.50 ml). On standing bright yellow crystals (55 mg, *c.* 70%) separated; these were washed with methanol/water, a few drops of methanol, then light petroleum and dried in a vacuum.

(Found:	C, 53.6; H, 4.1; Br, 6.6; Cl, 8.7; P, 10.3
$C_{55}H_{50}BrCl_3MoO_2P_4$ requires:	C, 54.5; H, 4.2; Br, 6.6; Cl, 8.8; P, 10.2%).

The PF_6^- salt was prepared similarly, using $NaPF_6$.

$[Mo(CO)_2(dpe)_2I]I_3$

A solution of iodine (480 mg, 1.89 mmol) in dichloromethane (14 ml) was added dropwise to a suspension of $Mo(CO)_2(dpe)_2$ (148 mg, 0.156 mmol) in dichloromethane (6 ml) with vigorous magnetic stirring over a period of 8 min. Methanol (40 ml) was added; the solution was filtered to remove the precipitated iodine and slowly concentrated (water pump). The brown crystals (110 mg) were filtered, washed free of iodine with ethanol, washed with light petroleum and dried in a vacuum.

(Found:	C, 42.3; H, 3.2; I, 34.8; P, 8.0
$C_{54}H_{48}I_4MoO_2P_4$ requires:	C, 44.5; H, 3.3; I, 34.9; P, 8.5%).

$[Mo(CO)_2(dpe)_2I]BPh_4$

A concentrated solution of $NaBPh_4$ in methanol was added to a solution of $[Mo(CO)_2(dpe)_2I]I_3$ (100 mg) in dichloromethane (0.85 ml) until crystallization commenced. The bright yellow precipitate (62 mg, 60-65%) was collected, washed with methanol and light petroleum, and dried in a vacuum.

(Found:	C, 65.7; H, 4.8; I, 9.5; P, 8.8
$C_{78}H_{68}BIMoO_2P_4$ requires:	C, 67.2; H, 4.9; I, 9.1; P, 8.9%).

Further Reaction of $[Mo(CO)_2(dpe)_2Br]Br_3$

$[Mo(CO)_2(dpe)_2Br]Br_3$ was prepared from $Mo(CO)_2(dpe)_2$ (119 mg) and bromine (46 mg) in dichloromethane/carbon tetrachloride (9 ml + 6 ml) as described above. The mixture was stirred under dry nitrogen for 4–5 h. The colour changed to deep red, then to cloudy orange. The solution was filtered to collect the orange CO-free precipitate (Found: C, 45.3; H, 3.4; Br, 29.8; Cl, *c.* 2.5; P, 8.5%). Light petroleum (12 ml) was added to precipitate an insoluble orange compound; ν_{CO} (Nujol mull) 1936vs, 1855vs cm^{-1} (Found: C, 44.2; H, 3.9; Br, 19.8; Cl, 7.2; P, 9.2%). The yellow filtrate was concentrated, carbon tetrachloride (20 ml) was added and the solution was concentrated to precipitate any unchanged $[Mo(CO)_2(dpe)_2Br]Br_3$. Light petroleum was added to the filtrate to precipitate $[Mo(CO)_2(dpe)_2Br_2]$ (*c.* 40 mg) as a yellow powder, which was washed with carbon tetrachloride and light petroleum, and dried in a vacuum.

(Found:* C, 54.6; H, 4.4; Br, 15.9; P, 10.3
$C_{54}H_{48}Br_2MoO_2P_4$ requires: C, 58.5; H, 4.4; Br, 14.4; P, 11.2%).

$[W(CO)_2(dpe)_2Br]Br_3,1.5CCl_4$

Bromine (37 mg, 0.23 mmol) in carbon tetrachloride (6 ml) was added dropwise with stirring to a suspension of $W(CO)_2(dpe)_2$ (104 mg, 0.10 mmol) in dichloromethane (7.5 ml). Carbon tetrachloride (20-22 ml) was slowly added to the bright yellow solution until turbidity was produced and the mixture was placed in a refrigerator to complete the precipitation. The bright yellow microcrystals (140 mg, 90%) were filtered, washed with carbon tetrachloride and light petroleum, and dried in a vacuum.

(Found: C, 41.7; H, 3.2; Br, 21.7; Cl, 14.4; P, 6.0
$C_{55}H_{48}Br_4Cl_6O_2P_4W$ requires: C, 42.0; H, 3.1; Br, 20.2; Cl, 13.4; P, 7.8%).

---

* The compound contains a small amount (*c.* 15%) of $[Mo(CO)_2(dpe)_2Br]Br_3$.

$[W(CO)_2(dpe)_2Br]BPh_4$

The procedure is identical to that for the analogous molybdenum salt, yielding bright yellow crystals of $[W(CO)_2(dpe)_2Br]BPh_4$ (80-85%).

$[W(CO)_2(dpe)_2I]I_3$

A solution of iodine (310 mg, 1.2 mmol) in dichloromethane (8 ml) was added dropwise and with vigorous stirring to a suspension of $W(CO)_2(dpe)_2$ (104 mg, 0.10 mmol) in dichloromethane (4 ml). Methanol (30-35 ml) was added and the solution was filtered. The filtrate was slowly concentrated to precipitate $[W(CO)_2(dpe)_2I]I_3$ as brown crystals (98 mg, 63%),which were filtered, washed with ethanol and light petroleum,and dried in a vacuum. A second crop of crystals (30 mg) was obtained by further concentration of the filtrate.

(Found:	C, 41.7; H, 3.1; I, 33.3; P, 7.8
$C_{54}H_{48}I_4O_2P_4W$ requires:	C, 42.0; H, 3.1; I, 32.9; P, 8.0%).

$[W(CO)_2(dpe)_2I]BPh_4$

The procedure is identical to that for the molybdenum complex; $[W(CO)_2(dpe)_2I]BPh_4$ was obtained as bright yellow crystals (65%).

Reactions with NO_2

The nitrogen dioxide cylinder was connected to the reaction flask by way of an inverted Dreschel bottle (250 ml) and a 3-way tap. After the apparatus had been completely flushed with dry nitrogen, the Dreschel bottle was filled with NO_2 gas. Nitrogen was then used as a carrier gas to transfer the NO_2 into the reaction flask. This procedure gave some degree of control over the amount of NO_2 used.

Reactions with $AgClO_4$

Solid $AgClO_4$ was added to suspensions or solutions of $[Mo(CO)_2(dpe)_2X]Y$ ($X = Br, I; Y = Br_3, I_3, ClO_4, BPh_4$) in the appropriate solvent. The solid dissolved as silver halide precipitated to give yellow solutions of the solvento complexes, which were identified by infrared spectroscopy.

CHAPTER 4

PERCHLORATO DERIVATIVES OF MANGANESE CARBONYL

4.1 Introduction

The perchlorate ion is generally considered to be non-coordinating and inert. Perchlorate salts are often used in kinetic studies to provide a medium of constant ionic strength and in electrochemical investigations as an inert supporting electrolyte. However, under the appropriate circumstances the ion will form complexes with transition metal ions[272-275] (e.g. $M(pyridine)_4(OClO_3)_2$; M = Ni, Cu). The only metal carbonyl complexes presently known to contain coordinated perchlorate are $M(CO)(PPh_3)_2(OClO_3)$ (M = Rh, Ir) and $Co(CO)_2(PPh_3)_2(OClO_3)$.[198]

In order to investigate the possibility of preparing perchloratocarbonyl complexes, manganese(I) compounds were chosen for several reasons. Firstly, this oxidation state is easily attained by halogen oxidation of $Mn_2(CO)_{10}$. The manganese pentacarbonylhalides are stable crystalline solids which are precursors to a wide variety of other complexes. The maximum stability of the metal carbonyl halides is attained with manganese and thus, there is reason to believe that a manganese carbonyl perchlorate would also be the most stable representative of this class of compound. Finally, manganese(I) complexes are very resistant to oxidation [see Chapter 1.4(b)].

The subject of this Chapter is the preparation, characterization and reactions of the first example of a perchlorate ion bonded to an unsubstituted metal carbonyl group together with substituted derivatives containing nitrogen- and phosphorous-donor ligands.

4.2 Preparation of $Mn(CO)_5(OClO_3)$

The complex, $Mn(CO)_5(OClO_3)$, was prepared by adding a slight excess of finely divided silver perchlorate to a solution of $Mn(CO)_5Br$ in dichloromethane as shown in the equation:

$$Mn(CO)_5Br + AgClO_4 \xrightarrow{CH_2Cl_2} Mn(CO)_5(OClO_3) + AgBr\downarrow$$

The reaction mixture, shielded from direct light, was stirred at room temperature (*c*. 25°C) under an atmosphere of dry nitrogen for 50-60 minutes. The colour of the solution changed from orange to pale yellow as silver bromide precipitated. The product was isolated as yellow microcrystals by filtering the reaction mixture into light petroleum.

Silver perchlorate has only very slight solubility (if any at all) in dichloromethane and the reaction probably occurs at the solvent-solid interface. It is for this reason that finely divided silver perchlorate was used. The time required for complete reaction depends on the ambient temperature and thus, the progress of the reaction was always monitored by infrared spectroscopy before the product was isolated.

$Mn(CO)_5(OClO_3)$ was found to be deliquescent and was, therefore, stored in a desiccator. When the compound is exposed to the atmosphere, it slowly absorbs water vapour forming a yellow solution. In a dry atmosphere the complex is very stable and can be kept for several months. Over a long period of time a slight amount of decomposition occurs, producing an insoluble compound, probably a manganese salt. $Mn(CO)_5(OClO_3)$, like the pentacarbonyl halides,[148] can be sublimed in a vacuum, although a slightly higher temperature (65-70°, 0.02 mm) is required. In comparison, attempts to sublime $Mn(CO)_5(ONO_2)$ by heating to 55°C/0.01 mm resulted in disproportionation to give sublimed $Mn_2(CO)_{10}$ and a residue containing $Mn(NO_3)_2$ and some oxides of manganese.[193] On the other hand, $Re(CO)_5(ONO_2)$ can be sublimed because of the inertness of rhenium.[196]

4.2.1 Characterization of $Mn(CO)_5(OClO_3)$

(a) Infrared Spectrum

The local symmetry of the carbonyl groups in a monosubstituted carbonyl complex, $M(CO)_5L$, is C_{4v}. Accordingly, these complexes should have three infrared-active carbonyl stretching fundamentals,[10,13,19,20] which are classified as A_1^{1a}, A_1^{1b} and E respectively (see Figure 4.1).[13] The relative band intensities have been deduced from symmetry arguments.[12,13] The E band will be very strong and the A_1^{1a} band will be less strong by a factor of roughly four. The A_1^{1b} band will be of weak intensity since it is almost totally forbidden. However, the two A_1 modes interact and some of the intensity of the strongly allowed one must be transferred to the other. The A_1^{1b} band will be at higher frequency relative to the E band, while the position of the A_1^{1a} band cannot be predicted.

Three carbonyl stretching bands (Table 4.1) are present in the infrared spectrum of $Mn(CO)_5(OClO_3)$. The relative band intensities (Figure 4.2) are consistent with C_{4v} symmetry. This indicates that the perchlorato group can be considered simply as a spherically symmetrical ligand which does not perturb the symmetry of the carbonyl groups. The bands are at higher frequency relative to the pentacarbonyl halides[12,276,277] (see Table 4.1), presumably because the perchlorato group is more strongly electron-withdrawing than the halide ions. Furthermore, since the perchlorato group coordinates through oxygen, there can be no metal-ligand π bonding.

The uncoordinated perchlorate ion has a regular tetrahedral structure and belongs to point group T_d; it has nine vibrational degrees of freedom, but due to the high symmetry of the ion there are only four normal modes of vibration. These are described as symmetric (A_1) and asymmetric (T_2) stretching and symmetric (E) and asymmetric (T_2) bending respectively;[278,279] only the two asymmetric modes are infrared active. The infrared spectrum

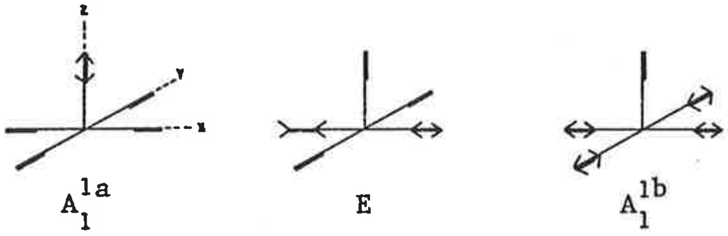


Fig. 4.1 The allowed carbonyl stretching Vibrations of [M(CO)$_5$L] Molecules. (Only One Component of the E Mode is Shown.)

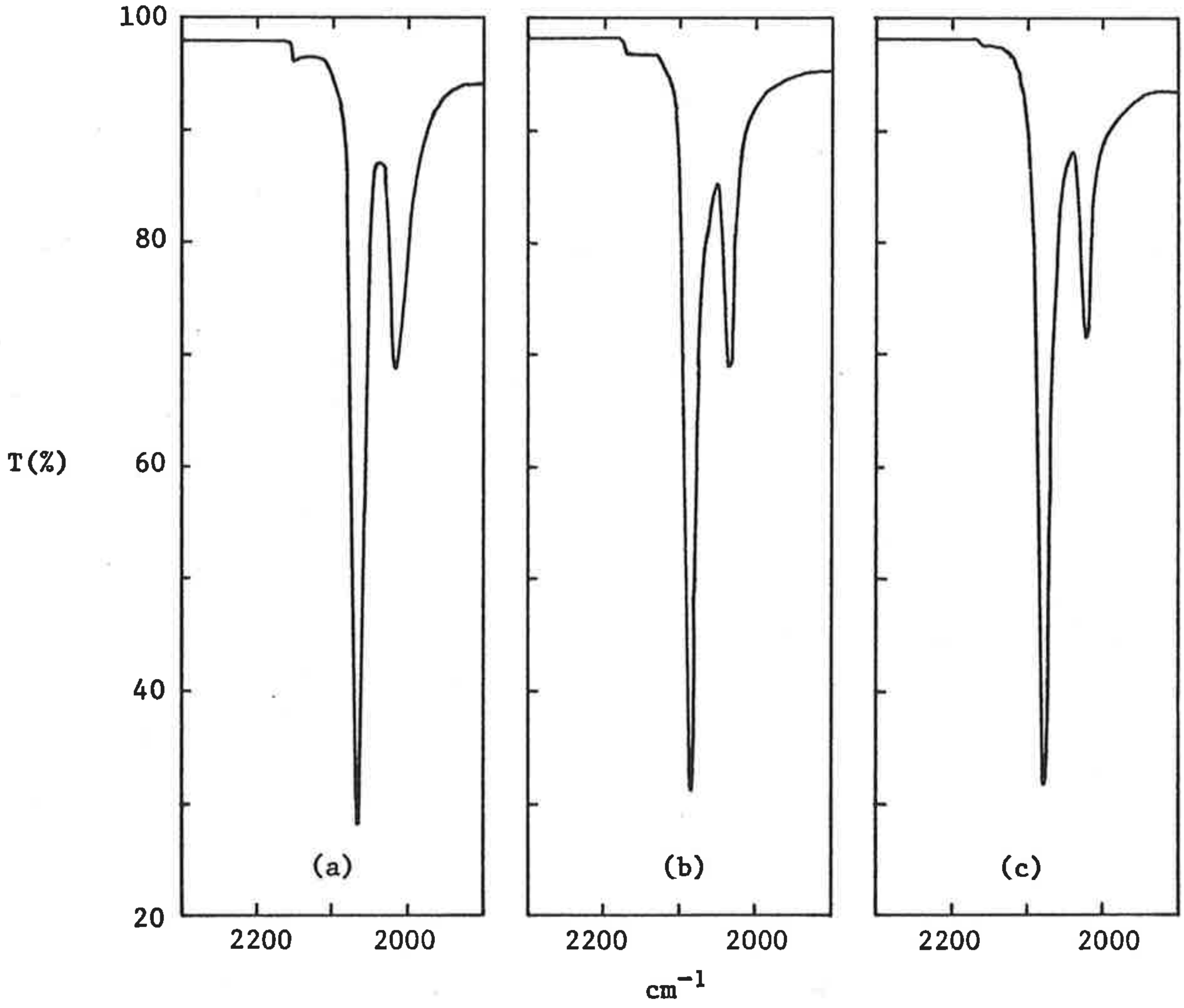


Fig. 4.2 Infrared Spectra of (a) Mn(CO)$_5$Cl, (b) Mn(CO)$_5$(OClO$_3$) and (c) Mn(CO)$_5$(PO$_2$F$_2$) in Dichloromethane.

consists of a very strong, broad band at 1110 cm^{-1} due to the stretching mode and weaker band at 626 cm^{-1} due to the bending mode.[278,279] The symmetric stretching mode, although theoretically infrared inactive, usually appears as a weak absorption at 932 cm^{-1} due to distortion of the ion in the crystal field.[279] All four modes of vibration are Raman active. The symmetric bending mode has been assigned to the band in the Raman spectrum at 460 cm^{-1}.[278]

If the perchlorate ion becomes coordinated to a metal ion through a single oxygen atom, the symmetry is lowered to C_{3v}. As a result, the triply degenerate asymmetric stretching band splits into two well defined bands (A_1 + E) with maxima between 1200 and 1000 cm^{-1}. Likewise the asymmetric bending mode also splits into two bands (A_1 + E). Furthermore, the symmetric stretching and bending modes become infrared active.[279,280] The former mode is now due to stretching of the ClO_3 moiety[273] while the latter mode becomes a rocking vibration.

The infrared spectrum of $Mn(CO)_5(OClO_3)$ in the 1200 - 300 cm^{-1} region is illustrated in Figure 4.3. The bands due to the perchlorato group (see Tables 4.1 and 4.10) are consistent with monodentate coordination of the ion. The asymmetric stretching band is split by approximately 140 cm^{-1}. The asymmetric ClO_3 bending absorption is buried beneath the very intense δ(MCO) band, while the corresponding symmetric absorption is present as a shoulder. The doubly degenerate rocking absorption was not observed. This band usually occurs in the region 480 - 420 cm^{-1} and is generally of medium-to-weak intensity.[279]

(b) Mass Spectrum

The mass spectrum of $Mn(CO)_5(OClO_3)$ is presented in Table 4.2. Molecular ions of moderate intensity were present at *m/e* 296 and 294 in the ratio of 1:3. These are due to the two isotopes of chlorine (^{35}Cl and ^{37}Cl); manganese itself, consists solely of one naturally occurring iso-

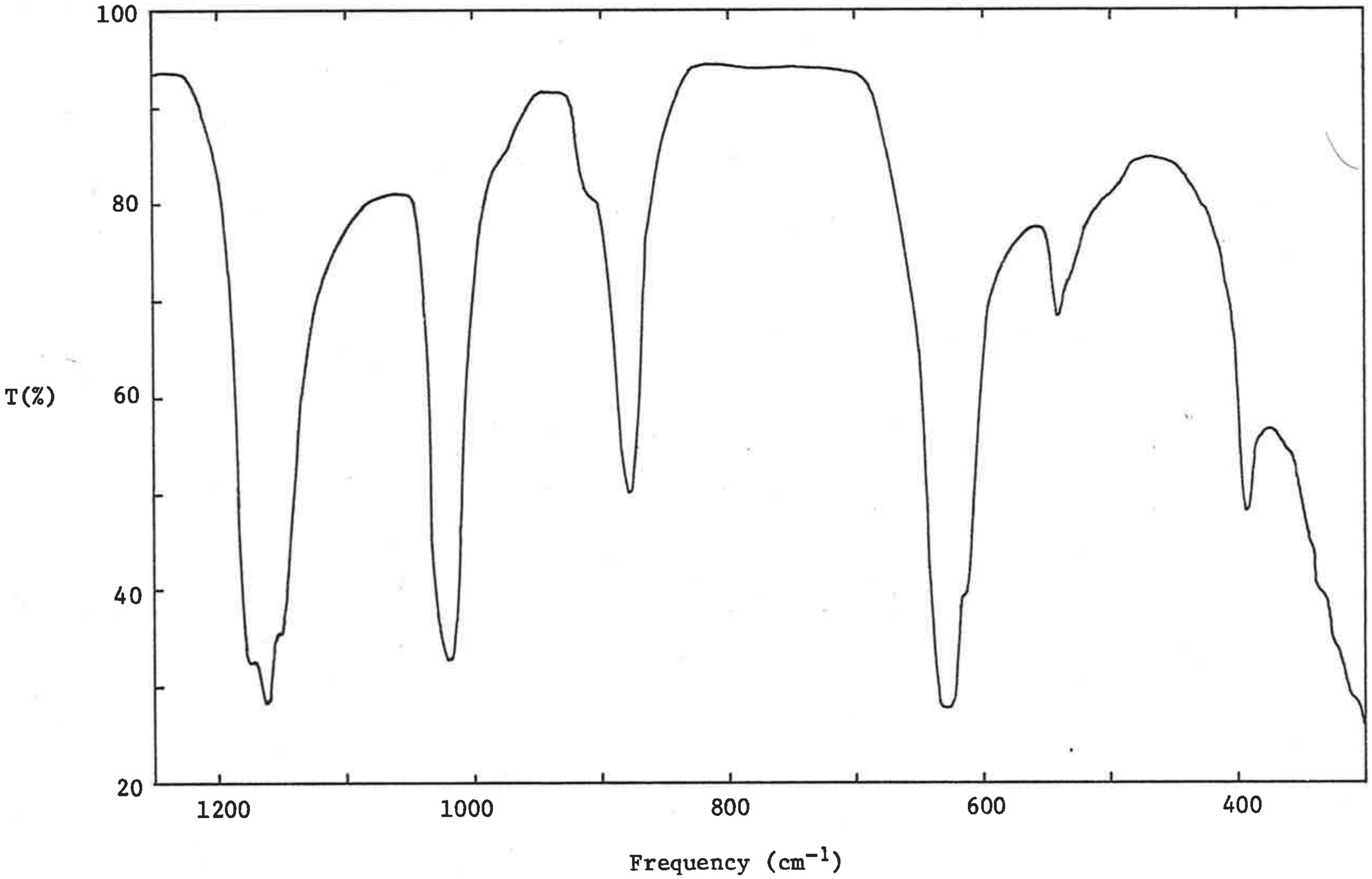


Fig. 4.3 Infrared Spectrum of $Mn(CO)_5(OClO_3)$

tope.[246(c)] Two modes of decomposition may be suggested. The molecular ions fragment by loss of ClO_4 according to the equation:

$$[Mn(CO)_5(OClO_3)]^+ \longrightarrow Mn(CO)_5^+ + ClO_4$$

Peaks were observed for both of these fragments. The $Mn(CO)_5^+$ ion then decomposes by successive loss of carbon monoxide. Peaks were present for all the ions $Mn(CO)_n^+$ ($n = 0 - 5$). The other mode of fragmentation for the molecular ion appears to involve the sequential loss of carbon monoxide:

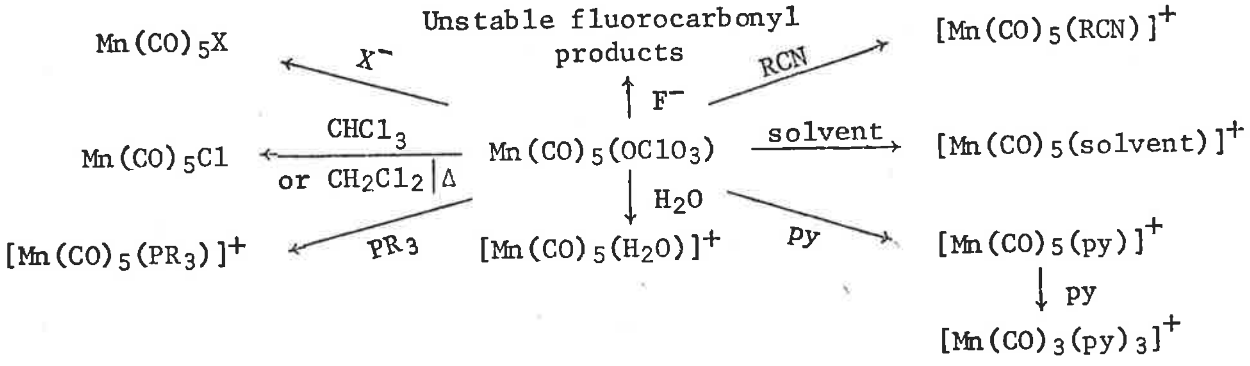
$$\begin{tikzcd}
{[Mn(CO)_5(OClO_3)]^+} \arrow[r] & {[Mn(CO)_4(OClO_3)]^+ + CO} \arrow[d, "-CO\ (4\ times)"] \\
Mn^+ \text{ and } ClO_4^+ & {[Mn(OClO_3)]^+} \arrow[l]
\end{tikzcd}$$

Peaks were observed for all the ions in this series. The only metastable peak present was at *m/e* 36.5, which corresponds to the loss of carbon monoxide from $Mn(CO)^+$. The relative intensities of the peaks for the fragmentation of $[Mn(CO)_5(OClO_3)]^+$ by the loss of either the perchlorato or the carbonyl groups suggest that these processes occur concurrently with no route being particularly favoured.

In the mass spectra of $Mn(CO)_5X$ (X = Cl, Br, I) the molecular ions also fragment by two routes involving the loss of either carbon monoxide or the halide.[281,282]

4.2.2 Reactions of $Mn(CO)_5(OClO_3)$

The perchlorato group is easily substituted and the complex can be used to prepare a wide range of manganese(I) pentacarbonyl complexes as shown in Scheme 4.1.



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Scheme 4.1 Substitution Reactions of $Mn(CO)_5(OClO_3)$

(X = Cl, Br, I; solvent = MeOH, Me_2CO, $MeNO_2$; R = Me, Ph)

(a) <u>with Solvents</u>

$Mn(CO)_5(OClO_3)$ is insoluble in diethyl ether and light petroleum, sparingly soluble in benzene and slightly soluble in dichloromethane and chloroform. The complex is very soluble in polar organic solvents because rapid substitution of the perchlorato group takes place (see below).

$Mn(CO)_5(OClO_3)$ is reasonably stable in dichloromethane at room temperature and shows only a slight tendency to react with the solvent. After a period of two hours a shoulder of medium intensity was present in the infrared spectrum at 2065 cm^{-1} (due to the formation of $Mn(CO)_5Cl$). The complex reacts fairly quickly with hot dichloromethane forming $Mn(CO)_5Cl$. The reaction was conveniently monitored by leaving a solution of the complex in the infrared beam. Under these conditions the conversion was complete after approximately 14 minutes. The perchlorato complex reacts with chloroform at room temperature forming $Mn(CO)_5Cl$ over a period of 10-15 minutes.

When $Mn(CO)_5(OClO_3)$ was dissolved in the cyano solvents, acetonitrile and benzonitrile, at room temperature, the perchlorato group was rapidly substituted (i.e. in a few seconds) to give the corresponding nitrile complexes, $[Mn(CO)_5(RCN)]ClO_4$ (R = Me, Ph). The colour of the complex fades during the reaction producing either colourless (R = Me) or very pale yellow (R = Ph) solutions. The isolation and characterization of these complexes is described in section 4. The molar conductance of $Mn(CO)_5(OClO_3)$ in acetonitrile (Table 4.3) confirms the ionization of the perchlorato group.

The perchlorato complex also undergoes complete ionization in the polar organic solvents, acetone, methanol and nitromethane, according to the equation:

$$Mn(CO)_5(OClO_3) \ + \ solvent \ \longrightarrow \ [Mn(CO)_5(solvent)]^+ \ + \ ClO_4^-$$

as evidenced by conductance measurements (Table 4.3) and the infrared spectra (Table 4.4) of the resultant solutions. In nitromethane the colour quickly fades to give an almost colourless solution. The carbonyl stretching frequencies of the nitromethane complex are similar to those of $[Mn(CO)_5(MeCN)]^+$ (see Table 4.4). The preparation of this complex is described in section 4. On the other hand, no colour change occurs in acetone solution and the carbonyl stretching frequencies of the acetone complex resemble those of $Mn(CO)_5Br$. This trend parallels that observed for the isoelectronic tungsten complexes; i.e. the carbonyl stretching frequencies decrease in the order $W(CO)_5(MeCN) > W(CO)_5(Me_2CO) \approx [W(CO)_5Br]^-$.[51,192] The perchlorato ligand in $M(CO)(PPh_3)_2(OClO_3)$ (M = Rh, Ir) is also labile and the complexes undergo similar ionizations in polar organic solvents.[198]

$Mn(CO)_5(OClO_3)$ dissolves in neat pyridine with evolution of carbon monoxide to afford a bright yellow solution which consists mainly of $[Mn(CO)_3(py)_3]^+$; no pentacarbonyl species were present. $[Mn(CO)_5(py)]^+$ was formed when pyridine was carefully added to a solution of $Mn(CO)_5(OClO_3)$ in dichloromethane. The addition of excess pyridine resulted in the formation of $[Mn(CO)_3(py)_3]^+$. A similar reaction occurred with 4-methylpyridine. The carbonyl stretching frequencies of the complexes are summarized in Table 4.4.

$[Mn(CO)_5(MeCN)]PF_6$ has been prepared previously by treating either $Mn_2(CO)_{10}$ or $Mn(CO)_5Br$ with nitrosonium hexafluorophosphate in acetonitrile.[167,216,283] $[Mn(CO)_5(py)]PF_6$ was prepared by stirring the acetonitrile complex with an excess of pyridine in chloroform for 15 hours at room temperature.[286,287] $[Mn(CO)_5(MeCN)]^+$ reacts rapidly with neat pyridine at room temperature to produce $[Mn(CO)_3(py)_3]^+$.[286,287]

The reaction of $Mn(CO)_5(OClO_3)$ with water is described in section 5.

(b) with Phosphines

The preparation of monosubstituted group VIa metal carbonyl derivatives of the type $M(CO)_5L$ (L = group Vb Lewis base) is generally a straightforward process involving either photochemical or thermal substitution of the hexacarbonyls. On the other hand, the isoelectronic $[Mn(CO)_5L]^+$ cations, which may be considered as derivatives of $[Mn(CO)_6]^+$, can only be prepared by indirect methods. Furthermore, surprisingly little work has been done on the preparation of these complexes.

Kruck and Hofler[288] have prepared mono- and di-substituted cationic manganese carbonyl derivatives according to the following high pressure synthesis:

$$Mn(CO)_{5-n}L_nCl \;+\; AlCl_3 \xrightarrow[250\ atm]{CO} [Mn(CO)_{6-n}L_n]AlCl_4$$

where L = PPh_3, $P(cyclohexyl)_3$ and 1,10-phenanthroline. Darensbourg and co-workers[286,287] have developed two procedures for the preparation of the analogous monosubstituted complexes under mild conditions. The first method can be summarized by the following equations:

$$[Mn(CO)_4L]_2 \xrightarrow{Na/Hg} Na^+\,[Mn(CO)_4L]^- \xrightarrow{ClCO_2Et} \xrightarrow[or\ BF_3]{HBF_4} [Mn(CO)_5L]BF_4 + EtOH + NaCl$$

where L = PPh_3, PMe_2Ph and $P(OPh)_3$. The source of carbon monoxide is ethyl chloroformate and the overall yield is about 18% (based on Mn_2CO_{10}). In addition to the poor yield, this method is limited by the availability of the dimers $[Mn(CO)_4L]_2$. The other method of preparation consists of stirring $[Mn(CO)_5(MeCN)]PF_6$ with an excess of phosphine (L = PPh_3, $P(p\text{-}Tol)_3$, dpe etc.) in a solvent such as acetone or chloroform, as shown in the equation:

$$[Mn(CO)_5(MeCN)]PF_6 + L \longrightarrow [Mn(CO)_5L]PF_6 + MeCN$$

The reaction times varied between 5 and 24 hours and the products were obtained in good yield. Monosubstituted complexes have also been prepared in moderate yield by treating the dimers $[Mn(CO)_4L]_2$ (L = $P(OMe)_3$, $P(OMe)_2Ph$, $P(OMe)Ph_2$) with nitrosonium hexafluorophosphate in dichloromethane.[158]

$Mn(CO)_5(OClO_3)$ reacts with an excess of phosphine (PR_3; R = Ph, *p*-Tol, *m*-Tol) in warm dichloromethane (30-33°C) to form $[Mn(CO)_5(PR_3)]^+$ over a period of 15-20 minutes, as shown in the equation:

$$Mn(CO)_5(OClO_3) + PR_3 \xrightarrow{CH_2Cl_2} [Mn(CO)_5(PR_3)]ClO_4$$

The perchlorato complex also reacts with the ditertiary phosphines, dpe and dpm, under the same conditions to form $[Mn(CO)_5(dpe)]^+$ in approximately 18 minutes and $[Mn(CO)_5(dpm)]^+$ after 25 minutes; the ligands are monodentate in these complexes. In the above reactions the colour of the solutions faded to pale yellow, except for tris(*p*-tolyl)phosphine where the yellow colour increased in intensity. No reaction occurred with triphenylarsine, triphenylphosphite or tris(*o*-tolyl)phosphine. The failure of the latter ligand to react is probably due to steric factors. Darensbourg and co-workers[287] reported that $[Mn(CO)_5(MeCN)]PF_6$ did not react with triphenylphosphite either under reflux conditions in chloroform and acetone or in warm pure triphenylphosphite solution.

The infrared spectra of the monophosphine complexes in dichloromethane solution showed three carbonyl stretching bands as expected for a pentacarbonyl species of C_{4v} local symmetry. The frequencies are recorded in Table 4.5 and a typical spectrum is reproduced in Figure 4.4. The A_1^{1b} band (Figure 4.1) is more intense than those usually observed for complexes of this type (typical examples are shown in Figure 4.2). This may be due to the phosphine ligand distorting the coplanarity of the radial carbonyl groups. Although the A_1^{1a} vibration is at higher frequency relative to the E vibration, it is to some extent buried beneath the intense E absorption and appears as a shoulder. Accidental degeneracy of the A_1^{1a} and E bands has been observed in the infrared spectrum of $Cr(CO)_5(PPh_3)$.[10] Darensbourg and co-workers[286,287] have also reported the carbonyl stretching frequencies of the $[Mn(CO)_5(PR_3)]^+$ complexes using acetonitrile as the solvent. Although there are slight differences in the frequencies between the two sets of data, which may be partly due to solvent effects, the spectra overall compare favourably.

The perchlorato complexes $M(CO)(PPh_3)_2(OClO_3)$ (M = Rh, Ir) react with triphenylphosphine in benzene to give $[M(CO)(PPh_3)_3]ClO_4$.[198]

(c) with Halide Ions

$Mn(CO)_5(OClO_3)$ reacts extremely rapidly with halide ions (X^- = Cl, Br, I), as either the tetraphenylarsonium or tetraethylammonium salt, in dichloromethane at room temperature to form the corresponding halo complexes:

$$Mn(CO)_5(OClO_3) + X^- \xrightarrow{CH_2Cl_2} Mn(CO)_5X + ClO_4^-$$

The colour changes during the reactions were characteristic of each halide; thus, with chloride the colour faded to pale yellow, with bromide the colour intensified to orange and with iodide a deep orange-red solution was obtained. The products were also identified by their infrared spectra.

This substitution reaction appears to be general and thus, should proceed with any anion provided it is soluble in dichloromethane; this limits the reaction to salts of large organic cations and possibly crown ether complexes. There was no significant reaction with salts of very low solubility such as potassium thiocyanate. If polar solvents or dichloromethane-polar solvent mixtures are used, there is the possibility of a competing reaction with the solvent.

No successful synthesis of $Mn(CO)_5F$ has been reported. The reaction between $Mn(CO)_5(OClO_3)$ and the fluoride ion would appear to be a potential route to this complex. Tetraethylammonium fluoride has only slight solubility in dichloromethane, but is highly soluble in alcohols. The reaction was carried out by adding either solid tetraethylammonium fluoride or a solution of the salt in methanol to a solution of $Mn(CO)_5(OClO_3)$ in dichloromethane. When the latter method was used, carbon monoxide was evolved and the colour of the reaction mixture intensified to bright yellow. The infrared spectrum of the solution showed strong carbonyl absorptions at 2059 and 1939 (br) cm^{-1} and this is consistent with the formation of $Mn(CO)_3F_3$. On standing, the colour of the solution faded and a yellow insoluble precipitate with no distinct carbonyl absorptions was formed. A similar reaction occurred in pure dichloromethane, but the rate was slower and what appears to be $Mn(CO)_5F$ (ν_{CO} similar to $Mn(CO)_5Br$*) was initially formed. These solutions also decomposed on standing with the formation of a yellow precipitate. The above reactions did not always proceed cleanly and other carbonyl bands were sometimes present in the infrared spectra.

$Mn(CO)_3F_3$ has been previously prepared by stirring $Mn(CO)_5Br$ with a large excess of silver fluoride in dichloromethane at room temperature. The carbonyl stretching frequencies (nujol mull) are 2037 (vs) and 1944 (vs,br) cm^{-1}. A weak shoulder, which is believed to be due to crystal effects, was also present at 1922 cm^{-1}. When two equivalents of silver fluoride were used, the fluoro-bridged dimer, $[Mn(CO)_4F]_2$, was formed.[179] The only other known fluorocarbonyl complex of manganese is $[Mn_2(CO)_9F]^-$, which was prepared photochemically from manganese carbonyl.[289]

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* In the halo complexes $[Cr(CO)_5X]^-$,[50,51] $[W(CO)_5X]^-$[50,51] and $[Mn_2(CO)_9X]^-$[289] ($X = F, Cl, Br, I$) the carbonyl stretching frequencies usually decrease in the order $F \simeq Cl \simeq Br > I$.

TABLE 4.1

Infrared Spectra of $Mn(CO)_5(OClO_3)^A$ and $Mn(CO)_5Br^A$

Assignment[B]	Symmetry	Frequency (cm^{-1}) $Mn(CO)_5(OClO_3)$	 $Mn(CO)_5Br$
ν(CO)	A_1^{1b}	2168 w	2145 w
ν(CO)	E	2085 vs	2060 vs
ν(CO)	A_1^{1a}	2034 ms	2018 s
$\nu_{as}(ClO_3)$	E	1163 vs[D]	-
ν(Cl-O*)[C]	A_1	1020 vs	-
$\nu_{sym}(ClO_3)$	A_1	879 s	-
δ(MCO)	?	630 vs	636 vs
$\delta_{sym}(ClO_3)$	A_1	615 sh[E]	-
δ(MCO)	?	541 m	549 m
-	-	-	477 vw
ν(MC)	E	394 s	419 s

A. Carbonyl stretching bands recorded in dichloromethane; other bands recorded as nujol mulls between either potassium bromide (1500 - 400 cm^{-1}) or polyethylene (600 - 250 cm^{-1}) plates.

B. Perchlorato assignments based on reference 273; see also Table 4.10.

C. O* refers to oxygen coordinated to manganese.

D. Band consists of a triplet of absorptions at 1175, 1163 and 1151 cm^{-1} (see Fig. 4.3).

E. Partially obscured by δ(MCO) absorption.

TABLE 4.2

Mass Spectrum of the Compound $Mn(CO)_5(OClO_3)$

m/e	Relative Intensity[A]	Assignment
296, 294	30	$Mn(CO)_5(OClO_3)^+$
268, 266	10	$Mn(CO)_4(OClO_3)^+$
240, 238	45	$Mn(CO)_3(OClO_3)^+$
212, 210	60	$Mn(CO)_2(OClO_3)^+$
195	45	$Mn(CO)_5^+$
184, 182	80	$Mn(CO)(OClO_3)^+$
167	40	$Mn(CO)_4^+$
156, 154	75	$Mn(OClO_3)^+$
139	55	$Mn(CO)_3^+$
111	80	$Mn(CO)_2^+$
101, 99	50	ClO_4^+
83	100	$Mn(CO)^+$
55	100	Mn^+

A. For ions containing perchlorate only the intensity of the ion containing the ^{35}Cl isotope is recorded.

TABLE 4.3

Molar Conductance of $Mn(CO)_5(OClO_3)$ at 25°C

Solvent	Λ_M(S cm^2)	Concentration (M × 10^3)
Acetonitrile	132	1.30
Acetone	104	1.53
Methanol	91.0	1.05
Nitromethane	77.2	1.18
Nitrobenzene	15.0	1.13

TABLE 4.4

Properties of the Solvento Complexes

Complex[A]	Colour	CO Stretching Frequencies (cm^{-1})	Medium
$[Mn(CO)_5(MeCN)]^+$	white	2171 (w), 2082 (vs), 2059 (s)	Acetonitrile
$[Mn(CO)_5(PhCN)]^+$	white	2171 (w), 2084 (vs), 2060 (s)	Acetonitrile
$[Mn(CO)_5(Me_2CO)]^+$	yellow	2144 (w), 2060 (vs), 2020 (s)	Acetone
$[Mn(CO)_5(MeNO_2)]^+$	white	2170 (w), 2084 (vs), 2057 (s)	Nitromethane
$[Mn(CO)_5(py)]^+$	pale yellow	2163 (w), 2078 (vs), 2049 (s)	Dichloromethane
$[Mn(CO)_3(MeCN)_3]^+$	yellow	2072 (vs), 1970 (vs)	Acetone
$[Mn(CO)_3(PhCN)_3]^+$	yellow	2068 (vs), 1970 (vs)	Benzonitrile
$[Mn(CO)_3(py)_3]^+$	yellow	2049 (s) , 1943 (s)	Dichloromethane

A. All complexes exist as the perchlorate salt.

TABLE 4.5

Infrared Data for the $[Mn(CO)_5(PR_3)]^+$ Complexes

Complex [A]	ν_{CO} (cm^{-1})[B] A_1^{1b}	A_1^{1a}	E
$[Mn(CO)_5(PPh_3)]^+$	2151 mw	2080 sh	2060 vs
$[Mn(CO)_5\{P(p\text{-}Tol)_3\}]^+$	2150 mw	2075 sh	2060 vs
$[Mn(CO)_5\{P(m\text{-}Tol)_3\}]^+$	2149 mw	2077 sh	2060 vs
$[Mn(CO)_5(dpe)]^+$	2151 mw	2079 sh	2060 vs
$[Mn(CO)_5(dpm)]^+$	2151 mw	-	2059 vs

A. All complexes existed as the ClO_4^- salt. B. In dichloromethane.

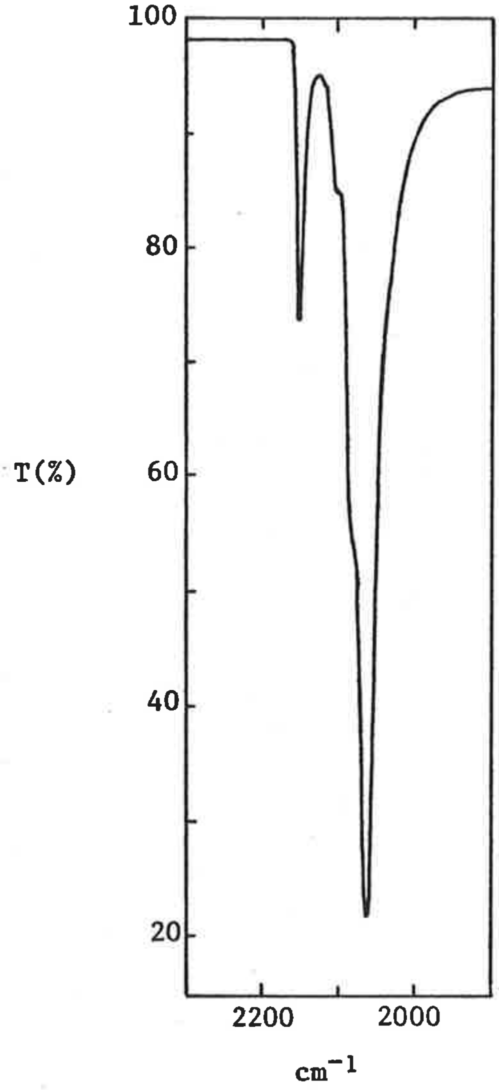

Fig. 4.4 Infrared Spectrum of $[Mn(CO)_5(PPh_3)]^+$ in Dichloromethane

4.3 Attempted Syntheses of Other Perchlorato Complexes

Following the successful preparation of $Mn(CO)_5(OClO_3)$, the synthesis of a bis-perchlorato complex was investigated. Silver perchlorate (2.5 - 3 equivalents) was added in one-molar portions to a stirred solution of $Et_4N[Mn(CO)_4Br_2]$ in dichloromethane at room temperature. The colour of the solution faded from deep yellow to pale yellow as silver bromide precipitated. Infrared monitoring showed that a rearrangement had occurred during the halide abstraction process resulting in the formation of $Mn(CO)_5(OClO_3)$; there was no evidence for the formation of the bis-perchlorato complex. When the reaction was carried out at approximately -5°C, decomposition with total loss of carbon monoxide was observed.

In $Mn(CO)_5(OClO_3)$ the strong electron-withdrawing ability of the perchlorate ion results in a reduction in the amount of metal to carbonyl backbonding relative to $Mn(CO)_5Br$, as evidenced by the increase in the carbonyl stretching frequencies. It would appear that any attempt to incorporate a second perchlorate ion into the coordination sphere of manganese reduces the backbonding to such an extent that the carbonyl groups become labile and the molecule decomposes.

The preparation of a group VIa perchlorato derivative was also attempted. However, the addition of an equimolar quantity of silver perchlorate to a solution of $Et_4N[Mo(CO)_5Br]$ in dichloromethane at room temperature resulted in a rapid oxidation reaction as indicated by the formation of a black precipitate of metallic silver. The molybdenum(I) product is unstable with respect to disproportionation and decomposes to give a zerovalent and a high oxidation-state species respectively. The latter complex is also unstable and decomposes by total loss of carbon monoxide forming a blue precipitate. The deep yellow colour of the starting material disappears during this process which is accompanied by the vigorous evolution of carbon monoxide to give a clear solution. The molybdenum(0) species reacts with the liberated carbon monoxide to give $Mo(CO)_6$ which precipitated as white crystals when the filtered reaction mixture was concentrated. The properties were identical to those of an authentic sample.

4.4 Preparation of the Solvento Complexes

The acetonitrile complex, $[Mn(CO)_5(MeCN)]ClO_4$, was prepared by filtering a freshly prepared solution of $Mn(CO)_5(OClO_3)$ in dichloromethane into acetonitrile. The colour of the solution faded to pale yellow and the product precipitated as white crystals upon the addition of diethyl ether. The overall yield was 40% and this appears to be limited by the formation of $Mn(CO)_5(OClO_3)$ since the solvolysis step is quantitative. Evaporation of the filtrate to dryness produced a small quantity of pale yellow crystals with two carbonyl stretching bands (acetone solution) at 2072 (vs) and 1970 (vs) cm^{-1} respectively. These are consistent with the formation of $[Mn(CO)_3(MeCN)_3]^+$.[287,292] The conversion of $[Mn(CO)_5(MeCN)]^+$ to the tris-acetonitrile complex is a reasonably facile process and occurs readily on warming the complex in acetonitrile solution.[287]

$[Mn(CO)_5(MeCN)]ClO_4$ is very soluble in polar organic solvents (acetonitrile, acetone) giving colourless solutions and insoluble in dichloromethane and chloroform. The molar conductance of the complex in acetonitrile (1.24×10^{-3} M) was 135 S cm^2, which is typical of a 1:1 electrolyte. The carbonyl and nitrile stretching frequencies were recorded in both acetonitrile and acetone solution and these, together with the complete infrared spectrum, are presented in Table 4.6.

The carbonyl stretching frequencies are in reasonable agreement with those reported previously.[287] However, the C-N stretching frequency does not appear to have been reported. This absorption mode was observed as a rather broad band of weak intensity shifted to higher frequency relative to neat acetonitrile (see Chapter 2.5). In addition, a very weak band was present at 2310 cm^{-1} (acetone solution). It is thought that this band is due to the combination of the symmetric CH_3 deformation and the C-C stretching mode, as explained in Chapter 2.5. The C-N stretching frequency for the isoelectronic $W(CO)_5(MeCN)$ complex is 2347 cm^{-1} (KBr disc.).[192]

The complex reacts with both acetonitrile and acetone in the infrared beam and the spectra were therefore recorded as quickly as possible. In acetone solution substitution to give $[Mn(CO)_5(Me_2CO)]^+$ occurs, while in acetonitrile $[Mn(CO)_3(MeCN)_3]^+$ is slowly formed and the solution develops a yellow colour. The complex $[Mn(CO)_3(MeCN)_3]^+$ also undergoes a substitution reaction when acetone solutions of the complex are left in the infrared beam, forming $[Mn(CO)_3(Me_2CO)_3]^+$.[287]

The benzonitrile complex, $[Mn(CO)_5(PhCN)]ClO_4$, was prepared in a manner identical to that for the acetonitrile complex and was isolated as white crystals in comparable yield. The infrared spectrum of the yellow filtrate, after the volatile solvents had been removed, showed strong carbonyl absorptions at 2068 and 1970 cm^{-1}, these are consistent with the formation of a small amount of $[Mn(CO)_3(PhCN)_3]ClO_4$. No attempt was made to isolate this complex because of the involatility of benzonitrile.

$[Mn(CO)_5(PhCN)]ClO_4$ has the same solubility properties as the acetonitrile analogue. The molar conductance in acetonitrile (1.05×10^{-3} M) was 130 S cm^2. The carbonyl stretching frequencies in acetonitrile solution (Table 4.7) are virtually identical to those for the acetonitrile complex. The spectrum of the benzonitrile complex, in acetone solution, changed very rapidly due to substitution by the solvent and thus, had to be recorded with the utmost celerity. The weak C-N stretching absorption (Table 4.7) is shifted to higher frequency relative to neat benzonitrile as expected. The complete infrared spectrum is recorded in Table 4.7.

The nitromethane complex, $[Mn(CO)_5(NO_2Me)]ClO_4$, was also prepared by the aforementioned method, but the yield of the product, which was isolated as white crystals, was low, possibly due to the very high solubility of the complex in nitromethane. The complex was not studied in detail. The carbonyl stretching frequencies in nitromethane are given in Table 4.4. When the spectrum of the complex in acetone was being recorded, a rapid substitution by the solvent occurred to give $[Mn(CO)_5(Me_2CO)]^+$.

Attempts to prepare the solvento complexes by direct reaction of $Mn(CO)_5Br$ with silver perchlorate (1.2 equivalents) in the polar solvents, acetonitrile and nitromethane, at room temperature were unsuccessful. The silver salt dissolves but no halide abstraction occurs, possibly due to complex formation between the silver ion and the solvent. Warming the solutions resulted in the evolution of carbon monoxide to give a mixture of penta- and tri-carbonyl complexes. Both $Mn(CO)_5Br$ and $[Mn(CO)_5(MeCN)]^+$ are known to react with acetonitrile on warming.[285,287,292]

TABLE 4.6

Infrared Spectrum of $[Mn(CO)_5(MeCN)]ClO_4$

Assignment	Frequency (cm^{-1}) Nujol	 Acetonitrile	 Acetone
$\nu(C{\equiv}N)$	2340 w	2337 w	2335 w,br
combination band	2317 w	2300 w,sh	2310 w,sh
$\nu(CO)$, $(A_1^{1b}$, eq)	2174 w	2171 w	2170 w
$\nu(CO)$, (E, eq)	2080 vs	2082 vs	2080 vs
$\nu(CO)$, $(A_1^{1a}$, ax)	2055 s	2059 vs	2059 vs
Perchlorate $\nu_{as}(Cl-O)$	1098 vs		
$\delta(MCO)$	639 s		
Perchlorate $\delta_{as}(OClO)$	630 s		
$\delta(MCO)$	540 m		
$\nu(M-C)$	409 vs		

TABLE 4.7

Infrared Spectrum of $[Mn(CO)_5(PhCN)]ClO_4$

Assignment	Frequency (cm^{-1}) Nujol	Acetonitrile	Acetone[A]
$\nu(C{\equiv}N)$	2296 w	-	2286 w
$\nu(CO)$, (A_1^{1b}, eq)	2174 w	2171 w	
$\nu(CO)$, (E, eq)	2078 vs	2084 vs	
$\nu(CO)$, (A_1^{1a}, ax)	-	2060 s	
$\nu(C{=}C)$	1597 w		
Perchlorate $\nu_{as}(Cl{-}O)$	1095 vs		
C-H out of plane def.	767 s 693 m		
$\delta(MCO)$ (?)	649 ms		
Perchlorate $\delta_{as}(OClO)$	627 vs		
?	559 ms		
$\delta(MCO)$	537 m		
$\nu(M{-}C)$	406 s		

A. The compound reacts rapidly with acetone in the infrared beam to give $[Mn(CO)_5(Me_2CO)]^+$.

4.5 Reaction of $Mn(CO)_5(OClO_3)$ with Water (Preparation of $[Mn(CO)_5(H_2O)]^+$)

When a solution of $Mn(CO)_5(OClO_3)$ in dichloromethane was vigorously stirred with a small amount of water at room temperature, the aqueous phase developed a bright yellow colour while the organic phase faded until it was almost colourless. Infrared monitoring of the dichloromethane layer showed the rapid formation of carbonyl stretching bands at 2148 (w), 2060 (vs) and 2019 (s) cm^{-1} as the bands due to $Mn(CO)_5(OClO_3)$ disappeared. The intensity of these bands then decreased slowly as the product was transferred into the aqueous phase. Approximately 30 minutes were required for complete reaction. The amount of complex remaining in the organic phase was found to be negligible.

The aqueous solution of the product slowly evolved carbon monoxide on standing and attempts to concentrate the solution in a vacuum resulted in vigorous effervescence. The product is very soluble in water and could only be isolated by the addition of solid sodium tetraphenylborate, which resulted in the precipitation of bright yellow microcrystals in low yield. A large amount of the complex still remained in solution as indicated by the bright yellow colour of the filtrate. Accordingly, the amount of water used in the reaction should be kept to a minimum. The solid complex is very unstable and decomposes over a period of 24 hours to give brown crystals.

The product initially formed in the above reaction is formulated as the aquo complex, $[Mn(CO)_5(H_2O)]ClO_4$, which is subsequently isolated as the tetraphenylborate salt, $[Mn(CO)_5(H_2O)]BPh_4$. Unfortunately, due to the high molecular weight of the tetraphenylborate ion, elemental microanalysis could not be used to conclusively demonstrate the presence of the aquo ligand.

The aquo complex has remarkable solubility properties. As mentioned above, $[Mn(CO)_5(H_2O)]ClO_4$ is very soluble in water and even the tetraphenylborate salt has slight solubility in this solvent. $[Mn(CO)_5(H_2O)]BPh_4$ is very soluble in polar organic solvents (acetone, methanol, acetonitrile, nitromethane) and, unlike other solvento complexes such as $[Mn(CO)_5(MeCN)]ClO_4$, is soluble in dichloromethane and chloroform. This may be due to the larger size of the tetraphenylborate ion. The complex is insoluble in benzene and dry diethyl ether although very soluble in wet ether.

The carbonyl stretching frequencies of freshly prepared samples of $[Mn(CO)_5(H_2O)]BPh_4$ in various media are recorded in Table 4.8. The local symmetry of the carbonyl groups is C_{4v} and hence, three carbonyl stretching fundamentals ($2A_1 + E$) are expected. Three of the four bands observed in the solid-state spectrum can be assigned to these modes of vibration, while the band at 2122 cm^{-1} is assigned as the B_1 mode, which is infrared inactive for rigorous C_{4v} symmetry. Its appearance may be due to crystal effects lowering the symmetry of the complex. Alternatively, it is reasonable to assume that the crystal lattice contains water molecules of crystallization and thus, the hydrogen bonding between the lattice water and the coordinated water molecules (see below) will result in a reduction in the symmetry of the complex. Under these conditions, splitting of the E mode should occur[10,13] and this is indeed observed. The B_1 absorption is also present in the infrared spectra of the fluoro anions $[M(CO)_5F]^-$ (M = Cr, W)[50,51] and of phosphine substituted complexes of the type $Cr(CO)_5PR_3$.[10]

The infrared spectrum in wet diethyl ether showed, in addition to the three expected modes of vibration, a shoulder due to the B_1 mode and a band of medium intensity at 1945 cm^{-1}; the origin of the latter band is at present unclear. Extra bands in this region have also been observed in the spectra of acyl complexes of the formula $RCORe(CO)_5$.[13] The carbonyl stretching frequencies of the aquo complex in acetone solution are similar to those of $[Mn(CO)_5(Me_2CO)]^+$ and this may be indicative of substitution by the solvent. The aquo ligand is displaced in acetonitrile solution giving $[Mn(CO)_5(MeCN)]^+$.

The complete infrared spectrum of $[Mn(CO)_5(H_2O)]BPh_4$ is presented in Table 4.8. The broad hydroxyl stretching absorption at 3386 cm^{-1} is indicative of coordinated water. The sharp absorptions at approximately 3600 cm^{-1} and the shoulder at 3425 cm^{-1} are assigned to lattice water; one arm of which is hydrogen bonded and the other is free. Hydrogen bonding between these molecules and the aquo ligand may be responsible for the reduction in the symmetry of the complex as mentioned above.

The infrared spectra[290] of a series of complexes of general formula $M(III)(Saen)_2X \cdot H_2O$ (M = Cr, Fe, Co; X = Cl, Br, I) show, in the O-H stretching region, a very sharp band at 3620 cm^{-1} and a slightly broader band in the region 3350 - 3450 cm^{-1}, the position of the latter band depending on the nature of both the metal and the anion. The former band was assigned as a free O-H stretch and the latter band as a hydrogen bonded O-H stretch. This has been verified by the X-ray molecular structure determination of $Fe(Saen)_2Cl \cdot H_2O$[290] which showed that the water molecule was not coordinated and that one of the hydrogen atoms was hydrogen bonded to the chloride ion, while the other was free. Evidence from NMR and conductance studies suggests that the water remains bound in solution.

The molar conductance of $[Mn(CO)_5(H_2O)]BPh_4$ in acetone (1.10×10^{-3} M) was 95 S cm^2. The value is slightly low for a 1:1 electrolyte, but this can be attributed to the low ionic mobility of the tetraphenylborate ion.[222]

$[Mn(CO)_5(H_2O)]^+$ has been postulated[211] as one of the products of the acidic hydrolysis of the 3- and 4-pyridiomethylmanganesepentacarbonyl cations in aqueous solution. The workers did not isolate or characterize the complex. Aquo complexes of the general formula $[(C_6F_5)M(PR_3)_2(H_2O)]ClO_4$ (M = Ni, Pt; R = Ph, Et) have been prepared by stirring either benzene or dichloromethane solutions of the corresponding perchlorato complexes, $(C_6F_5)M(PR_3)_2(OClO_3)$, with water.[201,291]

TABLE 4.8

Infrared Spectrum of $[Mn(CO)_5(H_2O)]BPh_4$

	Frequency (cm^{-1})		
Assignment	Nujol	Wet ether	Acetone
lattice H_2O, ν(OH) free	3632 w,shp		
	3561 w,shp		
" " , ν(OH) H bonded	3425 sh		
coord. H_2O , ν(OH)	3386 ms,br		
aromatic ν(C-H)	3055 mw		
ν(CO), (A_1^{1b})	2169 w	2148 w	2146 w
ν(CO), (B_1)	2122 ms	2092 sh	
ν(CO), (E)	2079 vs		
	2066 vs	2060 vs	2059 vs
ν(CO), (A_1^{1a})	2036 vs	2008 s	2020 s
–		1945 ms	
δ(H_2O)	1610 w		
ν(C=C)	1580 w		
C-H out of plane def.	744 s		
	715 s		
δ(MCO)	630 s		
	543 w		
ν(M-C)	399 ms		

4.6 Substituted Perchlorato Complexes

(a) Preparation and Characterization

The substituted bromo complexes, $Mn(CO)_3L_2Br$ ($L = P(OPh)_3$; L_2 = bpy), react smoothly with an excess of silver perchlorate in dichloromethane at room temperature to produce the corresponding perchlorato derivatives, as shown in the equation:

$$Mn(CO)_3L_2Br + AgClO_4 \xrightarrow{CH_2Cl_2} Mn(CO)_3L_2(OClO_3) + AgBr\downarrow$$

The amount of silver perchlorate did not seem to be critical provided an excess was used.

In the preparation of the bis-triphenylphosphite complex, the colour of the reaction mixture changed from pale to bright yellow and the product, which is very soluble in dichloromethane, was isolated as bright yellow needles by adding light petroleum to the concentrated filtrate. The bipyridyl-perchlorato complex, on the other hand, is only slightly soluble in dichloromethane. In the preparation of this complex, the colour of the solution changed from orange to yellow and most of the product precipitated as yellow microcrystals. These were extracted with a large volume of dichloromethane and precipitated by the addition of light petroleum.

The complexes are very stable in the solid state; they do not appear to be hygroscopic and no decomposition was observed over a period of several months. When solutions of the complexes in dichloromethane were left in the infrared beam, the spectrum of $Mn(CO)_3\{P(OPh)_3\}_2(OClO_3)$ was unchanged after 60 minutes, while 50% of the $Mn(CO)_3(bpy)(OClO_3)$ had reacted with the solvent to give $Mn(CO)_3(bpy)Cl$ after 30 minutes.

$Mn(CO)_3(PPh_3)_2Br$, suspended in dichloromethane, reacts with an excess of silver perchlorate (1.3 moles) to give an orange solution of the perchlorato complex, $Mn(CO)_3(PPh_3)_2(OClO_3)$. A small amount of uncharacterized by-product with a carbonyl stretching band at 1997 cm^{-1} is always formed in the reaction. If less than 1.3 equivalents of silver perchlorate are used, the reaction does not proceed to completion because of the reverse reaction of the product with the solvent (see below); if more than this quantity is used, the side reaction increases markedly. The product was isolated either by crystallization with light petroleum or by filtration of the reaction mixture directly into light petroleum. The perchlorato group is very labile and some $Mn(CO)_3(PPh_3)_2Cl$ is always formed when the former method is used, even if the process is carried out rapidly. Slow crystallizations result in almost complete conversion to the chloro complex. The reaction with the solvent is more rapid at elevated temperatures. When a freshly prepared solution of the perchlorato complex in dichloromethane was left in the infrared beam, complete conversion to the chloro complex occurred in a period of < 10 minutes.

The carbonyl stretching frequencies of the perchlorato complexes are summarized in Table 4.9. The bands are at higher frequency relative to the bromo complexes as was observed for $Mn(CO)_5(OClO_3)$. The bands due to the perchlorato group (see Table 4.10) are consistent with monodentate coordination of the ion. The band assignments for the bipyridyl complex are straightforward due to the absence of ligand vibrations. On the other hand, the absorptions due to the perchlorato group in the infrared spectra of the triphenylphosphine and triphenylphosphite complexes are somewhat more difficult to identify because of the intense bands arising from the ligands themselves. The ClO_3 bending absorptions are always partially obscured by the band due to the $\delta(MCO)$ vibrational mode.

Complexes of the formula $Mn(CO)_3L_2Br$ can exist in three distinct isomeric forms: *mer-cis*-L_2, *mer-trans*-L_2 and *fac*, as illustrated in Figure 4.5. The *mer-cis*-form can be eliminated because, as a general rule, carbonyl substitutions occur in the *cis*- position relative to the bromo group. Although three carbonyl stretching fundamentals are expected for both the

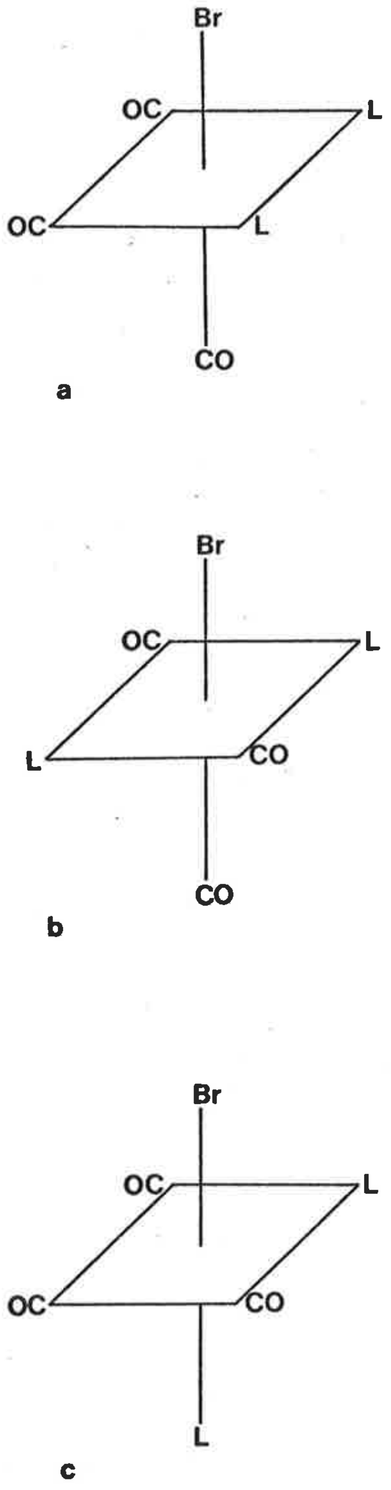

Fig. 4.5 Isomers of $Mn(CO)_3L_2Br$: (a) *fac*, (b) *mer-trans* and (c) *mer-cis*.

mer-trans- (referred to hereafter as *mer*; C_{2v} symmetry) and the *fac-* (C_s symmetry) isomers, they can be distinguished by the relative band intensities. Three strong bands (2A' + A") of roughly equal intensity are expected for the *fac-* isomer, while the *mer-* form gives rise to one weak (A_1^{1b}) and two strong (A_1^{1a} + B_1) absorptions.[159,293] This has been confirmed in the case of *fac-* and *mer*-$Mn(CO)_3\{PPh(OMe)_2\}_2Br$[160] by the X-ray molecular structure determinations.[294]

$Mn(CO)_3(PPh_3)_2Br$ has only been isolated in the *mer*-form;[148] attempts to prepare the *fac*-isomer were unsuccessful.[159] The bis-triphenylphosphite complex has been isolated in both forms.[159] Substitution of $Mn(CO)_5Br$ under mild conditions (37°C) affords the *fac*-isomer, while the same reaction at higher temperatures (55 - 60°C) yields the *mer*-isomer. The *mer*-form was used to prepare the complexes described in this thesis. Due to steric constraints, the bipyridyl complex can only exist as the *fac*-isomer.

No significant changes were observed in the relative intensities of the carbonyl stretching bands of the perchlorato derivatives compared with the corresponding bromo complexes and this indicates similar geometries.

(b) Reactions

The perchlorato complexes, $Mn(CO)_3L_2(OClO_3)$ (L = PPh_3, $P(OPh)_3$; L_2 = bpy), react extremely rapidly with an excess of halide ion (X = Cl, Br, I), as either the tetraphenylarsonium or tetraethylammonium salt, in dichloromethane at room temperature to yield the corresponding halo complexes, as shown in the equation:

$$Mn(CO)_3L_2(OClO_3) + X^- \xrightarrow{CH_2Cl_2} Mn(CO)_3L_2X + ClO_4^-$$

The colour changes during the reactions were characteristic of each particular halo complex and the products were identified by their infrared spectra. However, consistent results could not be obtained in similar reactions with tetraethylammonium fluoride, carried out under anhydrous conditions.

The perchlorato complexes undergo complete ionization in acetonitrile according to the equation:

$$Mn(CO)_3L_2(OClO_3) + MeCN \longrightarrow [Mn(CO)_3L_2(MeCN)]^+ + ClO_4^-$$

as evidenced by conductance measurements (Table 4.9) and the carbonyl stretching frequencies of the products (Table 4.11). During the reactions the colour of the solutions decreased in intensity to yield either yellow ($L = PPh_3$, L_2 = bpy) or very pale yellow ($L = P(OPh)_3$) solutions. Similar ionizations are expected to occur in other polar organic solvents.

The perchlorato group in substituted complexes of the type $[(C_6F_5)M(PR_3)_2(OClO_3)]$ (M = Ni, Pt; R = Ph, Et) is also very labile and the complexes react with a wide variety of ligands.[201,291]

Several routes to phosphine-substituted acetonitrile carbonyl complexes have been reported. $[Mn(CO)_3(MeCN)_3]^+$ reacts with an excess of dimethylphenylphosphine in refluxing chloroform to give *fac*-$[Mn(CO)_3(PMe_2Ph)_2(MeCN)]^+$.[292] This method has recently been extended to bidentate ligands by Edwards and Marshalsea.[284] Halide abstraction from *mer-trans*-$Mn(CO)_3L_2Br$ ($L = P(OMe)_2Ph$, $P(OMe)_3$, PMe_2Ph) with either silver perchlorate or silver hexafluorophosphate in warm acetonitrile gave *mer-trans*-$[Mn(CO)_3L_2(MeCN)]^+$.[292] These complexes have also been prepared by treatment of the hydrides, $[Mn(CO)_3L_2H]$, with HPF_6 in acetonitrile.[158]

In conclusion, the preparation of substituted manganese(I) perchlorato derivatives appears to be a general type of reaction. Furthermore, although not all the possible substitution reactions of these complexes were investigated, it appears that the perchlorato group can be easily displaced by a wide variety of ligands and thus, these derivatives may be used to prepare a wide range of manganese(I) carbonyl complexes.

TABLE 4.9

Properties of the Substituted Perchlorato Complexes

Complex	Colour	ν_{CO} (cm^{-1})A	Λ_M ($S\ cm^2$)B
$Mn(CO)_3(bpy)(OClO_3)$	yellow	2055 (ms), 1951 (sh), 1938 (ms)C	133
$Mn(CO)_3(PPh_3)_2(OClO_3)$	orange	2059 (w), 1969 (vs), 1916 (s)	110
$Mn(CO)_3\{P(OPh)_3\}_2(OClO_3)$	yellow	2091 (w), 2005 (vs), 1960 (s)	120

A. Recorded in dichloromethane.

B. Measured in acetonitrile; concentrations approx. 1.0×10^{-3} M.

C. Compound is only slightly soluble.

TABLE 4.10

Perchlorato Frequencies of $Mn(CO)_3L_2(OClO_3)$[A]

			Assignments[B]		
	E	A_1	A_1	E	A_1
Compound	ClO_3 Asy. Str.	Cl-O* Str.[C]	ClO_3 Sym. Str.[D]	ClO_3 Asy. Bend	ClO_3 Sym. Bend
$Mn(CO)_5(OClO_3)$	1163 vs	1020 vs	879 s	-	615 sh
$Mn(CO)_3(bpy)(OClO_3)$	1146 vs	1020 vs	884 m[E]	633 m	615 m
$Mn(CO)_3(PPh_3)_2(OClO_3)$	1148 vs	1021 ms	890 w	-	625 m,sh
$Mn(CO)_3\{P(OPh)_3\}_2(OClO_3)$	1158 vs	1020 vs	885 s	622 m	610 sh (?)

A. Recorded in nujol between KBr plates.

B. Based on ref. 273.

C. O* refers to the oxygen coordinated to manganese.

D. Analogous to the A_1 symmetric breathing frequency of ionic perchlorate.

E. Bands also present at 898 m and 905 m cm^{-1}.

TABLE 4.11

Infrared Data for the $[Mn(CO)_3L_2(MeCN)]^+$ Complexes

Complex	ν_{CO} $(cm^{-1})^A$
$[Mn(CO)_3(bpy)(MeCN)]^+$	2060 vs, 1951 vs
$[Mn(CO)_3(PPh_3)_2(MeCN)]^+$	2053 w, 1972 vs, 1945 s
$[Mn(CO)_3\{P(OPh)_3\}_2(MeCN)]^+$	2098 w, 2025 vs, 1985 s

A. Measured in acetonitrile.

4.7 Experimental

General

All preparations and reactions were carried out in an atmosphere of high-purity dry nitrogen. Solvents were of analytical grade purity and were dried over Linde 4A molecular sieves before use. The light petroleum used in the experiments had b.p. < 40°. The halide abstraction reactions are dependent on the ambient temperature and the times given should be regarded as a guide; the progress of the reactions was monitored by infrared spectroscopy. The perchlorato complexes were stored in a desiccator in the dark although only the pentacarbonyl complex was water sensitive. Although these complexes do not appear to be explosive, they are, nevertheless, potentially hazardous and the appropriate precautions should be taken. The preparations of the starting materials together with the instruments used for the physical measurements are described in Appendix 1.

$Mn(CO)_5(OClO_3)$

$Mn(CO)_5Br$ (200 mg, 0.727 mmol) and finely divided silver perchlorate (176 mg, 0.850 mmol) were stirred in dichloromethane (6 ml) at room temperature for 50-60 min. The mixture was filtered into light petroleum (40 ml) and the solvent decanted. The yellow powder was dried and sublimed (65-70°, 0.02 mm) to give $Mn(CO)_5(OClO_3)$ (90 mg, 42%).

(Found:	C, 19.4;	Cl, 12.5;	Mn, 18.7;	O, 49.5
C_5ClMnO_9 requires:	C, 20.4;	Cl, 12.0;	Mn, 18.7;	O, 48.9%)

The compound is deliquescent and was stored in a desiccator.

$Mn(CO)_3(bpy)(OClO_3)$

Finely divided silver perchlorate (30 mg; 0.15 mmol) was added to a solution of $Mn(CO)_3(bpy)Br$ (40 mg; 0.11 mmol) in dichloromethane (4 ml) and the mixture was stirred at room temperature for 40-60 min. The solution was filtered and the yellow precipitate was extracted with dichloromethane (*c.* 15 ml). The extracts and the filtrate were combined and then concentrated until crystallization commenced. Light petroleum was added to precipitate $Mn(CO)_3(bpy)(OClO_3)$ as fine yellow crystals (75-85%), which were filtered, washed with light petroleum and dried in a vacuum.

(Found:	C, 38.8;	H, 2.0;	Mn, 13.8;	N, 6.9
$C_{13}H_8ClMnN_2O_7$ requires:	C, 39.6;	H, 2.0;	Mn, 13.9;	N, 7.1%)

$Mn(CO)_3(PPh_3)_2(OClO_3)$

This complex was prepared similarly by adding silver perchlorate (25.5 mg, 0.12 mmol) to a suspension of $Mn(CO)_3(PPh_3)_2Br$ (70 mg, 0.094 mmol) in dichloromethane (2.5 ml) and stirring the mixture for 45-55 min. The orange solution was either filtered and the product rapidly crystallized by adding light petroleum or filtered directly with stirring into light petroleum (20-25 ml). The orange crystals of $Mn(CO)_3(PPh_3)_2(OClO_3)$ (70-80%) were filtered, washed with light petroleum and dried in a vacuum.

The compound reacts fairly readily with dichloromethane and samples which were isolated by crystallization generally contained a small amount of $Mn(CO)_3(PPh_3)_2Cl$.

(Found:	C, 59.9;	H, 4.0;	Mn, 7.0
$C_{39}H_{30}ClMnO_7P_2$ requires:	C, 61.4;	H, 4.0;	Mn, 7.2%)

$Mn(CO)_3\{P(OPh)_3\}_2(OClO_3)$

The complex was prepared as above from $Mn(CO)_3\{P(OPh)_3\}_2Br$ (65 mg, 0.077 mmol) and silver perchlorate (23.0 mg, 0.11 mmol) in dichloromethane (3.5 ml). The mixture was stirred for 30-35 min. The bright yellow solution was filtered, concentrated and light petroleum was slowly added to crystallize $Mn(CO)_3\{P(OPh)_3\}_2(OClO_3)$ as bright yellow needles (48 mg, 73%).

(Found:	C, 54.4;	H, 3.5;	Mn, 6.4
$C_{39}H_{30}ClMnO_{13}P_2$ requires:	C, 54.5;	H, 3.5;	Mn, 6.4%)

$[Mn(CO)_5(MeCN)]ClO_4$

A solution of $Mn(CO)_5(OClO_3)$ in dichloromethane (3 ml), prepared from $Mn(CO)_5Br$ (100 mg) and silver perchlorate (90 mg), was filtered into acetonitrile (2.6 ml). The pale yellow solution was gently warmed for a few minutes before being concentrated to a minimum volume. Diethyl ether was added to give white crystals of $[Mn(CO)_5(MeCN)]ClO_4$ (49 mg, 40%) which were filtered, washed free of acetonitrile with diethyl ether and dried in a vacuum.

(Found:	C, 24.6;	H, 0.9;	Mn, 16.3;	N, 4.2
$C_7H_3ClMnNO_9$ requires:	C, 25.1;	H, 0.9;	Mn, 16.4;	N, 4.2%)

$[Mn(CO)_5(PhCN)]ClO_4$

A solution of $Mn(CO)_5(OClO_3)$, prepared as above, was filtered into benzonitrile (1.5 ml) to give a yellow solution. The dichloromethane was removed (water pump) and diethyl ether was added to crystallize $[Mn(CO)_5(PhCN)]ClO_4$ as white crystals (54 mg, 37%), which were filtered, washed free of benzonitrile with ether and dried in a vacuum.

(Found:	C, 36.3;	H, 1.3;	Mn, 13.7;	N, 3.6
$C_{12}H_5ClMnNO_9$ requires:	C, 36.3;	H, 1.3;	Mn, 13.8;	N, 3.5%)

$[Mn(CO)_5(H_2O)]BPh_4$

A solution of $Mn(CO)_5(OClO_3)$ in dichloromethane (3 ml), prepared as described above from $Mn(CO)_5Br$ (100 mg) and silver perchlorate (90 mg), was vigorously stirred with water (2 ml) for 25-30 min. The bright yellow aqueous phase was separated from the organic layer and solid sodium tetraphenylborate was slowly added with shaking to precipitate $[Mn(CO)_5(H_2O)]BPh_4$ as bright yellow microcrystals (50 mg), which were filtered, washed with water and dried in the air.

The compound decomposes over a period of 24 hours to give brown crystals

CHAPTER 5

DIFLUOROPHOSPHATO DERIVATIVES OF MANGANESE CARBONYL

5.1 Introduction

Although the difluorophosphate ion ($PO_2F_2^-$) can behave as either a mono- or as a bi-dentate ligand, little work has been done with this ion as a ligand[295-299] and no metal carbonyl derivatives have been prepared. Metal carbonyl complexes containing the difluorothiophosphate (PF_2OS^-)[300] and difluorodithiophosphate ($PS_2F_2^-$)[300,301] ions have been reported as well as diorganodithiophosphinate ($R_2PS_2^-$; R = Et, Ph) derivatives.[302]

The hexafluorophosphate ion is generally considered to be non-coordinating and inert and is often used as a substitute for perchlorate because it does not have the explosive tendencies of the latter ion. However, under the appropriate circumstances, this ion will coordinate to transition metal ions (e.g. $M(pyridine)_4(PF_6)_2$; M = Ni, Cu[303,304]). However, no metal carbonyl derivatives have been reported.

Following the successful preparation of the manganese(I) perchlorato complexes as described in the previous chapter, it was proposed to investigate the preparation of the analogous hexafluorophosphato complexes. In our attempts to prepare these derivatives, the hexafluorophosphate ion was observed to undergo a novel decomposition to the difluorophosphate ion. The subject of this chapter is the preparation and characterization of the first examples of metal carbonyl complexes containing the difluorophosphate ion.

5.2 Difluorophosphatopentacarbonylmanganese(I)

(a) Preparation

The hexafluorophosphate ion is a potential source of fluoride by way of the following equation:

$$PF_6^- \longrightarrow PF_5 + F^-$$

and this has an effect on some reactions of the hexafluorophosphate ion with transition metal complexes. Thus, oxidation of $Mo(CO)_2(dpe)_2$ with nitrosonium hexafluorophosphate in inert solvents results in the formation of molybdenum(II) fluoro complexes (see Chapter 2). Moreover, the reaction of $(Cp)Mo(CO)_3GeCl_3$ with silver hexafluorophosphate results in the formation of $(Cp)Mo(CO)_3GeF_3$.[242] Although the manganese pentacarbonyl halides (X = Cl, Br, I) have been known for many years,[147,148] attempts to prepare the analogous fluorine complex have been unsuccessful.[179,204] Halide abstraction by silver hexafluorophosphate would appear to be a potential route to this complex.

When $Mn(CO)_5Br$ was stirred with a slight excess of silver hexafluorophosphate in dichloromethane at -3°C, hydrolysis of the hexafluorophosphate ion occurred together with the abstraction of bromide resulting in the formation of the difluorophosphato complex, $Mn(CO)_5(PO_2F_2)$. The colour of the solution changed from orange to pale yellow over a period of 70 - 80 minutes and the product was isolated as fluffy yellow needles by filtering the reaction mixture into cold light-petroleum.

When the reaction was carried out at room temperature, carbon monoxide was vigourously evolved and a mixture of complexes was formed. Infrared monitoring showed that complete conversion to $Mn(CO)_5(PO_2F_2)$ had occurred after approximately four minutes. The complex then reacts further to give a tricarbonyl species with carbonyl stretching bands at 2061 (s) and 1945 (s,br) cm^{-1}. These are consistent with the formation of $Mn(CO)_3F_3$. This complex has been previously prepared by stirring $Mn(CO)_5Br$ with a large excess of silver fluoride in dichloromethane. The carbonyl stretching frequencies in nujol were reported as 2037 (s), 1944 (s,br) and 1922 (w,sh) cm^{-1}.[179]

$Mn(CO)_5(PO_2F_2)$ is stable at low temperatures and can be stored at -15°C for several weeks. The complex is, however, unstable at room temperature and decomposes to a yellow gum over a period of 12 - 15 hours. The infrared spectrum of this gum showed carbonyl absorptions at 2060 (s) and 1940 (s,br) cm^{-1}. A similar reaction occurred when the pentacarbonyl complex was heated in an atmosphere of nitrogen at 60°C for 15 minutes. The gum subsequently decomposed over a period of days with the total loss of carbon monoxide to give a pale yellow insoluble residue.

On gentle warming to approximately 41°C, $Mn(CO)_5(PO_2F_2)$ sublimes in a vacuum (0.02 mm) producing fluffy yellow needles. On the other hand, rapid heating in a vacuum to a temperature > 45°C causes the compound to melt, carbon monoxide is then evolved and the molten mass resolidifies to give an orange solid with carbonyl stretching absorptions (dichloromethane solution) at 2060 (s) and 1945 (s,br) cm^{-1}. Further heating to about 100°C leads to total decomposition, probably by way of a series of disproportionation reactions. One of the products is $Mn_2(CO)_{10}$, which can be recovered by sublimation. The infrared spectrum, melting point and X-ray powder pattern were identical to those of an authentic sample.

(b) Characterization

Three carbonyl stretching bands (Table 5.1) are present in the infrared spectrum of $Mn(CO)_5(PO_2F_2)$. The relative band intensities (see Fig. 4.2) are consistent with the formulation of the complex as a pentacarbonyl species. The frequencies are intermediate between those for the pentacarbonyl halides and $Mn(CO)_5(OClO_3)$ and this indicates that the difluorophosphato group is not as strongly electronwithdrawing as the perchlorato group. The bands due to the difluorophosphate ion are also recorded in Table 5.1 (see section 3).

The mass spectrum of $Mn(CO)_5(PO_2F_2)$ (Table 5.2) can be explained in terms of two simultaneous fragmentation processes. The molecular ion, observed at *m/e* 296, fragments by the loss of PO_2F_2 according to the equation:

$$[Mn(CO)_5(PO_2F_2)]^+ \longrightarrow Mn(CO)_5^+ + PO_2F_2$$

No peak corresponding to the $PO_2F_2^+$ ion was observed, but a peak attributable to POF_2^+ was present. The $Mn(CO)_5^+$ ion fragments by successive loss of carbon monoxide. Peaks were present for all the ions $Mn(CO)_n^+$ (n = 0 - 5). The other mode of fragmentation for the ion $[Mn(CO)_5(PO_2F_2)]^+$ appears to involve the sequential loss of carbon monoxide:

$$\begin{tikzcd}
{[Mn(CO)_5(PO_2F_2)]^+} \arrow[r] & {[Mn(CO)_4(PO_2F_2)]^+ + CO} \arrow[d, "-CO\ (4\ times)"] \\
Mn^+ + PO_2F_2 & {[Mn(PO_2F_2)]^+} \arrow[l]
\end{tikzcd}$$

Peaks were observed for all the ions in this series. The relative intensities of the peaks for the fragmentation of $[Mn(CO)_5(PO_2F_2)]^+$ by the loss of either the difluorophosphato or the carbonyl groups suggest that these processes occur concurrently, with no route being particularly favoured.

Peaks observed at *m/e* higher than 296 can be accounted for by the formation and subsequent fragmentation of $Mn_2(CO)_{10}$. These were present for the ions $Mn_2(CO)_n^+$ (n = 0 - 8). It is believed that the dimanganese species are formed in the spectrometer from the monomanganese fragments, either by molecular combination or by ion-molecule reactions, since: (a) the infrared spectrum of $Mn(CO)_5(PO_2F_2)$ showed no evidence for any $Mn_2(CO)_{10}$ impurity and (b) $Mn_2(CO)_{10}$ is produced in the thermal decomposition of $Mn(CO)_5(PO_2F_2)$.

In the mass spectrum of $Mn(CO)_5(O_2CCF_3)$[206] fragmentation of the molecular ion occurs by two routes involving the loss of either carbon monoxide or the trifluoroacetate ion. In addition, peaks of significant intensity were observed for $Mn_2(CO)_{10}$ and its fragmentation products. Thermal decomposition of $Mn(CO)_5(O_2CCF_3)$ afforded carbon monoxide, $Mn_2(CO)_{10}$ and manganese salts.[204]

The ^{19}F NMR spectrum of $Mn(CO)_5(PO_2F_2)$ (Table 5.4), recorded in CD_2Cl_2 at 240°K, consisted of a doublet with a ^{31}P-^{19}F coupling constant of 968 Hz. This is in good agreement with the values obtained for the free ion[305] and for $[\{(C_5Me_5)Rh\}_2(O_2PF_2)_3]^+$, which contains bridging difluorophosphato groups[298,299] (see Table 5.4).

(c) Reactions

Due to the instability of the complex, its reactions were not extensively studied, but they appear to be similar to those of $Mn(CO)_5(OClO_3)$.

$Mn(CO)_5(PO_2F_2)$ shows no tendency to react with dichloromethane at room temperature. The complex reacts slowly with dichloromethane to give $Mn(CO)_5Cl$ when solutions of the complex are left in the infrared beam. In chloroform, under these conditions, complete conversion to $Mn(CO)_5Cl$ occurs within 10 minutes. $Mn(CO)_5(PO_2F_2)$ reacts very rapidly with halide ions (X = Cl, Br, I) in dichloromethane at room temperature to form the corresponding halo complexes:

$$Mn(CO)_5(PO_2F_2) + X^- \xrightarrow{CH_2Cl_2} Mn(CO)_5X + PO_2F_2^-$$

The colour changes were the same as those observed in the reactions of $Mn(CO)_5(OClO_3)$ [Chapter 4.2.2(c)]. The difluorophosphato group is rapidly displaced by cyano solvents (RCN; R = Me, Ph) to give the corresponding nitrile complexes, $[Mn(CO)_5(RCN)]^+$, as shown in the equation:

$$Mn(CO)_5(PO_2F_2) + RCN \longrightarrow [Mn(CO)_5(RCN)]PO_2F_2$$

TABLE 5.1

Infrared Spectrum of $Mn(CO)_5(PO_2F_2)$

Assignment	Frequency (cm^{-1}) Nujol	Dichloromethane
ν_{CO}, (A_1^{1b}, eq)	2166 w	2166 vw
ν_{CO}, (E , eq)	2061 vs	2080 vs
ν_{CO}, (A_1^{1a}, ax)	2030 s	2024 ms
combination band[A]	1344 w,sh	
ν_{as} PO_2, (B_1)	1315 s	
ν_{sym} PO_2, (A_1)	1140 s	
ν_{as} PF_2, (B_2)	880 ms	
ν_{sym} PF_2, (A_1)	849 ms	
–	650 sh	
δ MCO	634 vs	
δ MCO ; δ PO_2, (A_1)[B]	550 m	
δ POF, (B_1)	510 m	
δ POF, (B_2)	495 m	
–	462 w	
ν MC	398 s	

A. Assigned to 849 + 495.

B. These two modes of vibration occur at identical frequency.

TABLE 5.2

Mass Spectrum of $Mn(CO)_5(PO_2F_2)$

m/e	Relative Intensity	Assignment
334	5	$Mn_2(CO)_8^+$
306	25	$Mn_2(CO)_7^+$
296	20	$[Mn(CO)_5(PO_2F_2)]^+$
278	25	$Mn_2(CO)_6^+$
268	20	$[Mn(CO)_4(PO_2F_2)]^+$
250	40	$Mn_2(CO)_5^+$
240	20	$[Mn(CO)_3(PO_2F_2)]^+$
222	50	$Mn_2(CO)_4^+$
212	35	$[Mn(CO)_2(PO_2F_2)]^+$
195	50	$Mn(CO)_5^+$
194	45	$Mn_2(CO)_3^+$
184	45	$[Mn(CO)(PO_2F_2)]^+$
167	40	$Mn(CO)_4^+$
166	35	$Mn_2(CO)_2^+$
156	75	$Mn(PO_2F_2)^+$
139	40	$Mn(CO)_3^+$
138	20	$Mn_2(CO)^+$
111	30	$Mn(CO)_2^+$
110	35	Mn_2^+
85	40	POF_2^+
83	40	$Mn(CO)^+$
74	70	MnF^+
55	100	Mn^+

5.3 Substituted Difluorophosphato Complexes

(a) Preparation and Characterization

When the substituted bromo complexes $Mn(CO)_3L_2Br$ ($L = PPh_3$, $P(OPh)_3$; L_2 = bpy) were stirred with an excess of silver hexafluorophosphate in dichloromethane at 0°C, the corresponding difluorophosphato complexes, $Mn(CO)_3L_2(PO_2F_2)$, were formed. The colour changes in these reactions were similar to those occurring in the preparations of the analogous perchlorato complexes (see Chapter 4.6). The amount of silver hexafluorophosphate did not seem to be critical provided an excess was used, except in the case of $Mn(CO)_3(PPh_3)_2(PO_2F_2)$. A small amount of uncharacterized by-product with a carbonyl stretching band at 1997 (m) cm^{-1} is always formed during the preparation of this complex and,for this reason, the amount of silver hexafluorophosphate should be kept to a minimum (see experimental section). The products, which are very soluble in dichloromethane, were isolated as crystalline solids by adding light petroleum to the concentrated filtrate; the entire procedure being carried out at 0°C under an atmosphere of dry nitrogen.

These complexes are more stable in the solid state than $Mn(CO)_5(PO_2F_2)$, but they decompose over a period of several days on standing at room temperature. They are quite stable at low temperatures and can be stored at -15°C in an atmosphere of dry nitrogen for several months. The bipyridyl and bis-triphenylphosphite complexes showed no tendency to react with dichloromethane even at elevated temperatures, since there was no change in the infrared spectra when solutions of these complexes were left in the infrared beam for one hour. The bis-triphenylphosphine complex, however, reacts very rapidly with dichloromethane under these conditions forming $Mn(CO)_3(PPh_3)_2Cl$.

The carbonyl stretching frequencies of the difluorophosphato complexes (Table 5.3) are intermediate between those of the analogous perchlorato

(Table 4.9) and bromo (Appendix 1) complexes, as was observed for $Mn(CO)_5(PO_2F_2)$. Furthermore, there were no significant changes in the relative band intensities compared to the bromo complexes and this indicates that no structural rearrangement has taken place during the halide abstraction process. The bands due to the difluorophosphato group are recorded in Table 5.5 (see Section 3).

The ^{19}F NMR spectra of the difluorophosphato complexes (Table 5.4), recorded in CD_2Cl_2, consisted of a doublet due to coupling with the phosphorous atom. The chemical shifts and coupling constants of the various derivatives are similar. The small change in the coupling constants between the free and coordinated anions indicates that only a small change in the P-F bond character has occurred upon complex formation[307] and this is consistent with coordination through oxygen.

(b) Reactions

The rate of reaction of the difluorophosphato complexes, $Mn(CO)_3L_2(PO_2F_2)$, with halide ions increases in the order $P(OPh)_3 << bpy < PPh_3 \approx CO$. $Mn(CO)_3(PPh_3)_2(PO_2F_2)$ reacts very rapidly with halide ions (X = Cl, Br, I), as either the tetraphenylarsonium or tetraethylammonium salts, in dichloromethane at room temperature to give the corresponding halo complexes, as shown in the equation:

$$Mn(CO)_3(PPh_3)_2(PO_2F_2) + X^- \xrightarrow{CH_2Cl_2} Mn(CO)_3(PPh_3)_2X + PO_2F_2^-$$

The products were identified by their infrared spectra and their characteristic colours.

The same reaction with $Mn(CO)_3(bpy)(PO_2F_2)$ was slow at room temperature, but proceeded reasonably quickly on warming. On the other hand, $Mn(CO)_3\{P(OPh)_3\}_2(PO_2F_2)$ reacted very slowly even in hot dichloromethane. For these complexes the rate of reaction increased in the order $I^- < Br^- < Cl^-$.

$Mn(CO)_3(PPh_3)_2(PO_2F_2)$ reacts very rapidly with acetonitrile at room temperature to give $[Mn(CO)_3(PPh_3)_2(MeCN)]^+$, as shown by the infrared spectrum. The molar conductance of a solution of $Mn(CO)_3(bpy)(PO_2F_2)$ in acetonitrile (1.10×10^{-3} M), measured as quickly as possible, was 60 S cm^2. On standing for one hour at 25°C, the conductance increased to an equilibrium value of 120 S cm^2 mol^{-1}, which corresponds to complete displacement of difluorophosphate by acetonitrile. The rate of substitution of $Mn(CO)_3\{P(OPh)_3\}_2(PO_2F_2)$ was even slower. The initial conductance of an acetonitrile solution of similar molarity was 8.4 S cm^2 mol^{-1} and the equilibrium value of 100 S cm^2 mol^{-1} was reached after 8 hours. The value is slightly low for a 1:1 electrolyte and this may be due to either decomposition or incomplete reaction with the solvent. In comparison, the perchlorato complexes dissociate virtually instantaneously upon dissolution in polar solvents.

These results indicate that the difluorophosphate ion is a better ligand than perchlorate and this is consistent with the relative electron-withdrawing abilities, deduced from the carbonyl stretching frequencies.

TABLE 5.3

Carbonyl Stretching Frequencies of the Difluorophosphato Complexes

Compound	Colour	$\nu_{CO}(cm^{-1})^A$
$Mn(CO)_3(bpy)(PO_2F_2)$	deep yellow	2051 (vs), 1942 (vs), 1930 (vs)
$Mn(CO)_3(PPh_3)_2(PO_2F_2)$	orange-yellow	2051 (w), 1956 (vs), 1914 (s)
$Mn(CO)_3\{P(OPh)_3\}_2(PO_2F_2)$	pale yellow	2085 (w), 1999 (vs), 1950 (s)

A. Measured in dichloromethane

TABLE 5.4

^{19}F NMR Spectra^A of the Difluorophosphato Complexes

Compound	Chemical Shift^B (ppm)	J(Hz)^C	T(°K)	Ref.
$(HO)POF_2$	-	978	-	306
$PO_2F_2^-$	-	952	-	305
$Mn(CO)_5(PO_2F_2)$	+ 0.7	968	240	-
$Mn(CO)_3(bpy)(PO_2F_2)$	+ 1.2	962	300	-
$Mn(CO)_3(PPh_3)_2(PO_2F_2)$	- 0.3	954	255	-
$Mn(CO)_3\{P(OPh)_3\}_2(PO_2F_2)$	- 1.5	957	300	-
$[\{(C_5Me_5)Rh\}_2(O_2PF_2)_3]^+$	+ 3.4	952	-	298,299

A. Recorded in CD_2Cl_2.

B. Measured relative to CF_3CO_2H (external reference).

C. $^{31}P - {}^{19}F$ coupling.

5.4 Infrared Spectrum of the Difluorophosphate Ion

In its K^+, Rb^+, Cs^+ and NH_4^+ salts the difluorophosphate ion has been shown to have C_{2v} symmetry[308-310] and is expected to have nine fundamental modes of vibration. These are approximately described as PO_2 and PF_2 symmetric and asymmetric stretches, PO_2 and PF_2 bending, two POF rocking modes, and a torsional mode. Only the last mode, which belongs to group A_2, is infrared inactive. The infrared[311,312] and Raman[311] spectra of the difluorophosphate ion as the alkali metal salt together with the band assignments have been reported. These are summarized in Table 5.5.

Upon monodentate coordination of the ion through an oxygen atom, the symmetry is reduced to C_s and the A_2 mode should now be infrared active, albeit of medium-to-weak intensity. The bands due to the coordinated difluorophosphate ion in the complexes $Mn(CO)_3L_2(PO_2F_2)$ (L = CO, PPh_3, $P(OPh)_3$; L_2 = bpy) are recorded in Table 5.5 and the infrared spectrum of $Mn(CO)_5(PO_2F_2)$ in the region 1400 - 350 cm^{-1} is illustrated in Figure 5.1. Some of the low frequency bands in the spectra of the phosphine-substituted complexes are obscured by absorptions due to the ligands. As can be seen from the table, only seven of the fundamentals could be assigned.

All complexes show strong asymmetric and symmetric PO_2 stretching modes in the region 1320 - 1120 cm^{-1}. The asymmetric mode, with the exception of the bis-triphenylphosphite complex, is increased slightly relative to the free ion, while the symmetric mode is slightly decreased in all cases. A weak band due to the combination of the symmetric PF_2 stretching mode and one of the POF rocking modes is present, except for the triphenylphosphite complex, as a shoulder at approximately 1340 cm^{-1}. The asymmetric and symmetric PF_2 stretching modes in the region 890 - 835 cm^{-1} are also increased relative to the free ion; the extent of the increase depending on the ligand L. An increase was observed in the PO_2 bending mode, while only slight changes occurred in the POF rocking modes. In the spectrum of

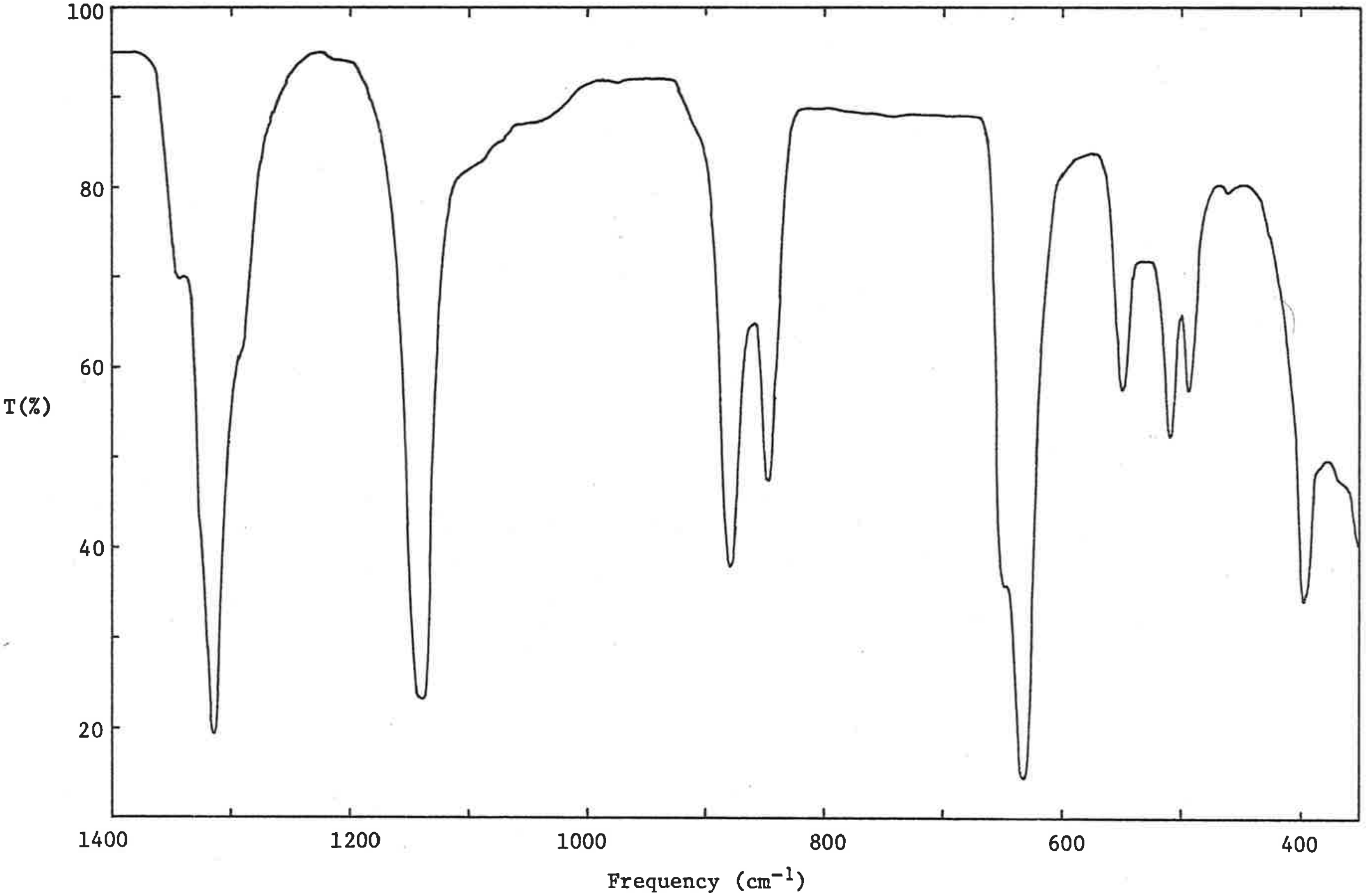

Fig. 5.1 Infrared Spectrum of $Mn(CO)_5(PO_2F_2)$

$Mn(CO)_5(PO_2F_2)$ the frequency of the PO_2 bending mode corresponded exactly with one of the $\delta(MCO)$ modes.

It was not possible to conclusively demonstrate the presence of either the POF torsional mode (A_2) or the PF_2 bending mode (A_1). Bühler and Bues[311] assigned the Raman band at 365 cm^{-1} in molten KPO_2F_2 to the A_2 absorption and the weak band in the infrared spectrum at 286 cm^{-1} to the A_1 mode. Thompson and Reed[312] were unable to observe the band at 286 cm^{-1} and assigned the A_1 absorption to the band at 360 cm^{-1}. This band was of weak intensity for the sodium salt and was not present for the other alkali metal salts (K^+, Rb^+, Cs^+; NH_4^+).

In the previously reported difluorophosphato complexes[295-297] the ion is bidentate and thus, the symmetry remains C_{2v}. The frequencies of the asymmetric PO_2 stretching modes are decreased relative to the free ion, while the symmetric PO_2 and both PF_2 stretching modes are increased. The PF_2 bending mode is not always observed in the spectra and when it is present, it varies between 260 and 350 cm^{-1}.

TABLE 5.5

Difluorophosphato Frequencies of $Mn(CO)_3L_2(PO_2F_2)^A$ and KPO_2F_2 (cm^{-1})

Assignment	KPO_2F_2 Raman[B]	KPO_2F_2 IR[C]	L = CO	$L = PPh_3$	$L = P(OPh)_3$	L_2 = bpy
combination	–	1332 w	1344 mw[D]	1335 mw	–	1335 mw
ν_{as} PO_2, (B_1)	1290 w	1310 s	1315 s	1319 s	1308 s	1315 s
ν_{sym} PO_2, (A_1)	1145 s	1148 s	1140 s	1142 m	1129 s	{ 1143 m 1129 m
ν_{as} PF_2, (B_2)	–	850 s	880 ms	870 m	882 s	856 m
ν_{sym} PF_2, (A_1)	824 s	832 s	849 ms	839 m	851 s	838 m
δ_{sym} PO_2, (A_1)	517 m	535 w	550 m[E]	546 w,sh	548 mw	542 mw
δ POF, (B_1)	–	503 s	510 m	502 m	–[F]	505 mw
δ POF, (B_2)	–	495 s	495 m	–[F]	495 m	495 w
δ_{sym} PF_2, (A_1)	277[G]	–[G,H]	–	–	–	–

A. Infrared spectra recorded as nujol mulls between either KBr (1400 – 400 cm^{-1}) or polyethylene (600 – 250 cm^{-1}) plates.

B. Molten KPO_2F_2 at 300°C, Reference 311. C. Reference 312.

D. Assigned to 849 +495, similar assignments for the other complexes.

E. Coincides exactly with δ MCO.

F. Obscured by ligand vibrations.

G. See text.

H. In $NaPF_6$ this band occurs at 360 (w) cm^{-1}.

5.5 Discussion

The hexafluorophosphate ion is normally considered as being extremely stable and many salts have been prepared. The ion is virtually completely resistant to hydrolysis under alkaline and neutral conditions,[238,268] but undergoes very slow hydrolysis in acidic media to form the orthophosphate ion.[238,239] On standing in 4M nitric acid for 26 hours at 25°C only 16.5% of the ion had been hydrolyzed.[240] A dissociative mechanism with the rate determining step being the initial dissociation of one of the phosphorous-fluorine bonds has been postulated.[239] The phosphorous pentafluoride thus formed is then rapidly hydrolyzed. The aquation reaction is accelerated by alkali metal ions in the order $K^+ < Na^+ << Li^+$ and this has been attributed to the formation of ion pairs.[240] Metal ion catalysis, under acidic conditions, has been observed for beryllium(II), aluminium(III), zirconium(IV) and thorium(IV).[241] In the aluminium(III) catalyzed reactions kinetic evidence was given for the build-up of an intermediate.

Silver hexafluorophosphate was found to be very water sensitive and fumed when exposed to the air. The infrared spectrum of the compound as a nujol mull, prepared in a nitrogen filled dry-box and recorded between potassium bromide plates, showed in addition to the hexafluorophosphate bands at 840 (s) and 563 (m) cm^{-1}[311,313] a number of medium-intensity bands due to hydrolysis products. When the mull was exposed to the air for a few minutes, the bands due to the hexafluorophosphate ion disappeared and they were replaced by bands which could be assigned to the difluorophosphate ion. The frequencies were in good agreement with the reported values.[311,312] A similar result was obtained when silver hexafluorophosphate was exposed to the air for a short time before the mull was prepared. Accordingly, silver hexafluorophosphate was always manipulated in a dry-box except for the moment when it was transferred into the reaction flask. Although the hexafluorophosphate ion may have been partly hydrolyzed when it was added to the reaction mixture, it is believed that complete conversion to difluorophosphate occurred during the halide abstraction process. However, we are at present unsure about the mechanism of the reaction.

$[(C_5Me_5)RhCl_2]_2$ reacts with silver hexafluorophosphate in polar solvents (acetone, acetonitrile, pyridine etc.) to give $[(C_5Me_5)Rh(solvent)_3]$-$(PF_6)_2$. When attempts were made to isolate the acetone complex, or when the acetone solution was heated (50°C/12 hr.), a complex decomposition reaction occurred to give $[(C_5Me_5)Rh(OPF_2O)_3Rh(C_5Me_5)]PF_6$ which contains three bridging difluorophosphato ligands. This was confirmed by an X-ray molecular structure determination. The addition of water did not significantly increase the rate of formation of the dimer.[298,299]

5.6 Experimental

General

All preparations were carried out in an atmosphere of high-purity dry nitrogen. Analytical grade dichloromethane was dried over Linde 4A molecular sieves before use. The light petroleum used in the experiments had b.p. < 40°. Silver hexafluorophosphate was stored in a desiccator over potassium hydroxide and was manipulated in a nitrogen filled dry-box. The progress of the reactions was monitored by infrared spectroscopy. The difluorophosphato complexes were stored in a freezer at -15°C under an atmosphere of dry nitrogen. The preparations of the starting materials are described in Appendix 1.

The instruments used for the physical measurements are described in Appendix 1. Carbonyl stretching frequencies were measured in dichloromethane and complete spectra were recorded as nujol mulls between either potassium bromide or polyethylene plates. The triphenylphosphine complex, $Mn(CO)_3(PPh_3)_2(PO_2F_2)$, gave consistently low carbon analyses, presumably because of the presence of a by-product which could not be removed during the isolation of the complex.

$Mn(CO)_5(PO_2F_2)$

A suspension of $Mn(CO)_5Br$ (120 mg, 0.436 mmol) in dichloromethane (4.7 ml) was cooled to -3°C in an ice/ethanol bath. Silver hexafluorophosphate (132 mg, 0.522 mmol) was added and the mixture was stirred at this temperature for 70 - 80 min. The yellow solution was filtered with stirring into light petroleum (40 ml) which had been precooled to 0°C. The volume was reduced to *c.* 25 ml (vacuum line), the solvent was decanted and the yellow needles were dried on a vacuum line; the entire procedure being carried out at 0°C.

(Found:	C, 20.3;	Mn, 18.3
$C_5F_2MnO_7P$ requires:	C, 20.3;	Mn, 18.6%).

$Mn(CO)_3(bpy)(PO_2F_2)$

A solution of $Mn(CO)_3(bpy)Br$ (40 mg, 0.11 mmol) in dichloromethane (3.2 ml) was cooled to 0°C in an ice bath. Silver hexafluorophosphate (38 mg, 0.15 mmol) was added and the mixture was stirred at this temperature for 25 - 30 min. The yellow solution was filtered into a cold flask and concentrated to minimum volume. Light petroleum was slowly added to precipitate $Mn(CO)_3(bpy)(PO_2F_2)$ as deep yellow crystals. The solvent was decanted and the product dried on a vacuum line; the entire procedure being carried out at 0°C.

(Found: C, 37.7; H, 2.1; F, 7.3; Mn, 13.0; N, 6.6; P, 6.9
$C_{13}H_8F_2MnN_2O_5P$ requires: C, 39.4; H, 2.0; F, 9.6; Mn, 13.9; N, 7.1; P, 7.8%)

$Mn(CO)_3(PPh_3)_2(PO_2F_2)$

This complex was prepared in a similar manner from a suspension of $Mn(CO)_3(PPh_3)_2Br$ (70 mg, 0.094 mmol) and silver hexafluorophosphate (27 mg, 0.11 mmol) in dichloromethane (2.4 ml). The mixture was stirred for 25 - 30 min. and the product was isolated as orange-yellow crystals.

(Found: C, 59.3; H, 4.0
$C_{39}H_{30}F_2MnO_5P_3$ requires: C, 61.3; H, 4.0%).

$Mn(CO)_3\{P(OPh)_3\}_2(PO_2F_2)$

This complex was prepared as described above from $Mn(CO)_3\{P(OPh)_3\}_2Br$ (55 mg, 0.066 mmol) and silver hexafluorophosphate (25 mg, 0.099 mmol) in 3.2 ml of dichloromethane. The mixture was stirred for 65 min. After the yellow filtrate had been concentrated to minimum volume, petroleum ether (40 - 60°, *c.* 10 ml) was added and the solution was gently concentrated until $Mn(CO)_3\{P(OPh)_3\}_2(PO_2F_2)$ began to crystallize as pale-yellow needles.

(Found: C, 54.4; H, 3.5; F, 3.1; Mn, 6.3; P, 10.4
$C_{39}H_{30}F_2MnO_{11}P_3$ requires: C, 54.4; H, 3.5; F, 4.4; Mn, 6.4; P, 10.8%).

APPENDICES

APPENDIX 1

EXPERIMENTAL

This appendix contains a detailed account of the reagents and instruments used throughout this work, the preparations of the starting materials and a general summary of experimental details presented previously.

1.1 General

All preparations and reactions, except metatheses involving the molybdenum(II) and tungsten(II) halo complexes, were carried out in an atmosphere of dry nitrogen. All compounds were stored in the dark. The group VIa complexes developed either a brown or green colour when exposed to the light for a few hours. $Mn(CO)_5(OClO_3)$ is hygroscopic and needs to be stored in a desiccator. The substituted perchlorato complexes were not hygroscopic, but were stored in a dessicator as a routine precaution. The manganese difluorophosphato complexes were stored in a freezer at -15°C. Although we have experienced no accidents in our work with the perchlorato complexes, they are potentially hazardous and the normal precautions should be taken.

1.2 Physical Measurements and Instrumentation

Elemental Analyses

Elemental microanalyses (C, H, P, O, N, F, Cl, Br, I) were determined by the Australian Microanalytical Service, Melbourne. Carbon, hydrogen and nitrogen were also determined using a Perkin Elmer Model 240 C, H, N Analyser situated at The Levels campus of the South Australian Institute of Technology. The manganese difluorophosphato samples were sent to Melbourne by air express in a dry-ice cooled package and were analyzed immediately upon arrival.

Manganese analyses were obtained using a Varian 1200 Atomic Absorption

Spectrophotometer. The manganese standards were prepared by reducing a solution of potassium permanganate to the manganous ion by boiling with ethanol, according to the method of Vogel.[314(a)] The permanganate solution was prepared from analytical grade potassium permanganate and standardized by titration with dry sodium oxalate (AR grade) as described by Vogel.[314(b)] The manganese complexes were digested by boiling in a mixture of sulphuric and nitric acids (both AR grade).

Balances

For conductiometric and atomic absorption work samples were weighed on a Cahn Model G2 electrobalance. For routine preparative work weighings were done on a Mettler H16 balance weighing to 0.01 mg.

Infrared Spectra

These were recorded using a Perkin Elmer 457 or Jasco IRA-2 double-beam Grating Infrared Spectrophotometer in the range 4000-250 cm^{-1} and were calibrated with polystyrene. The Perkin Elmer instrument has incorporated into it a scale changing mechanism at 2000 cm^{-1}, which produces a discontinuity in the spectrum thus interfering with any carbonyl absorptions near this wavenumber. The Jasco instrument has a smooth scale changing mechanism, which does not interfere with the recording of the spectra. Carbonyl stretching frequencies were, if possible, recorded in solution between KBr plates using a standard solution cell. The solvent was usually dichloromethane. Complete spectra were recorded as nujol mulls between KBr plates (4000 - 400 cm^{-1}). Very low wavenumber spectra (600 - 250 cm^{-1}) were recorded as nujol mulls between polyethylene plates. Spectra were also obtained using KBr discs, prepared by subjecting a ground mixture of the compound and KBr to 10 tons of pressure delivered by a Research and Industrial Instruments Company K32 MkI press.

Raman Spectra

Attempts were made to record spectra using a Carey-83 Argon Laser Spectrophotometer (488 nm), situated at The Levels campus of the South Australian Institute of Technology, but extensive decomposition of all samples occurred in the laser beam before a spectrum could be obtained.

Electronic Spectra

Spectra were recorded using a Perkin Elmer Model 402 and a Zeiss Model DMR10 spectrophotometer.

NMR Spectra

Proton NMR spectra were recorded relative to TMS on a Varian T60 spectrometer at 60 MHz. Broadband proton-decoupled Fourier transform ^{31}P and ^{19}F NMR spectra were recorded on a computer equipped Bruker HX-90E spectrometer at 36.43 and 84.67 MHz respectively. The spectra were determined in deuterochloroform or deuterodichloromethane in 5mm tubes. Deuterated solvents were required for the deuterium resonance lock. Dpe was used as an internal reference for the ^{31}P spectra and was then calibrated against 85% orthophosphoric acid. For the ^{19}F spectra, trifluoroacetic acid was used as an external reference. Concentrations of the samples were in the range 7 - 12% (w/v). Good ^{19}F spectra were usually obtained after 100 - 150 scans, while the ^{31}P spectra required roughly 500 scans.

Conductivity Measurements

Measurements were made using a conductivity cell fitted with two taps allowing the cell to be flushed and then filled with an inert gas. Solutions were thermostatted in a water bath at 25.0 ± 0.5°C and the resistance measured using a Philips PR 9500 AC bridge incorporating a cathode ray indicator to detect the balance point. Molar conductances of the complexes were estimated from approximately 1.0 × 10^{-3} M solutions. AR grade solvents dried over molecular sieves were used.

Magnetic Measurements

The magnetic moment of the fluoro complex (Chapter 2.2.1) was determined in a dichloromethane/3% cyclohexane solution (0.0844 M) using the Evan's method.[217]

X-Ray Powder Photographs

A four track Nomius Guinier-De Wolff camera was used, in conjunction with Cu K_α radiation.

Electrochemistry

(a) Reagents

All solvents used were of reagent grade purity. Tetraethylammonium perchlorate was used as the supporting electrolyte at a concentration of 0.1M in acetone and nitromethane at room temperature and as a saturated solution in dichloromethane. For low temperature work a saturated solution of the supporting electrolyte was used in all cases. All solutions were degassed with argon.

(b) Instrumentation

Cyclic voltammograms were recorded at a platinum sheet working electrode in acetone, dichloromethane and nitromethane using a Princeton Applied Research (PAR) Model 170 electrochemistry system. The reference electrode was Ag/AgCl (0.1M LiCl; acetone) separated from the test solution by a salt bridge containing 0.1M tetraethylammonium perchlorate in acetone. The third or auxiliary electrode was platinum wire. Solutions were thermostatted at 25°C and unless otherwise stated results refer to this temperature. Low temperature electrochemistry at -70°C was carried out using an acetone-dry ice mixture. Scan rates of dc potential of 100 or 200 mV/sec were used. All voltammograms were recorded with a three electrode circuit plus positive feedback circuitry to minimize ohmic losses.

Mass Spectra

Mass Spectra were recorded on an AEI MS30 spectrometer with a 70eV beam.

1.3 Reagents, Solvents and Gases

Solvents

All solvents including those used as reagents were of analytical grade purity and were dried over Linde 4A molecular sieves before use, except for methanol, which was dried over magnesium turnings and distilled under nitrogen. The light petroleum used in the experiments had b.p. < 40°.

Gases

High purity nitrogen was obtained from Commonwealth Industrial Gases (CIG) Limited and nitrogen dioxide from Matheson Gas Products; both were used as received.

Reagents and Ligands

The common reagents (Et_4NBr, Et_4NI, NH_4PF_6, $NaBPh_4$, $AgClO_4$, PPh_3, bpy), of AR grade purity if possible, were obtained from BDH and were used as received; the tetraethylammonium salts were dried in a vacuum over potassium hydroxide. Manganese and chromium carbonyls and the phosphine and arsine ligands (dpe, dpae, $(Tol)_3P$) were obtained from Strem Chemicals and were used directly. Triphenylphosphite was from Ralph N. Emanuel Ltd. Tungsten hexacarbonyl was purchased from the Climax Molybdenum Company and molybdenum carbonyl from Kochlight. Silver hexafluorophosphate was purchased from Pfaltz and Bauer and was stored in a desiccator and manipulated in a dry box. Nitrosonium hexafluorophosphate, obtained from Ralph N. Emanuel Ltd., was stored in a freezer at -15°C and manipulated in a dry box.

Nitrosyl chloride was prepared by the literature method[315] and was stored in glass ampoules. The ampoule was broken inside a large flask and the nitrosyl chloride was transferred to the reaction vessel by using dry nitrogen as a carrier gas.

Silver fluoride

Silver fluoride was prepared according to Brauer's method[316] by adding silver carbonate to hydrofluoric acid (40%) in a plastic vial, shielded from direct light, until evolution of carbon dioxide ceased. The solution was filtered and the water was removed under high vacuum to yield a yellow solid, which was stored in the dark. Nevertheless decomposition quickly occurred to afford a black solid of indeterminate composition.

Silver tetrafluoroborate

The compound was prepared by adding silver carbonate to aqueous fluoroboric acid (40%) until evolution of carbon dioxide ceased. The filtered solution was evaporated to dryness on a vacuum line to yield the product as a white powder. The solid is very hygroscopic and extensive pumping and warming were required to remove the water of crystallization. Infrared spectra, prepared under anhydrous conditions, still showed an absorption of medium intensity due to residual water.

Tetraethylammonium fluoride

The compound was prepared by two methods.

A. An aqueous solution of silver fluoride was added to a concentrated aqueous solution of tetraethylammonium bromide in a polyethylene beaker. The coarse white curds of silver bromide settled rapidly and the solution was periodically decanted and filtered through cotton wool. When precipitation of silver bromide had ceased, the solution was filtered through filter paper to remove finely divided particles. The water was removed on a rotary evaporator to yield a viscous solution containing white crystals. These were dissolved in a minimum quantity of alcohol and acetone was added to crystallize the product as white needles, which were filtered, washed with ether, and dried in a vacuum.

When this method is used, it is essential that no hydrofluoric acid remains in the preparation of silver fluoride, because the unreacted acid will attack the glass to form hexafluorosilicate ($SiF_6^=$), which can be identified by its infrared spectrum.[313]

B. An aqueous solution of tetraethylammonium perchlorate was prepared by mixing equimolar quantities of tetraethylammonium bromide and silver perchlorate. The solution was periodically decanted and filtered. When precipitation of silver bromide had ceased, the solution was evaporated to minimal volume. Tetraethylammonium perchlorate crystallized as white flakes, which were dissolved in a minimum quantity of warm water. An ice-cold saturated solution of potassium fluoride (equimolar amount) was added and the mixture was cooled to crystallize potassium perchlorate. The mother liquor was decanted and concentrated on a rotary-evaporator until crystallization of potassium perchlorate ceased. The mother liquor was then concentrated until viscous, extracted with a minimum amount of ethanol, a few mls of acetone were added and tetraethylammonium fluoride was crystallized by the addition of ether. The crystals were filtered, washed with ether and dried in a vacuum. A second crop of crystals was obtained from the filtrate. The product was recrystallized from an ethanol/acetone mixture by the addition of ether.

The compound is deliquescent and was stored over phosphorous pentoxide. It is very soluble in water, alcohol, nitromethane, slightly soluble in dichloromethane and sparingly soluble in acetone. The infrared spectrum was identical to that of tetraethylammonium bromide.

1.4 Starting Materials

cis-$Cr(CO)_2(dpe)_2$

The dicarbonyl complex was prepared by an improvement of the literature method.[109] Chromium hexacarbonyl (0.6g) and dpe (2.8g) were refluxed in diglyme (60ml) for 140 hours. The deep red solution was filtered while hot to remove decomposition products. On cooling, the filtrate deposited yellow-orange crystals of *cis*-$Cr(CO)_2(dpe)_2$ (2.0g), which were filtered, washed with a few mls of diglyme and then liberally with light petroleum. The compound was purified by rapid recrystallization from dichloromethane with methanol.

The isolation and purification procedures were carried out in an atmosphere of dry nitrogen.* Once isolated, the complex is air stable.

(ν_{CO} 1835(vs), 1774(vs) cm^{-1} ($CHCl_3$ solution))

trans-$Cr(CO)_2(dpe)_2$

The method of Chatt and Watson[58] was used, producing, in our hands, a mixture of *trans*- and *cis*-$Cr(CO)_2(dpe)_2$ in the ratio of roughly 3:1 (yield 33%).

(ν_{CO} (*trans*-isomer) 1790(vs) cm^{-1} (CH_2Cl_2 solution))

cis-$Mo(CO)_2(dpe)_2$

The complex was prepared by the procedure of Zingales and Canziani[109] in nearly quantitative yield and was recrystallized from benzene-methanol.

(ν_{CO} 1849(vs), 1780(vs) cm^{-1} ($CHCl_3$ solution))

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* These conditions were necessary to prevent oxidation of the complex, see Appendix 3.

cis-$W(CO)_2(dpe)_2$

The complex was prepared by the procedure of Zingales and Canziani[109] in 75% yield and was recrystallized from chloroform-methanol.

(ν_{CO} 1848(vs), 1780(vs) cm^{-1} ($CHCl_3$ solution))

$Mo(CO)_4(dpe)$

The procedure of Zingales and Canziani[109] was used. $Mo(CO)_6$ (1.0g) and dpe (1.5g) were refluxed in *n*-butylether (50ml) for 60 min. On cooling, yellow crystals of $Mo(CO)_4(dpe)$ (1.7g, 76%) separated. These were recrystallized from acetone-methanol to give the product as white crystals. (m.p. 193 - 194°C).

(ν_{CO} 2031(ms), 1917(sh), 1905(vs), 1880(vs) (CH_2Cl_2 solution))

(Mesitylene) $Mo(CO)_3$

$Mo(CO)_6$ (4.0g) and dry redistilled mesitylene (20ml) were refluxed according to the method of Angelici.[317] Four hours of reflux were required for complete reaction. The product was obtained in 66% yield after recrystallization from dichloromethane-hexane.

(Mesitylene) $Cr(CO)_3$

$Cr(CO)_6$ (3.0g) and mesitylene (15ml) were refluxed for 4 hours. The hexacarbonyl readily sublimed into the condenser and was mechanically returned to the reaction flask. After cooling, hexane (50ml) was added to the filtered reaction mixture to precipitate the product as yellow crystals (0.4g), which were sublimed in a vacuum (100°C, 0.1mm).

$Et_4N[Mo(CO)_5Br]$

The compound was prepared by the method of Abel *et al.*[175] $Mo(CO)_6$ (1.20g) and Et_4NBr (0.74g) were heated in diglyme (30ml) at 110°C for

60 min. The hot solution was filtered under an atmosphere of nitrogen. Light petroleum was added to the cooled yellow filtrate to give yellow crystals of $Et_4N[Mo(CO)_5Br]$ (1.30g, 83%), which were filtered, washed with light petroleum and dried in a vacuum. The compound decomposes over a period of months, developing a green colour.

(ν_{CO} 2069(w), 1926(vs), 1850(s) cm^{-1} (CH_2Cl_2 solution))

$\underline{Mn(CO)_5Br}$

The method described by Abel and Wilkinson[148] was used. Bromine (2.1g) was added to $Mn_2(CO)_{10}$ (3.8g) in carbon tetrachloride (40ml) and the mixture was stirred at 40°C for 60 min. resulting in extensive precipitation of $Mn(CO)_5Br$. The solvent was removed and the residue was sublimed (55°, 0.1mm) to yield $Mn(CO)_5Br$ as orange crystals (4.4g, > 80%).

(ν_{CO} 2145(w), 2060(vs), 2017(s) cm^{-1} (CH_2Cl_2 solution))

$\underline{Et_4N\ [Mn(CO)_4Br_2]}$

The method described by Angelici[154] was used. $Mn(CO)_5Br$ (0.21g) and Et_4NBr (0.15g) were stirred in methanol (7ml) at 45 - 50°C for 60 min. The solvent was evaporated and the residue dissolved in dichloromethane (20ml). Light petroleum was added to the filtered solution to precipitate the product as deep yellow crystals (85%), which were filtered, washed with light petroleum and dried in a vacuum.

(ν_{CO} 2100(w), 2032(vs), 1980(s), 1934(vs) cm^{-1} (CH_2Cl_2 solution))

mer-$\underline{Mn(CO)_3(PPh_3)_2Br}$

The procedure of Abel and Wilkinson[148] was used. $Mn(CO)_5Br$ (0.30g) and PPh_3 (1.1g) were heated with stirring in petroleum ether (32ml) at 110 - 120°C for 15 min. After cooling, the deep yellow crystals of $Mn(CO)_3(PPh_3)_2Br$ were filtered, washed with diethylether to remove excess

PPh_3 and recrystallized from chloroform-light petroleum (0.61g, 75%).

(ν_{CO} 2046(w), 1947(vs), 1913(s) cm^{-1} (CH_2Cl_2 solution))

$Mn(CO)_3(bpy)Br$

The procedure is identical to that used to prepare the bis-triphenylphosphine complex. $Mn(CO)_5Br$ (0.40g) and bpy (0.50g) were heated in petroleum ether (45ml) for 10 min. The orange crystals of $Mn(CO)_3(bpy)Br$ were washed free of excess ligand with light petroleum and recrystallized from chloroform-light petroleum (0.45g, 80%).

(ν_{CO} 2039(vs), 1933(vs), 1920(vs) cm^{-1} (CH_2Cl_2 solution))

mer-$Mn(CO)_3\{P(OPh)_3\}_2Br$

$Mn(CO)_5Br$ (0.20g) and $P(OPh)_3$ (1.0g) were heated, with stirring, in petroleum ether (20ml) at 100 - 110°C for 10 min. The yellow crystals (93%), which separated on cooling,were filtered, washed free of excess ligand with diethylether and recrystallized from chloroform-light petroleum to give yellow needles (0.46g, 75%), which were dried in a vacuum.

(Found:	C, 55.8; H, 3.5 ,
Calc. for $C_{39}H_{30}BrMnO_9P_2$	C, 55.8; H, 3.6%)

(ν_{CO} 2076(w), 1990(vs), 1949(s) cm^{-1} (CH_2Cl_2 solution))

APPENDIX 2

PREPARATION OF $M(CO)_2(DPE)_2$

The dicarbonyl complexes $M(CO)_2(dpe)_2$ (M = Cr, Mo or W) have been prepared by a number of synthetic routes. The method of Chatt and Watson,[58] which involves the heating of (mesitylene)$M(CO)_3$ (M = Cr, Mo) and dpe (2 equivalents), gave the *cis*-isomer for M = Mo[110] and the *trans*-isomer for M = Cr.[58] The *cis*-tungsten complex was prepared by ultraviolet irradiation of a mixture of $W(CO)_4(dpe)$ and dpe in refluxing 1,2-dimethoxyethane.[58] The method of Zingales and Canziani,[109] which consists of refluxing $M(CO)_6$ and excess dpe in diglyme, produced the *cis*-isomer for all three metals. *Cis*-$Mo(CO)_2(dpe)_2$ has been prepared by ultraviolet irradiation of $Mo(CO)_6$ and dpe in benzene.[60(a)]

The molybdenum complex was originally prepared in high yield (∿ 80%) by the method of Chatt and Watson. When their method was used to prepare $W(CO)_2(dpe)_2$, the complex was only obtained in low yield (∿ 10%). The major product of the reaction was a highly soluble bright yellow compound, which was not characterized, but appears to be a tricarbonyl complex.[255] Both of these methods were superseded by the method of Zingales and Canziani, which produces the molybdenum complex in virtually quantitative yield and the tungsten complex in very high yield ($\gtrsim$ 85%). The compounds can be recrystallized from a variety of solvent mixtures including benzene-methanol and chloroform-methanol.

Zingales and Canziani recommended a reaction time of 50 hours for the preparation of *cis*-$Cr(CO)_2(dpe)_2$. When the reactants were refluxed for this period of time, the yield of dicarbonyl complex was low. Infrared spectra of the red solution showed that the reaction mixture consisted mainly of $Cr(CO)_4(dpe)$, which did not crystallize on cooling, but could be precipitated by the addition of petroleum ether. Purification was effected by extraction of the tetracarbonyl complex with ethylmethylketone, which left *cis*-

$Cr(CO)_2(dpe)_2$ (∿ 6%). Refluxing the same mixture for 140 hours (or roughly 6 days) resulted in extensive formation of the dicarbonyl complex. Infrared spectra of the deep red reaction mixture still showed the presence of some $Mo(CO)_4(dpe)$ and it is doubtful whether complete conversion to the dicarbonyl complex is possible. Some decomposition had also occurred as shown by the small amount of green-black precipitate. Pure *cis*-$Cr(CO)_2(dpe)_2$ was obtained as yellow-orange crystals on cooling the reaction mixture to room temperature.

The preparation of *trans*-$Cr(CO)_2(dpe)_2$ consists of heating (mesitylene) $Cr(CO)_3$ with dpe (2 moles) for 5 hours at 190 - 195°C, recrystallizing the reaction mixture from toluene-petroleum ether (80 - 100°) and washing the product with ethylmethylketone to remove $Cr(CO)_4(dpe)$, which leaves the *trans*-dicarbonyl as deep red crystals.[58] When this reaction was carried out, a mixture of deep red and golden yellow crystals remained. These were characterized as *trans*- and *cis*-$Cr(CO)_2(dpe)_2$ respectively by both electrochemistry[113] and infrared spectroscopy.[255]

The carbonyl stretching frequencies of all the complexes were in good agreement with the published values.[58,109]

APPENDIX 3

ISOMERISM OF $Cr(CO)_2(DPE)_2$

Chatt and Watson[58] reported that *trans*-$[Cr(CO)_2(dpe)_2]$ (deep red) is isomerized by adding an excess of methanol to a solution of the complex in benzene or chloroform. The solution becomes yellow immediately and the *cis*-isomer separates completely. Complete reconversion of the *cis*- into the *trans*-isomer is attained by heating its solution in benzene, toluene or chloroform whereupon the reverse colour change is observed.

Chromium hexacarbonyl reacts with excess dpe in refluxing diglyme to yield a deep red solution,[109] which clearly indicates that *trans*-$Cr(CO)_2(dpe)_2$ is formed. When samples were removed so that infrared spectra could be recorded, the colour quickly changed to yellow-orange and the spectra showed two absorptions attributable to the *cis*-isomer and the complete absence of the band due to the *trans*-isomer. The *cis*-isomer crystallized from the reaction mixture on cooling to room temperature.

Crossing and Snow[110] reported that *trans*-$Cr(CO)_2(dpe)_2$ is easily oxidized by atmospheric oxygen to the cation, *trans*-$[Cr(CO)_2(dpe)_2]^+$, which they prepared by adding a methanolic solution of sodium perchlorate to a dichloromethane solution of the neutral *trans*-complex. In fact, the neutral complex is so easily oxidized in dichloromethane that it is difficult to obtain a satisfactory infrared spectrum of it in this solvent. The *cis*-isomer also undergoes a facile oxidation by atmospheric oxygen to the *trans*-cation, but an acidic medium is required to bring about a rapid reaction. This is in accordance with the halfwave potentials.[113]

It was proposed to examine the isomerism of $Cr(CO)_2(dpe)_2$ in a variety of solvents and, if possible, to measure the kinetics of the process, which appears to be extremely rapid. A comparison of reactions carried out both in an atmosphere of nitrogen and exposed to the air showed that it was generally not necessary to strictly exclude oxygen from the system. Oxidation was found to be a significant problem in only one case, as described below. Nevertheless, the reactions were usually carried out in an atmosphere of nitrogen. The different species can be distinguished by their carbonyl stretching frequencies, which are summarized in Table 3.1.

TABLE 3.1

Carbonyl Stretching Frequencies of the $Cr(CO)_2(dpe)_2$ Complexes

Compound	ν_{CO} (cm^{-1})	Solvent
trans-$Cr(CO)_2(dpe)_2$	1789	toluene
	1786	benzene
	1790	CH_2Cl_2
cis-$Cr(CO)_2(dpe)_2$	1835, 1773	$CHCl_3$
trans-$[Cr(CO)_2(dpe)_2]ClO_4$	1848	CH_2Cl_2

Cis-$Cr(CO)_2(dpe)_2$ has slight solubility in toluene. On standing at room temperature, a suspension of the complex dissolves to form an orange solution,which changes to deep red after approximately five minutes; i.e. the *trans*-isomer has greater solubility in this solvent. The *cis*-complex dissolves very rapidly in hot toluene to give a deep red solution. The infrared spectra showed that these solutions contained a mixture of *cis*- (30%) and *trans*- (70%) isomers. The *cis*-complex is very soluble in benzene and the colour changes to deep red over a period of 4 - 5 minutes, as an equilibrium mixture of *cis*- (40%) and *trans*- (60%) isomers is formed. The *trans*-isomer crystallizes, on standing, as dark red cubes.

The *cis*-complex is very soluble in tetrahydrofuran at room temperature producing a red solution, which consists of a 1:1 mixture of the two isomers. The complex is only slightly soluble in acetone at room temperature yielding a yellow solution. When hot acetone was used, the colour changed to yellow-orange and the *cis*-isomer crystallized on cooling. The complex is slightly soluble in hot carbon tetrachloride forming an orange-red solution.

The *cis*-complex is very soluble in chloroform and slightly soluble in dichloromethane forming yellow solutions, which change to red after a few minutes. The majority of the complex (> 80%), however, is still in the *cis*-form as shown by the infrared spectra. When a small amount of methanol is added to these solutions, the colour immediately changes to bright yellow, which indicates that the complex is now solely in the *cis*-form. However, the colour quickly fades to pale yellow and the infrared spectra show that oxidation to *trans*-$[Cr(CO)_2(dpe)_2]^+$ has occurred. The pure *cis*-complex can be isolated from these solvents by the addition of an excess of methanol. The crystallization must be done rapidly with minimal exposure to the air. The molar conductance of *cis*-$Cr(CO)_2(dpe)_2$ in nitrobenzene (9.93×10^{-4} M) was 1.0 S cm^2 and the value did not change significantly on standing. Chatt and Watson[58] noticed that the conversion of *trans*-$Cr(CO)_2(dpe)_2$ to the *cis*-isomer was accompanied by a side reaction, since no *trans*-isomer remained and the yield of the *cis*-isomer was variable. In retrospect it is realized that this is due to the competing oxidation process.

The addition of methanol to an equilibrium solution of $Cr(CO)_2(dpe)_2$ in benzene resulted in complete and rapid conversion to the *cis*-isomer. Oxidation to the *trans*-cation subsequently occurred as shown by conductance measurements. The molar conductance of the complex in a benzene/methanol (1:1) mixture open to the air was 43.4 S cm^2 (8.79×10^{-4} M) compared with 0.92 S cm^2 for a non-electrolyte ($Mo(CO)_2(dpe)_2$) of identical molarity.

A search for a polar solvent, which would not facilitate oxidation, was therefore undertaken. The addition of nitromethane to an equilibrium solution of $Cr(CO)_2(dpe)_2$ in chloroform resulted in partial oxidation. When acetonitrile was added to an equilibrium solution of the complex in chloroform, complete conversion to the *cis*-isomer occurred without a trace of oxidation and *cis*-$Cr(CO)_2(dpe)_2$ crystallized on standing. The molar conductance of *cis*-$Cr(CO)_2(dpe)_2$ in a 1:1 mixture of benzene and acetonitrile (9.09×10^{-4} M) was approximately 1.6 S cm^2 and only increased slowly on standing (e.g. after 2 hours, $\Lambda_M = 6.4$ S cm^2). No attempt was made to exclude air from the solution. In comparison, the molar conductance of $[Mo(CO)_2(dpe)_2F]PF_6$ in the same solvent mixture (8.86×10^{-4} M) was 81.5 S cm^2. Acetonitrile thus appears to be the solvent of choice in the study of this isomerism.

The isomerism also proceeds in the complete absence of air. Dry degassed benzene was vacuum distilled onto *cis*-$Cr(CO)_2(dpe)_2$ using a vacuum line. The yellow solution turned deep red within a few minutes. When degassed acetonitrile was distilled into the benzene solution, the colour changed very quickly back to golden yellow.

The electronic spectrum of *cis*-$Cr(CO)_2(dpe)_2$ in benzene/acetonitrile (1:1) showed an absorption at 340 nm. The spectrum of the mixture of isomers in benzene was virtually identical apart from a weak shoulder at approximately 510 nm. Although the ^{31}P NMR spectrum of *cis*-$Cr(CO)_2(dpe)_2$ was obtained without difficulty, the spectrum of the *trans*-isomer could not be recorded (see Chapter 3). The investigation of the isomerism was discontinued because of the lack of a suitable physical technique.

In conclusion, it seems that the *trans*-isomer, which has no dipole moment, is stabilized in non-polar solvents and the *cis*-isomer, which does have a dipole moment, is preferentially formed in polar solvents. The *trans*-isomer is the stable form at high temperatures and this isomer is initially formed in the synthesis of the complex. The pure *trans*-complex can be obtained by crystallization from benzene and the pure *cis*-isomer by precipitation from chloroform by a polar solvent.

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APPENDIX 4

ATTEMPTED PREPARATION OF DITERTIARY ARSINE AND MIXED PHOSPHINE-ARSINE COMPLEXES

4.1 Introduction

It was decided to synthesize and study the reactions of the group VIa metal carbonyl derivatives containing ditertiary arsine ligands and to compare them with the phosphine analogues. The only systematic investigation of this type has been the preparation and oxidation of $M(CO)_2(diars)_2$, (M = Cr, Mo, W).[63(a),90,92,93]

Although the literature contains a profusion of references to phosphine complexes, the number of known arsine complexes is minimal. Sandhu and Mehta[60(a)] synthesized tetracarbonyl and dicarbonyl complexes containing bidentate tertiary arsine ligands (dpae, dpab) by ultraviolet irradiation of an equimilar mixture of the metal carbonyl and the ligand in benzene. The published method is not clear, but it appears that the ligands form only one type of complex with each particular metal. Chromium carbonyl yielded $Cr(CO)_2(dpae)_2$ and $Cr(CO)_2(dpab)_2$, molybdenum carbonyl yielded $Mo(CO)_4(dpae)$ and $Mo(CO)_2(dpab)_2$ whereas tungsten carbonyl gave only tetracarbonyl complexes. Zingales, Canziani and Ugo[62] prepared complexes of the formula $M(CO)_4(dpae)$, (M = Cr, Mo, W) by refluxing equimolar quantities of $M(CO)_6$ and dpae in *n*-butylether. Refluxing $Mo(CO)_4(dpae)$ with a stoichiometric quantity of dpae in diglyme gave $Mo(CO)_2(dpae)_2$, whereas $Cr(CO)_2(dpae)_2$ was prepared indirectly by heating $(C_7H_8)Cr(CO)_3$ with excess dpae.

The methods commonly used to prepare tetra-substituted carbonyl complexes consist of (a) refluxing the metal carbonyl and excess ligand in diglyme or high-boiling hydrocarbon (*n*-decane, decalin) (b) heating a mixture of an (arene)$M(CO)_3$ complex and the ligand or (c) heating the disubstituted complex, $M(CO)_4L$, with the ligand in a sealed evacuated tube or under reflux. Most of these methods were used in an attempt to synthesize $Mo(CO)_2(dpae)_2$.

4.1.1 Attempted Preparation of $Mo(CO)_2(dpae)_2$

We could not repeat Zingales and co-workers' preparation of $Mo(CO)_2(dpae)_2$. Refluxing $Mo(CO)_6$ and dpae (2.5 moles) in diglyme resulted in rapid formation of $Mo(CO)_4(dpae)$. The solution developed a deep brown colour on further refluxing and red crystals, which did not contain any carbonyl groups, precipitated. There was no evidence for the formation of the dicarbonyl complex. The tetracarbonyl complex was also rapidly formed in refluxing *n*-decane. Further reflux resulted in decomposition to give a blue-green solution, which deposited a blue-green precipitate. $Mo(CO)_4(dpae)$ crystallized when the solution was cooled.

(Mesitylene)$Mo(CO)_3$ and dpae (2 equivalents) were heated in the solid state at 185 - 195°C for 4.75 hours to give a dark coloured gum. The infrared spectrum (dichloromethane solution) showed that the major product of the reaction was $Mo(CO)_4(dpae)$. In addition, a pair of medium intensity bands were present at 1845 and 1775 cm^{-1}, which are consistent with the formation of a minor amount of $Mo(CO)_2(dpae)_2$. A large amount of decomposition had also occurred. Under the same conditions, the reaction of (mesitylene)$Mo(CO)_3$ with dpe produces $Mo(CO)_2(dpe)_2$ in high yield and with minimal decomposition.

$Mo(CO)_4(dpae)$ was prepared by refluxing $Mo(CO)_6$ with a stoichiometric quantity of the ligand in *n*-butyl ether for 45 minutes. On cooling, the tetracarbonyl complex crystallized as white needles (75%). The complex was also prepared by refluxing equimolar quantities of the reactants plus sodium borohydride in ethanol for 2 hours according to the method of Chatt, Leigh and Thankarajan.[53] The product crystallized as white needles (60%, m.p.

182 - 183°C) on cooling. The carbonyl stretching frequencies in dichloromethane are 2032(s), 1917(sh), 1909(vs) and 1880(vs) cm^{-1}.

$Mo(CO)_4(dpae)$ was heated with an equimolar quantity of dpae in the solid state at 180°C in an atmosphere of dry nitrogen. After 3.5 hours, carbonyl absorptions of medium-strong intensity were present in the infrared spectrum at 1840 and 1780 cm^{-1}, which suggests that some $Mo(CO)_2(dpae)_2$ has been formed. The absorptions due to the starting material were still very strong. Further heating resulted in extensive decomposition, as shown by the reaction mixture becoming very dark. The infrared spectra showed that a large amount of the tetracarbonyl complex was still unreacted and the bands due to the product had decreased in intensity. In comparison, $Mo(CO)_4(dpe)$ reacts completely with dpe in the solid state at 180°C in a period of 3 hours to give $Mo(CO)_2(dpe)_2$. The reaction mixture consisted of a bright yellow crystalline solid with no sign of any decomposition.

$Mo(CO)_4(dpae)$ shows a distinct reluctance to react further with dpae, which is consistent with the decreased donor ability of the arsine ligand relative to dpe. It was shown in a kinetic study that reaction of $Mo(CO)_4(dpae)$ with triphenylphosphite resulted in substitution of the arsine ligand to form $Mo(CO)_4[P(OPh)_3]_2$.[318]

4.2 Attempted Preparation of Mixed Phosphine-Arsine Complexes

$Mo(CO)_4(dpe)$ reacts with monodentate Lewis bases under vigorous conditions to form *fac*-$[Mo(CO)_3(dpe)L]$, (L = py, MeCN, Ph_3Sb) and *mer*-$[Mo(CO)_3(dpe)L]$, (L = Ph_3P, Ph_3As, $(EtO)_3P$). Treatment of $Mo(CO)_4(dpe)$ with excess triphenylarsine under drastic conditions gave *cis*-$[Mo(CO)_2(dpe)(AsPh_3)_2]$. Similar reactions were observed with triphenylphosphine and triethylphosphite.[83] It was thought that the reaction with a bidentate arsine ligand should also be successful. Accordingly, an investigation of the reaction of $Mo(CO)_4(dpe)$ with dpae was undertaken.

Refluxing $Mo(CO)_4(dpe)$ with excess dpae in *n*-decane or diglyme resulted only in decomposition. $Mo(CO)_4(dpe)$ and dpae (1.4 moles) were ground and mixed and heated at 180 - 185°C in an atmosphere of nitrogen for 2.5 - 3 hours. Infrared spectra of the yellow glass showed that most of the starting material had reacted to form a dicarbonyl complex. The reaction mixture was extracted with hot benzene and methanol was added to the solution to crystallize the yellow product (yield 15 - 38%). The carbonyl stretching frequencies in chloroform are 1850(vs) and 1780(vs) cm^{-1}. A considerable amount of decomposition had also occurred since a large quantity of black insoluble residue remained. Extraction with chloroform yielded a red compound, which did not contain any carbonyl groups. The reaction was not continued with, because of the poor yields.

It was not ascertained whether a mixed phosphine-arsine complex had indeed been formed or if a rearrangement had occurred to yield $Mo(CO)_2(dpe)_2$. The low yield and the CO stretching frequencies favour the latter possibility. This type of rearrangement was observed in the reactions of $Mo(CO)_4(dpe)$ with cyclohexylamine, pyridine and dimethylformamide; the only isolatable product being $Mo(CO)_2(dpe)_2$.[83]

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COMMENTS AND CORRECTIONS

Summary, line 5; p.2, line 5; p.11, line -13; p.12, line 15; p.39, line -7; p.45, line -13; p.68, line 17; p.82, lines 10,16,17; p.83, line -9; p.123, line -1; p.174, lines 7,8......
phosphorus (not phosphorous)

p.1, line 3	vaporised (not vapourised)
p.38, line 12	electron transfer (not charge transfer)
p.38, line 14	accessible (not accessable)
p.38, line -6	Evans' (not Evan's)
p.60, line 11	comma (not semi-colon)
p.64	The carbon analysis for $[Mo(CO)_2(dpe)_2F]BPh_4$ is hardly acceptable without some comment. There may be some CH_2Cl_2 of solvation, the complex may be impure, or there may be some particular difficulty about combustion analysis on this type of compound. Similar remarks apply to the cationic benzonitrile complexes on p.66.
p.68, line 13 and p.116 line 4	It seems remarkable that sodium chloride could not be completely removed from $[Mo(CO)_2(dpe)_2Cl]BPh_4$ by washing with water. What is the evidence that the impurity is sodium chloride? Was a sodium analysis carried out? If the evidence lies only in the low C, H and P analyses and in the high Cl analysis, then this is equally consistent with the presence of CH_2Cl_2 of solvation.
p.82, line 4	It is incorrect to say that symmetrically equivalent atoms are not spin-spin coupled. The nuclei must be coupled but if they are equivalent the coupling cannot be observed directly. Frequently the coupling can be observed indirectly by NMR examination of a second nucleus attached to the equivalent nuclei, *e.g.* $^2J_{PP}$ in complexes such as *trans*-$Mo(CO)_4(PH_3)_2$ or $[RhCl(PF_3)_2]_2$ can be extracted from the ^1H or ^{19}F spectra respectively.

p.83, line 3 *et seq.*

The sign convention used here is unfortunately the reverse of that generally adopted nowadays, *viz.* all chemical shifts downfield of the reference are labelled positive.

p.84, line 6 *et seq.*

I cannot follow the argument here. If it is assumed that the $[Mo(CO)_2(dpe)_2X]^+$ complexes in solution have the capped trigonal prismatic structure shown in Fig.22, the phosphorus atoms are already in equivalent environments, so how can their environments be averaged by a polytopal rearrangement? The quadrupole moments of bromine and iodine would certainly prevent observation of coupling of these nuclei with ^{31}P; to my knowledge, no such couplings have ever been reported for metal-phosphine complexes, and one could only hope to see them if the nuclei were in highly symmetrical (O_h or T_d) environments, which is certainly not the case here. Thus, the suggested polytopal rearrangement does not account for the observed ^{31}P NMR spectrum and it has nothing to do with the failure to observe coupling to the halogen nuclei; this paragraph should be amended accordingly.

As noted in the second paragraph, the cations $[M(CO)_2(dmpe)_2I]$ (dmpe = $Me_2PCH_2CH_2PMe_2$), prepared by Connor *et al.* (Ref.119), which presumably also have a capped trigonal prismatic structure, show temperature-dependent ^1H NMR spectra. In this case, although the phosphorus atoms are equivalent, the methyl groups on each phosphorus atom are not, so that a polytopal rearrangement involving migration of iodine over the faces of the trigonal prism could account for the observed averaging of the $P-CH_3$ resonances, though it is not the only explanation. Unfortunately, a variable temperature ^{31}P NMR study has not been carried out on Connor's compounds. It seems at least possible that the observed effects in both the dpe and dmpe complexes arise from a slowing down of the inversion of the two chelate dpe rings, which could 'freeze' into different conformations.

p.94, line 14	stirred (not stirring)
p.96	The explicit distinction between the polymeric and dimeric forms of $Mo(CO)_2(dpe)_{1.5}X_2$ could well have been made much earlier in the thesis. Colton's work is mentioned in the Introduction and the candidate's own work leading to compounds of apparently the same formula is then described, but the reader is left in the dark until some 30 pages later as to whether the two series of compounds are really identical or not.
pp.111-112	I think it should be made much clearer than it is at present that the work reported on these two pages is a summary of pertinent literature results and is not the candidate's own work.
p.116, line 2	"more so" should read "more effectively"
p.117, line 10	ampoules (not ampules)
p.117 *et seq.*	The carbon analyses for $[Mo(CO)_2(dpe)_2Cl]Cl$, $[Mo(CO)_2(dpe)_2Cl]BPh_4$ (see comments above) $[Mo(CO)_2(dpe)_2Br]BPh_4$, $[Mo(CO)_2(dpe)_2I]I_3$ and $[Mo(CO)_2(dpe)_2I]BPh_4$ are all low, though no comment is made in the thesis.
p.124, line -2	Why can $Re(CO)_5(ONO_2)$ be sublimed *because of* the inertness of rhenium? (my italics)
p.141, line 12	"...is a reasonably facile process and...." is tautologous and should be omitted
p.141, lines 15-16	"...and *is* insoluble in dichloromethane and chloroform".

p.143, line 5	It is not clear to me why complex formation between Ag^+ and the solvents acetonitrile and nitromethane should inhibit bromide ion abstraction from $Mn(CO)_5Br$, since $AgClO_4$ or $AgPF_6$ in acetonitrile will abstract bromide from *mer-trans*-$Mn(CO)_3L_2Br$ (p.153).
p.161, line -6	vigorously (not vigourously)
p.167, line 16	comma (not semi-colon)
p.174, line 16 *et seq.*	We frequently use $AgPF_6$ as a reagent and we have never observed it to fume on exposure to air though, like $AgBF_4$ and $AgClO_4$, it is certainly hygroscopic. We have also exposed mulls of $AgPF_6$ to air for periods of up to 30 min and have observed very little, if any, formation of $PO_2F_2^-$. The only reason I can offer for this discrepancy is that our samples are bought from Ozark-Mahoning, whereas the candidate's sample comes from Pfaltz and Bauer. I suggest that the fuming and rapid hydrolysis are due to some impurity, possibly residual PF_5.
p.178, line 13	desiccator (not dessicator)
p.181, line 5	Evans' (not Evan's)
p.186, line -7	The yield of (mesitylene)$Cr(CO)_3$ seems poor in comparison with the 84% yield reported by Nicholls and Whiting, *J.Chem.Soc.*, 551 (1959).
p.191, line -4 p.194, line 14 p.194, line -6	isomerization (not isomerism); the former refers to the process of interconversion of isomers, the latter to the general phenomenon of the existence of isomers.
p.199, line -2	comma (not semi-colon)