

***Low-Valent Fluoro-Complexes***  
***of the Transition Metals***

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**in the**

**Department of Chemistry**

**of the**

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**at the University of Leicester**

**by**

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## Dedication

This thesis is dedicated to my parents, Jean Frances Brewer and Dennis Alfred Brewer, without whom this would not have been possible.

Thanks

## Statement

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry at the University of Leicester between October 1989 and September 1992.

The work has not been submitted, and is not presently being submitted, for any other degree at this or any other University.

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## PUBLICATIONS

The following papers contain work carried out during the Ph.D. study.

"Osmium L<sub>III</sub> Edge Extended X-ray Absorption Fine-Structure Studies on Osmium(VIII) Oxide-Fluorides"

S.A.Brewer, A.K.Brisdon, J.H.Holloway and E.G.Hope, *J.Fluorine Chem.*, 1993,60,13

"Fluorination of Tetrairidium Dodecacarbonyl"

S.A.Brewer, J.H.Holloway, E.G.Hope and P.G.Watson, *J.Chem.Soc.,Chem.Comm.*, 1992,1577.

"Mixed Metal Pentafluorides"

S.A.Brewer, J.Fawcett, P.J.Holliman, J.H.Holloway and E.G.Hope, *J.Fluorine Chem.*, 1991,54,17.

"Synthesis of Novel Transition Metal Carbonyl Fluorides"

S.A.Brewer, J.H.Holloway, E.G.Hope and D.R.Russell, *J.Fluorine Chem.*, 1991,54,127.

"EXAFS Elucidation of the Solvation of Metal Hexafluorides by Anhydrous Hydrogen Fluoride"

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## Fluoro-Complexes of the Transition Metals

Stuart Anson Brewer

### Abstract

Transition metal carbonyls ( $\text{Ir}_4(\text{CO})_{12}$ ,  $\text{Os}_3(\text{CO})_{12}$  and  $\text{M}(\text{CO})_3(\text{PPh}_3)_2$   $\text{M}=\text{Ru}$  or  $\text{Os}$ ) have been reacted with  $\text{XeF}_2$ , and  $\text{Os}_3(\text{CO})_{12}$  with fluorine gas. The products have been fully characterised by NMR spectroscopy,  $^{19}\text{F}$ ,  $^{13}\text{C}$ ,  $^{13}\text{C}\{^{19}\text{F}\}$  and  $^{31}\text{P}$ , where appropriate.

For the reactions between  $\text{Ir}_4(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$ , the presence of hydrogen fluoride was observed to be critical to the subsequent fluorinations, the first stage of the reaction being protonation of the carbonyl clusters. The resulting transition metal carbonyl fluorides are observed to be reactive towards tertiary phosphines, resulting in the formation of carbonyl phosphine fluoro-complexes.

For the reactions between the five coordinate species  $\text{M}(\text{CO})_3(\text{PPh}_3)_2$  ( $\text{M}=\text{Ru}$  or  $\text{Os}$ ) and  $\text{XeF}_2$ , oxidative addition not only results in the formation of a  $\text{M}-\text{F}$  bond, but also produces the novel fluoroacyl ligand ( $-\text{COF}$ ). These reactions were followed by variable temperature NMR spectroscopy. This enabled the elucidation of the overall mechanism for the reaction, which ultimately afforded the respective  $\text{MF}_2(\text{CO})_2(\text{PPh}_3)_2$  complexes.

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*Tables of bond length and bond angles data for  $\text{cis-RuF}_2(\text{CO})_2(\text{PPh}_3)_2$*

### List of Abbreviations

AHF	Anhydrous hydrogen fluoride
bipy	2,2'-bipyridine
Cp	Cyclopentadienyl
Cy	Cyclohexyl
$\delta$	Chemical shift (NMR)
DMSO	Dimethyl sulphoxide
dppe	1,2-bis(diphenylphosphino)ethane
dppm	1,2-bis(diphenylphosphino)methane
E.S.R.	Electron spin resonance
Et	Ethyl
EXAFS	Extended X-ray Absorption Fine Structure
FEP	Tetrafluoroethene/perfluoropropene copolymer
Kel-F	Polytrifluoroethylene
HOMO	Highest Occupied Molecular Orbital
Hz	Hertz
IR	Infra-Red
LUMO	Lowest Unoccupied Molecular Orbital
Me	Methyl
NMR	Nuclear Magnetic Resonance
O.D.	Outside diameter
Ph	Phenyl
PPN	Bis(triphenylphosphine)iminium
R	Alkyl
tmeda	N,N,N',N'-tetramethylethylenediamine
THF	Tetrahydrofuran
$\epsilon$	IR stretch

## CHAPTER ONE

### Introduction To Low-Valent Fluoro-Complexes Of The Transition Metals

## 1.1

### A Brief Synopsis of Low-Valent Fluoro-Complexes

It is well established that the fluoride ligand is particularly useful in stabilising high oxidation-states of the transition metals. For example compounds such as  $\text{RhF}_6$ ,<sup>1</sup>  $\text{IrF}_6$ ,<sup>2</sup> and  $\text{PtF}_6$ ,<sup>3</sup> are readily prepared by fluorination of the appropriate metals. However, there are only a limited number of reports of species in which a fluoride ligand is coordinated directly to a metal in a low oxidation state. This has very recently been highlighted in a review article on transition-metal fluoro-compounds containing carbonyl, phosphine, arsine or stibine ligands<sup>4</sup>, which has drawn attention to the relative paucity of these species compared with those of the heavier halogens. Indeed, there are many instances where a particular type of halo-complex has been established for all the halogens except fluorine e.g. the substitution of a carbonyl ligand in  $[\text{Rh}_5(\text{CO})_{15}]^-$  by chloride, bromide and iodide but not fluoride<sup>5</sup>. However, the literature does contain a few such fluoro-species. Those containing both a carbonyl and a fluoride ligand are presented below as a synopsis of the different synthetic routes available.

An overriding reason for this lack of study is probably the commonly held belief that problems will arise if attempts are made to introduce fluorine or fluoride into organometallic systems. However, there are a number of examples of fluorine being successfully incorporated and the

successful methods used so far are listed below.

- i) Fluorination of a metal carbonyl.
- ii) Carbonylation of a binary metal fluoride.
- iii) Metathesis: fluoride ion is exchanged with an anionic ligand, X<sup>-</sup>.
- iv) Unexpected fluoride abstraction, by a metal complex, e.g. from BF<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup>.

Considering each of these synthetic routes separately:-

- i) Commonly, HX or X<sub>2</sub> itself, where X=Cl, Br and I, are the reagents used in the halogenation of transition metal systems. By analogy, therefore, if HF or F<sub>2</sub> are considered as reagents for the introduction of fluorine or fluoride into transition metal species, the need for specialised equipment and expertise are probably the reasons for the lack of study of fluorine-containing species. The suitability of F<sub>2</sub> and HF as reagents has also been questioned from the view-point of the difficulties in controlling the reaction of these highly aggressive reagents<sup>4</sup>. However, it is noteworthy that in one of the most recent syntheses of a fluoro-complex<sup>5</sup>, the problems associated with handling hydrogen fluoride were overcome by utilising Olah's reagent (a solution of pyridine and HF). This provided a convenient means to prepare Mo<sub>2</sub>F<sub>4</sub>(PR<sub>3</sub>)<sub>4</sub>.
- ii) An alternative preparation of transition metal fluoro-complexes, which does not require the use of elemental fluorine is *via* carbonylation of a binary metal fluoride. The analogous method has been used extensively for chloro-

bromo- and iodo carbonyl complexes. For example,  $RuX_3$ ;  $X = Cl, Br$  or  $I$  are commonly used precursors for the syntheses of numerous organometallic species<sup>7</sup>. However, the corresponding carbonylation of binary metal fluorides are very limited (see literature survey).

iii) Other reagents which have been utilised in metal fluorine bond formation are those which provide a source of  $F^-$  in metathesis reactions with chloride, bromide and iodide complexes or, more successfully, replacement of weakly-coordinating anions or solvent. The order of stability for such halo-complexes is predicted by Pearson's hard/soft acid/base rules increases in the order  $F < Cl < Br < I^8$ . Thus, the fluoride ligand is considered as a hard base, chloride and bromide are borderline bases while iodide is a soft base. Hence, as low-valent organometallic systems are generally considered as soft acids, complexes containing a fluoride ligand are predicted to be the least stable. This trend is observed in the syntheses of rhodium and iridium Vaska's derivatives where the fluoride of  $M(CO)F(PPh_3)_2$  is very labile in methanol and easily replaced by  $X^-$  ( $X =$  a one electron donor)<sup>9</sup>. However, the opposite trend has been detected for various systems in aprotic solvent systems<sup>10</sup>. (see 1.11).

A practical problem associated with introducing fluorine via metathesis reactions is solubility. AgF is an obvious choice for F-/X- exchange, since the AgX by-product can be precipitated from solution, forcing the reaction to completion. However, AgF is not only light sensitive, but is also fairly insoluble in non-polar solvents such as CH<sub>2</sub>Cl<sub>2</sub>. This difficulty has been conveniently overcome by the *in situ* formation of AgF by the reaction of Ag<sub>2</sub>CO<sub>3</sub> with NH<sub>4</sub>F. Good examples are MF(CO)(PPh<sub>3</sub>)<sub>2</sub> (M= Rh and Ir) which are readily prepared in high yields from the chloro-analogues<sup>67</sup>.

Despite the success in forming fluoro- Vaska's derivatives, it is evident that there have been few concerted efforts to synthesis M-F bonds in organometallic complexes by either routes (i), (ii) or (iii). This is exemplified by the predominance of these complexes which have been isolated from reactions involving unexpected fluoride abstraction from the usually inert, weakly coordinating anions BF<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup>. This has recently been demonstrated in the synthesis of  $[\{W(CO)_2(PMe_2Ph)_2\}_2(\mu-F)_3]BF_4$ <sup>11</sup> via the reaction between  $[WH_6(PMe_2Ph)_3]$  and HBF<sub>4</sub> in THF saturated with carbon monoxide.

## 1.2

### Complexes of Chromium, Molybdenum and Tungsten

Molybdenum hexacarbonyl reportedly reacts with  $\text{MoF}_6$  in HF, with the elimination of carbon monoxide, affording  $[\text{Mo}(\text{CO})_2\text{F}_4]_2$  and  $\text{MoF}_5$ <sup>12</sup>. The dimeric carbonyl fluoride is suggested to contain bridging fluorides and possibly a Mo-Mo bond; the possibility of bridging carbonyl ligands being discounted on the basis of an IR analysis. Claims that  $\text{Mo}(\text{CO})_4\text{F}_2$  has been synthesised using HF as a metathesis reagent on  $\text{Mo}(\text{CO})_4\text{Cl}_2$  have been made<sup>13</sup>, and fluorination of this difluoride with various ratios of  $\text{XeF}_2$  is reported to give rise to  $\text{Mo}(\text{CO})_3\text{F}_3$ ,  $\text{Mo}(\text{CO})_3\text{F}_4$  and, ultimately,  $\text{MoF}_6$ <sup>13</sup>. Similar reactions were attempted with tungsten, affording  $\text{W}(\text{CO})_4\text{F}_2$  from  $\text{W}(\text{CO})_4\text{Cl}_2$  and HF<sup>13</sup>. However, the subsequent oxidation of this W(II) complex by  $\text{XeF}_2$  did not form higher oxidation state carbonyl fluorides. Instead  $\text{W}(\text{CO})_6$  and  $\text{WF}_6$  were the only products observed. The production of  $\text{W}(\text{CO})_6$  was presumed to occur via disproportionation. The apparent difference in behaviour between the two systems is consistent with the greater stability of tungsten hexafluoride compared with that of  $\text{MoF}_6$ <sup>14</sup>. However, the overall reaction schemes for both of these metals are, at present, incompletely characterised, and the assignments are best regarded as tentative.

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$\text{Mo}(\text{CO})_6$  has been shown to react thermally with KF in DMSO affording  $[\text{Mo}(\text{CO})_5\text{F}]^-$ <sup>15</sup>. The  $^{95}\text{Mo}$  NMR spectrum for this species indicated a clean quantitative reaction, but, surprisingly,  $^{19}\text{F}$  NMR data was not reported. This fluoride complex was also obtained by fluoride abstraction from  $\text{BF}_4^-$  in the reaction of  $\text{NaBF}_4$  with  $\text{Mo}(\text{CO})_6$ <sup>15</sup>. For  $[\text{M}(\text{CO})_5\text{F}]^-$  (M=Cr or W) the use of crown ethers has been shown to facilitate the preparation of these complex ions in non-polar solvents such as  $\text{CH}_2\text{Cl}_2$ . Hence the reaction of  $\text{F}^-$  ( $\text{KF}\cdot 2\text{H}_2\text{O}$ ) with  $[\text{M}(\text{CO})_5]^-$ , photochemically produced from  $\text{M}(\text{CO})_6$ , affords  $[\text{M}(\text{CO})_5\text{F}]^-$  M=Cr and W<sup>16</sup>. The chromium complex is observed in lower yields and is less stable than the tungsten species. An attempt to react  $[\text{NEt}_4]\text{F}$  with  $\text{W}(\text{CO})_6$  in  $\text{CH}_2\text{Cl}_2$  produced only low yields of the tungsten complex. This was ascribed by Ruff to a solubility problem<sup>17</sup>, whereas Liotta found that the use of crown ethers with KF enhances the reactivity of the fluoride ion<sup>18</sup>. These complexes have also been obtained from the reaction of  $(\text{PFN})_2\text{M}_2(\text{CO})_{10}$  with  $\text{AgF}$  in THF<sup>17</sup>, however the yield in the photochemical reaction is much higher than in the redox reactions. Attempts to obtain  $^{19}\text{F}$  NMR spectra of the anions  $[\text{Cr}(\text{CO})_5\text{F}]^-$  and  $[\text{W}(\text{CO})_5\text{F}]^-$  were unsuccessful due to the instability of the products in concentrated solutions<sup>17</sup>.

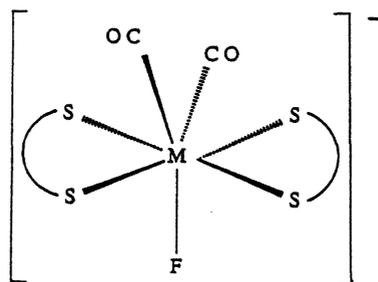
The seven-coordinate  $[\text{Mo}(\text{CO})_2(\text{dppe})_2\text{F}]\text{PF}_6$  has been obtained from the reaction of  $[\text{Mo}(\text{CO})_2(\text{dppe})_2]$  with nitrosonium hexafluorophosphate ( $\text{NOPF}_6$ ) in  $\text{CH}_2\text{Cl}_2$ <sup>19</sup>. Originally, this complex was formulated as

[Mo(CO)<sub>2</sub>(dppe)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub><sup>20</sup>, but, a later NMR investigation revealed the presence of a terminal fluoride ligand. The <sup>31</sup>P resonance (648) exhibits doublet coupling to a fluorine nucleus and the <sup>19</sup>F NMR resonance (δ-266) shows splitting consistent with coupling to four equivalent phosphines. From this evidence the stereochemistry was postulated as that of a capped trigonal prism with the four phosphorus atoms on a square face, a prediction which was later confirmed by a structural determination<sup>21</sup> (for an example of the structure see fig 1.1). Variable temperature <sup>31</sup>P NMR studies revealed that, unlike the bromo and iodo analogues, the fluoro-complex was rigid on the NMR timescale.

A solvent dependency for this reaction was also established. In nitromethane two fluoro-complexes were observed, the fluorine bridged dimer [ $\{\text{Mo}(\text{CO})_2(\text{dppe})_2\}_2(\mu\text{-F})\text{PF}_6\text{]}_3$  (80%) and  $[\text{Mo}(\text{CO})_2(\text{dppe})_2\text{F}]\text{PF}_6$  (20%). In nitroethane the product ratio is reversed, whereas in nitrobenzene only  $[\text{Mo}(\text{CO})_2(\text{dppe})_2\text{F}]\text{PF}_6$  is produced. NMR data for the dimer revealed a sharp singlet in both the <sup>19</sup>F and the <sup>31</sup>P spectra at δ-139 and 656 respectively. The lack of any observable coupling is presumably the result of intermolecular fluxionality. Conversion of the dimer to  $[\text{Mo}(\text{CO})_2(\text{dppe})_2\text{F}]^+$  in a dichloromethane solution is also conveniently achieved by the addition of NEt<sub>4</sub>F. This complex has also been synthesised electrochemically<sup>22</sup> from Mo(CO)<sub>2</sub>(dppe)<sub>2</sub> in the presence of F<sup>-</sup>.

Complexes structurally related to  $[\text{Mo}(\text{CO})_2(\text{dppe})_2\text{F}]^+$  have also been observed for a series of molybdenum and tungsten dithiocarbamate halide complexes  $[\text{M}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2\text{F}]^-$  ( $\text{M} = \text{Mo}$ ,  $\text{R}_2 = \text{Et}_2$  or  $\text{C}_4\text{H}_4$   $\text{M} = \text{W}$   $\text{R}_2 = \text{Me}_2$ ,  $\text{Et}_2$  or  $\text{C}_4\text{H}_4$ <sup>23, 24</sup>).

Fig 1.1 View of  $[\text{M}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2\text{F}]^-$



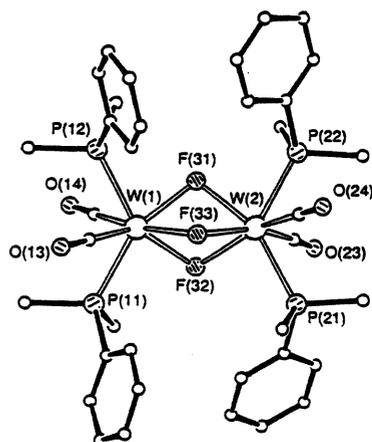
$\text{M} = \text{Mo}, \text{W}$

These species are readily obtained in high yield from the reaction of  $\text{NEt}_4\text{F}$  hydrate with  $\text{M}(\text{CO})_2(\text{S}_2\text{CNR}_2)_2$ . For the dialkyldithiocarbamate halide series<sup>23</sup>, the fluoride  $[\text{MoF}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2][\text{NEt}_4]$  is the only species which can be isolated as a solid, but it readily eliminates  $[\text{NEt}_4]\text{F}$  in solution to regenerate  $\text{Mo}(\text{CO})_2(\text{S}_2\text{CNEt}_2)_2$ . In contrast, the pyrrole-N-carbodithioate complexes<sup>24</sup> react with halides to afford stable crystalline solids for F, Cl and Br. The reactivity differences observed are postulated to result from the decrease in electron delocalisation from nitrogen into the  $\text{CS}_2$  fragment for  $\text{R}_2 = \text{C}_4\text{H}_4$  relative to the dialkyl ligand, hence the former have electron-poor metal centres.

[NEt<sub>4</sub>]F·2H<sub>2</sub>O has also been used to prepare the fluoro-analogue of the series of halocarbonyl complexes WX(CO)<sub>2</sub>(dppe)(CCH<sub>2</sub>Ph), from its reaction with [W(CO)<sub>2</sub>(dppe)(CCH<sub>2</sub>Ph)]BF<sub>4</sub><sup>25</sup>. NMR spectroscopy indicates that this is an octahedral complex, where the fluoride is trans- to the carbonyl ligand (<sup>31</sup>P 6373.7, doublet, <sup>2</sup>JPF 46Hz, <sup>1</sup>JPW 234Hz; <sup>13</sup>CO 6213.6, doublet of triplets, <sup>2</sup>JCP<sub>trans</sub> 51Hz, <sup>2</sup>JCP<sub>cis</sub>=<sup>2</sup>JCF<sub>cis</sub> 8Hz).

Treatment of [WH<sub>6</sub>(PMe<sub>2</sub>Ph)<sub>3</sub>], with HBF<sub>4</sub>·OEt<sub>2</sub> and carbon monoxide, gave an immediate clear yellow solution from which yellow crystals were isolated. An X-ray single crystal structure determination showed the material to be [{W(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>]<sub>2</sub>(μ-F)<sub>3</sub>]BF<sub>4</sub>. The structure was also supported by NMR spectroscopy where the <sup>31</sup>P and <sup>19</sup>F spectra showed couplings consistent with three equivalent fluorine atoms and four equivalent phosphine ligands<sup>11</sup>.

Fig 1.2 View of [{W(CO)<sub>2</sub>(PMePh)<sub>2</sub>]<sub>2</sub>(μ-F)<sub>3</sub>]<sup>+</sup>



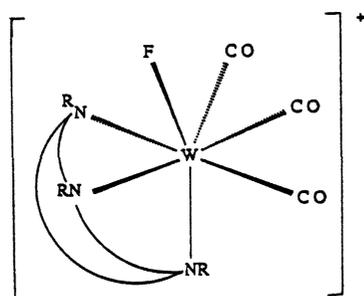
The low yield of this material (32%) prompted an investigation, by  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopy, of the reaction mixture from which it was isolated. This confirmed the presence of the above complex but also revealed two other structurally related fluoro-species,  $[\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-F})_2(\mu\text{-H})]^+$  and  $[\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-F})_2]^+$ , the latter being derived from  $[\{\text{W}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\}_2(\mu\text{-F})_3]^+$  where a bridging fluoride ligand is replaced by solvent (THF). The characteristic NMR spectral patterns were also used to identify the products resulting from the reaction of  $\text{MoH}_4(\text{PR}_3)_4$  ( $\text{R}_3 = \text{Et}_3$  or  $\text{MePh}_2$ ) and  $\text{HBF}_4 \cdot \text{OEt}_2$  in THF under an atmosphere of carbon monoxide. This revealed the analogous molybdenum derivatives,  $[\text{Mo}(\text{CO})_2(\text{PR}_3)_2]_2(\mu\text{-F})_3]^+$ , which could not be isolated because of contamination by the phosphonium salts,  $[\text{HPR}_3]\text{BF}_4$ . The  $^{19}\text{F}$  chemical shifts for all of these species fall within the range 6-191.7 to -201.9, as expected for a low-valent metal bound fluoride.

$\text{WF}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2$  has been prepared in high yield from the reaction of a methanol solution of  $[\text{Bu}_4\text{N}]\text{F}$  mixed with an acetone solution of  $\text{W}(\text{OCIO}_3)(\text{CO})_2(\text{NO})(\text{PPh}_3)_2$ <sup>26</sup>. It has also been shown to be produced in small amounts if samples of  $[\text{W}(\text{CO})_3(\text{NO})(\text{PPh}_3)_2]\text{PF}_6$  are heated, or allowed to stand at room temperature for extended periods of time. The  $^{31}\text{P}$  NMR spectrum comprised of a resonance at 613.9, exhibiting a doublet coupling ( $^2\text{JPF}$  42Hz). The phosphite derivative,  $\text{WF}(\text{CO})_2(\text{NO})(\text{P}(\text{O}^i\text{Pr})_3)_2$ , is also obtained from the analogous

reaction of  $[W(NO)(CO)_3(P(OiPr)_3)_2]PF_6$  with  $KF^{27}$ .

Halogenation reactions of  $LW(CO)_3$  (L= the tridentate ligands  $N,N',N''$ -trimethyl-1,4,7-triazocyclononane or  $N,N',N''$ -1,4,7-triazocyclononane) afford a variety of monomeric, air- and moisture-stable, tungsten (II) complexes<sup>28</sup>. The cationic seven-coordinate complexes,  $[LW(CO)_3X]^+$ , (X= F, Cl, Br and I), were obtained from the reaction of HX solutions of  $LW(CO)_3$  with oxygen. For the fluoride, aqueous HF is used in an open vessel, and the resulting complex is precipitated by addition of  $NaPF_6$ .

Fig 1.3 View of the Cationic Seven Coordinated Complex  $[LW(CO)_3X]^+$  L=  $N,N',N''$ -1,4,7-Trimethyltriazocyclononane and  $N,N',N''$ -1,4,7-Triazocyclononane



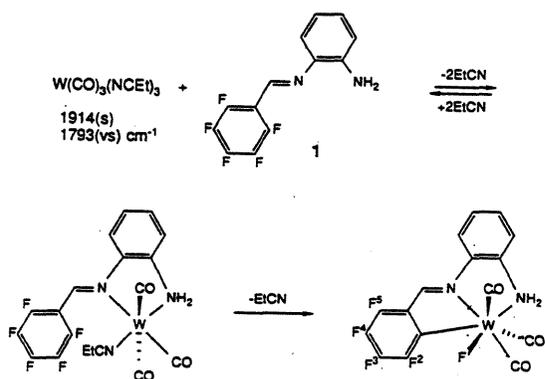
R= H, Me

The preparation of  $[WF(CO)_2(bipy)(L-L)]BF_4$  (L-L= dppe or dppm) results from the reaction of  $[W(CO)_2(bipy)_2][BF_4]_2$  with the appropriate L-L ligand<sup>29</sup>. The structures of these complexes were established by NMR spectroscopy. The  $^{31}P$  NMR spectrum of the dppe complex consists of a single resonance

at 650.4 with  $^{183}\text{W}$  satellites, exhibiting coupling to fluorine ( $^2\text{J}(\text{PF})=33.2\text{Hz}$ ). Corresponding results were obtained for the dpdm complex ( $^{31}\text{P}$   $\delta$ -8.84,  $^2\text{J}(\text{PF})=33.2$ ). The  $^{19}\text{F}$  spectrum of the dppe complex shows a singlet,  $\delta$ -151.7, assigned to the tetrafluoroborate anion, and a triplet signal centered at  $\delta$ -169.3 ( $^1\text{J}(\text{WF})=61.6$ ), assigned to the tungsten-bonded fluorine. It is not clear whether phosphorus coupling is observed.

Related seven-coordinate tungsten (II) tricarbonyl fluoro-complexes also result from the facile oxidative addition of an aromatic C-F bond to tungsten(0) complexes<sup>30</sup>. Hence, the treatment of a 1:1 Schiff base such as  $[(\text{C}_6\text{F}_5)\text{CHNC}_6\text{H}_4\text{NH}_2]$  with  $\text{W}(\text{CO})_3(\text{EtCN})_3$  in THF yields the fluoro-complex depicted in the reaction below.

Fig 1.4



**Table 1.1**

<b>Organometallic Fluoro-Complexes of Chromium Molybdenum and Tungsten</b>			
<b>Product</b>	<b>Reagents</b>	<b>Refs</b>	
[Mo(CO) <sub>2</sub> F <sub>4</sub> ]	[Mo(CO) <sub>6</sub> ] + [MoF <sub>6</sub> ]	12	
[M(CO) <sub>4</sub> F <sub>2</sub> ] (M = Mo, W)	[Mo(CO) <sub>4</sub> Cl <sub>2</sub> ] + HF	13	
[Mo(CO) <sub>3</sub> F <sub>3</sub> ]	[Mo(CO) <sub>4</sub> F <sub>2</sub> ] + XeF <sub>2</sub>	13	
[Mo(CO) <sub>3</sub> F <sub>4</sub> ]	[Mo(CO) <sub>4</sub> F <sub>2</sub> ] + XeF <sub>2</sub>	13	
[Mo(CO) <sub>5</sub> F] <sup>-</sup>	[Mo(CO) <sub>6</sub> ] + KF	15	
[Mo(CO) <sub>5</sub> F] <sup>-</sup>	[Mo(CO) <sub>6</sub> ] + NaBF <sub>4</sub>	15	
[M(CO) <sub>5</sub> F] <sup>-</sup> (M = Cr, W)	[M(CO) <sub>6</sub> ] + KF + hv	16	
[M(CO) <sub>5</sub> F] <sup>-</sup> (M = Cr, W)	[M <sub>2</sub> (CO) <sub>10</sub> ] <sup>2-</sup> + AgF	17	
[Mo(CO) <sub>2</sub> (dppe) <sub>2</sub> F][PF <sub>6</sub> ]	[NO][PF <sub>6</sub> ] + [Mo(CO) <sub>2</sub> (dppe) <sub>2</sub> ]	19	
[[Mo(CO) <sub>2</sub> (dppe) <sub>2</sub> ] <sub>2</sub> (μ-F)][PF <sub>6</sub> ] <sub>3</sub>	[NO][PF <sub>6</sub> ] + [Mo(CO) <sub>2</sub> (dppe) <sub>2</sub> ]	19	
[M(CO) <sub>2</sub> (S <sub>2</sub> CNR <sub>2</sub> ) <sub>2</sub> F]	[M(CO) <sub>2</sub> (S <sub>2</sub> CNR <sub>2</sub> ) <sub>2</sub> ] + [NEt <sub>4</sub> ]F	23 24	
(M = Mo, R <sub>2</sub> = Et <sub>2</sub> , C <sub>4</sub> H <sub>4</sub> ; M = W, R <sub>2</sub> = Me <sub>2</sub> , Et <sub>2</sub> , C <sub>4</sub> H <sub>4</sub> )			
[WF(CO) <sub>2</sub> (dppe)(CCH <sub>2</sub> Ph)]	[NEt <sub>4</sub> ]F + [W(CO) <sub>2</sub> (dppe)(CCH <sub>2</sub> Ph)] <sup>+</sup>	25	
{W(CO) <sub>2</sub> (PMe <sub>2</sub> Ph) <sub>2</sub> ] <sub>2</sub> (μ-F) <sub>2</sub> (μ-X)] <sup>+</sup>	[WH <sub>6</sub> (PMe <sub>2</sub> Ph) <sub>3</sub> ] + HBF <sub>4</sub> /CO	11	
(X = H, F, THF)			
[[Mo(CO) <sub>2</sub> (PR <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (μ-F) <sub>3</sub> ] <sup>+</sup>	[MoH <sub>4</sub> (PR <sub>3</sub> ) <sub>4</sub> ] + HBF <sub>4</sub> /CO	11	
(PR <sub>3</sub> = PEt <sub>3</sub> , PMePh <sub>2</sub> )			
[WF(CO) <sub>2</sub> (NO)(PPh <sub>3</sub> ) <sub>2</sub> ]	[Bu <sub>4</sub> N]F + [W(NO)(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> [ClO <sub>4</sub> ] <sup>-</sup>	26	
[WF(CO) <sub>2</sub> (NO)(PO <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub> ]	[W(NO)(CO) <sub>3</sub> (PO <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> [PF <sub>6</sub> ] <sup>-</sup> + KF	26	
[LW(CO) <sub>3</sub> F] <sup>+</sup>	[LW(CO) <sub>3</sub> ] + HF <sub>aq</sub> /air	28	
(L = N, N', N''-Trimethyl-1, 4, 7-triazocyclononane)			
[WF(CO) <sub>2</sub> (bipy)(L-L)][BF <sub>4</sub> ]	[W(CO) <sub>2</sub> (bipy) <sub>2</sub> ][BF <sub>4</sub> ] <sub>2</sub> + [L-L]	29	
[L-L] = dppe, dppm			
[WF(CO) <sub>3</sub> - (η <sup>3</sup> -NR <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -2-N=CHC <sub>6</sub> F <sub>4</sub> )]	[W(CO) <sub>3</sub> (EtCN) <sub>3</sub> ] + 1,2-NR <sub>2</sub> C <sub>6</sub> H <sub>4</sub> N=CHC <sub>6</sub> F <sub>5</sub>	30	
(R = H, Me)			
[WF(CO) <sub>3</sub> - (η <sup>3</sup> -NMe <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N=CHC <sub>6</sub> F <sub>4</sub> )]	[W(CO) <sub>3</sub> (EtCN) <sub>3</sub> ] + 1,2-NMe <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> N=CHC <sub>6</sub> F <sub>5</sub>	31	

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The structure was confirmed by a single-crystal X-ray structural determination, and can be approximated to a capped octahedron with a W-F bond of 2.032Å. This W-F bond is stable in solution in the presence of D<sub>2</sub>O, as observed by a <sup>19</sup>F NMR resonance at δ-226. Similar reactions are also observed for other Schiff base ligands<sup>31</sup>.

### 1.3

#### Complexes of Manganese

The reaction between  $\text{Mn}(\text{CO})_5\text{Br}$  and  $\text{AgF}^{32}$  demonstrates the difficulty in obtaining unambiguous assignment of products and their dependence on reaction conditions. Originally the reaction was formulated, on the basis of IR spectroscopy, mass spectrometry and elemental analysis, as yielding the dimer,  $[\text{Mn}(\text{CO})_4\text{F}]_2$ , or, with excess  $\text{AgF}$ ,  $\text{Mn}(\text{CO})_3\text{F}_3^{33}$ . However, a reinvestigation of this system by Horn *et al* <sup>34a</sup>, in which X-ray crystallography revealed the presence of the cluster  $[\text{Mn}_4(\text{CO})_{12}(\text{F}/\text{OH})_4]$  led to a reassignment of the products. In the overall reaction four structurally related clusters were observed,  $[\text{Mn}_4(\text{CO})_{12}\text{F}_x(\text{OH})_{4-x}]$  ( $x=0-4$ ). The hydroxyl contamination occurred from moisture within the system and, when water was added, the reaction rate was accelerated. The absence of moisture (which is difficult to eliminate completely since  $\text{AgF}$  is hydrated) significantly reduced the reaction time but the clusters  $[\text{Mn}_4(\text{CO})_{12}\text{F}_x(\text{OH})_{4-x}]$  for  $x=3$  and  $4$  were obtained in higher yields. This reaction, which might have been anticipated to produce  $\text{Mn}(\text{CO})_5\text{F}$ , demonstrates the distinctive difference in the properties of fluoro complexes to those of the heavier halogens, where  $\text{Mn}(\text{CO})_5\text{X}$  for Cl, Br and I, can be isolated as stable solids<sup>34b</sup>. Alternatively this difference may be due to the synthetic route employed. However, for  $\text{Re}(\text{CO})_5\text{F}$  and the related  $\text{ReF}(\text{CO})_3(\text{PPh}_3)_2$ , carbonyl lability is enhanced, within the halo series, for

the fluoride. Hence for  $\text{Mn}(\text{CO})_5\text{X}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$  and  $\text{I}$ ) the fluoro-complex can be expected to be the most unstable.

Another bridging fluoro-complex of manganese has been observed in the reaction of  $\text{BF}_3$  with  $[\text{Mn}_3(\text{CO})_9(\mu_3\text{-OEt})_2(\mu_2\text{-OEt})]^{36}$ , where fluoride abstraction from  $\text{BF}_3$  results in the formation of the structurally analogous fluoride-bridged trinuclear cluster,  $[\text{Mn}_3(\text{CO})_9(\mu_3\text{-OEt})_2(\mu_2\text{-F})]$ .  $^{19}\text{F}$  NMR analysis for this complex revealed one broad resonance at  $\delta$ -476. The very low frequency of this resonance, compared to that of organo-fluorine compounds, was attributed to the shielding of the fluorine nucleus by the two manganese atoms. This is comparable to that observed in  $^1\text{H}$  NMR spectroscopy for metal-bridging hydrides<sup>37</sup>. This investigation was extended to the other  $\text{BX}_3$  Lewis acids ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ ) which also afforded structurally related halo-complexes. However, for the reaction of  $[\text{Mn}_3(\text{CO})_9(\mu_3\text{-OEt})_2(\mu_2\text{-OEt}_3)]$  with  $\text{HX}$ , halo-complexes were only formed for  $\text{X} = \text{Cl}$  and  $\text{Br}$ . The lack of reaction with  $\text{HF}$  was attributed to the very strong  $\text{HF}$  bond in the acid. Fluoride ion abstraction from  $\text{BF}_3$  (and  $\text{BF}_4^-$ ) was also reported as a side-reaction in the synthesis of the monosubstituted manganese carbonyl cationic species,  $[\text{Mn}(\text{CO})_5(\text{PPh}_3)]\text{BF}_4$ , forming  $\text{MnF}(\text{CO})_3(\text{PPh}_3)_2$  in a low yield (15%)<sup>38</sup>. This species was formulated on the basis of elemental analysis and IR spectroscopy.

**Table 1.2**

<b>Organometallic Fluoro-Complexes of Manganese</b>			
<b>Product</b>	<b>Reagents</b>		<b>Refs</b>
$[\text{Mn}_4(\text{CO})_{12}\text{F}_x(\text{OH})_{4-x}]$ $x=0-4$	$[\text{Mn}(\text{CO})_5\text{Br}] + \text{AgF}$		34
$[\text{Mn}_2(\text{CO})_9\text{F}]^-$	$[\text{Mn}_2(\text{CO})_{10}] + [\text{KF dibenzo-18-crown-6}]$		35
$[\text{Mn}_3(\text{CO})_9(\mu^3\text{-OEt})_2(\mu^2\text{-F})]$	$[\text{Mn}_3(\text{CO})_9(\mu^3\text{-OEt})_3] + \text{BF}_3$		36
$[\text{Mn}(\text{CO})_3\text{F}(\text{PPh}_3)_2]$	$[\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2] + \text{i)Na/Hg, ii)HBF}_4$		38

**Table 1.3**

<b>Organometallic Fluoro-Complexes of Rhenium</b>			
<b>Product</b>	<b>Reagents</b>		<b>Refs</b>
$[\text{Re}(\text{CO})_6][\text{Re}_2\text{F}_{11}]$	$4[\text{ReF}_6] + [\text{Re}_2(\text{CO})_{10}]$		41, 42
$[\text{Re}(\text{CO})_5\text{FReF}_5]$	$2[\text{ReF}_6] + [\text{Re}_2(\text{CO})_{10}]$		41, 42
$[\text{Re}(\text{CO})_5\text{FReF}_5]$	$\text{XeF}_2 + [\text{Re}_2(\text{CO})_{10}]$		45
$[\text{Re}(\text{CO})_6][\text{ReF}_6]$	$[\text{Re}(\text{CO})_5\text{FReF}_5] + \text{CO}$		43
$[\text{Re}(\text{CO})_5\text{F}]$	$[\text{Re}(\text{CO})_5\text{Cl}] + \text{HF}$		45
$[\text{Re}(\text{CO})_5\text{F}]$	$[\text{Re}_2(\mu\text{-F})(\text{CO})_{10}] + \text{MeCN}$		48
$[\text{Re}(\text{CO})_3\text{F}]_4 \cdot 4\text{H}_2\text{O}$	$[\text{Re}(\text{CO})_5\text{Br}] + \text{AgF}$		47
$[\text{Re}_2(\mu\text{-F})(\text{CO})_{10}]$	$[\text{Re}(\text{CO})_5(\text{CH}_3)] + \text{HPF}_6, \text{ or } [\text{CPh}_3][\text{PF}_6]$		48
$[\text{ReF}(\text{CO})_3\text{L}_2]$	$[\text{ReBr}(\text{CO})_3\text{L}_2] + \text{AgF}_2\text{H}$		49
L=SbPh <sub>3</sub> or L <sub>2</sub> = tmeda, bipy or dppe.			
L=PPh <sub>3</sub>	$[\text{Re}(\text{CO})_3\text{Cl}(\text{PPh}_3)_2] + \text{AgSO}_3\text{CF}_3/[\text{PPN}]\text{F}$		50
$[\text{ReF}(\text{CO})(\text{NO})(\text{PPh}_3)_3]^+$	$[\text{ReH}_2(\text{NO})(\text{PPh}_3)_3] + \text{HBF}_4/\text{CO}$		51
$[\text{ReFX}(\text{CO})(\text{NO})(\text{PPh}_3)_2]$	$[\text{ReF}(\text{CO})(\text{NO})(\text{PPh}_3)_3]^+ + \text{X}^-$		52
X= H, OCH <sub>3</sub> or F			

#### 1.4

##### Complexes of Rhenium

A number of organometallic fluoro-complexes have been reported for rhenium, among which are those stabilised solely by carbonyl and fluoride ligands. For these, there are two general procedures for their preparation; fluorination of  $\text{Re}_2(\text{CO})_{10}$  with either  $\text{XeF}_2$  or  $\text{ReF}_6$ , or by a metathesis reaction of HF with  $\text{Re}(\text{CO})_5\text{Cl}$  or  $\text{AgF}$  with  $\text{Re}(\text{CO})_5\text{Br}$ . However, as with the complexes of manganese above, the earlier characterisations of some of the reaction products were later shown to be in error.

O'Donnell *et al*<sup>39</sup> suggested from IR spectroscopy, X-ray powder diffraction and elemental analysis that the reaction of  $\text{ReF}_6$  with  $\text{Re}_2(\text{CO})_{10}$  in anhydrous HF resulted in CO elimination and the formation of  $\text{ReF}_5$  and  $\text{Re}(\text{CO})_3\text{F}_3$  (an empirical formulisation). Holloway *et al*<sup>40</sup> independently investigated this system and revealed a more complex reaction, from which two rhenium carbonyl complexes were isolated and structurally characterised<sup>41,42</sup>. The relative proportions of these two complexes varied as the molar ratio of  $\text{ReF}_6:\text{Re}_2(\text{CO})_{10}$  was increased, such that, at the two extremes (2:1 and 4:1) pure samples of  $\text{Re}(\text{CO})_5(\mu\text{-F})\text{ReF}_5$  or  $[\text{Re}(\text{CO})_6][\text{Re}_2\text{F}_{11}]$  respectively were obtained. The reassignment of these two species to that previously observed by O'Donnell as  $\text{Re}(\text{CO})_3\text{F}_3$  is still not clear; the reported data on  $\text{Re}(\text{CO})_3\text{F}_3$  is not completely consistent with

those of either or both of these latter complexes. However, the  $\nu\text{CO}$  bands of  $\text{Re}(\text{CO})_3\text{F}_3$  are consistent with a  $[\text{Re}(\text{CO})_6]^-$  unit; which prompted Holloway *et al* to suggest that  $\text{Re}(\text{CO})_3\text{F}_3$  was a form of  $[\text{Re}(\text{CO})_6][\text{Re}_2\text{F}_{11}]$ , for which they have identified three similar crystal modifications  $\alpha$ ,  $\beta$  and  $\mu^{43}$ . The species was shown by XRPD not to be  $[\text{Re}(\text{CO})_6][\text{ReF}_6]^{43}$ .

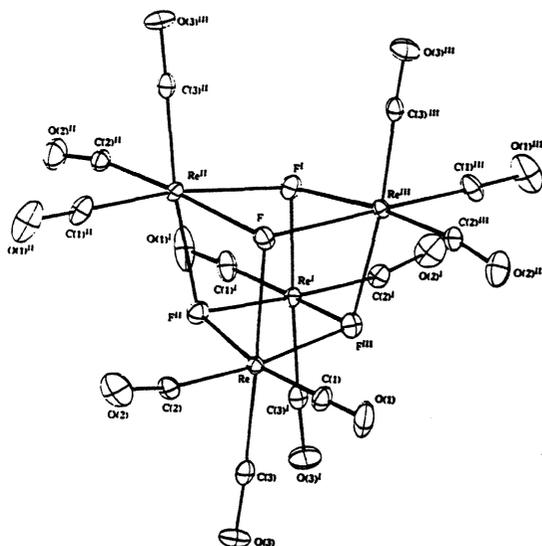
The reaction between  $\text{Re}_2(\text{CO})_{10}$  and  $\text{XeF}_2$  was also examined by both groups. O'Donnell<sup>44</sup> suggested that  $\text{Re}(\text{CO})_5\text{F}$  was the initial product from a 1:1 molar ratio reaction. This formulisation was on the basis of elemental analysis and an IR spectrum. The fluorination of this material, by  $\text{XeF}_2$ , yields " $\text{Re}(\text{CO})_3\text{F}_3$ " (characterised by analogy with the data from the  $\text{ReF}_6$  reaction) and, ultimately,  $\text{ReF}_5$ . However, the characterisation of this binary fluoride appears to be based purely on its colour. Holloway *et al* revealed a more complex reaction that, as well as being sensitive to the reagent ratio, is also dependent on CO pressure. With venting,  $\text{Re}(\text{CO})_5(\mu\text{-F})\text{ReF}_5$  is initially produced, and then further oxidised to  $\text{ReF}_6$  with increasing molar amounts of  $\text{XeF}_2^{45}$ . However, if the carbon monoxide that is eliminated from the reaction mixture is allowed to build-up within the reaction vessel, the initially formed  $\text{Re}(\text{CO})_5(\mu\text{-F})\text{ReF}_5$  is converted to the ionic complex  $[\text{Re}(\text{CO})_6][\text{ReF}_6]^{43}$ . For lower ratios,  $>1:3$  ( $\text{Re}_2(\text{CO})_{10}:\text{XeF}_2$ ),  $\text{Re}(\text{CO})_5(\mu\text{-F})\text{ReF}_5$  and unreacted  $\text{Re}_2(\text{CO})_{10}$  were observed. This  $\text{XeF}_2$  reaction was later investigated by Misra who claimed to have

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characterised the material as the tetramer,  $[\text{Re}(\text{CO})_3\text{F}_2]_4$ <sup>46</sup>. It is difficult to understand this formulation as, although it exhibits the same IR spectrum as the structurally determined  $\text{Re}(\text{CO})_5(\mu\text{-F})\text{ReF}_5$ , its assignment is not made accordingly even though Misra's work was published after this data was available in the literature.

The formation of  $\text{Re}(\text{CO})_5\text{F}$  via metathesis has also received some attention. Both O'Donnell and Holloway have reported its formation from the reaction of  $\text{Re}(\text{CO})_5\text{Cl}$  with HF. However, in an attempt to obtain metathesis between AgF and  $\text{Re}(\text{CO})_5\text{Br}$ , Horn *et al*<sup>47</sup> noticed an alternative reaction. The pentacarbonyl fluoro complex (observed in solution by IR spectroscopy) was not isolated as room temperature decarbonylation was detected in fluorobenzene, yielding a new complex. In this investigation the decarbonylation was observed to be accelerated by refluxing the solution. The resulting complex was isolated and structurally characterised as the tetramer,  $[\text{Re}(\text{CO})_3\text{F}]_4 \cdot 4\text{H}_2\text{O}$ .

Fig 1.5 View of  $[\text{Re}(\text{CO})_3\text{F}]_4 \cdot 4\text{H}_2\text{O}$

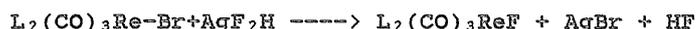


The water in this species was believed to have been derived from the hydrated  $\text{AgF}$ , and may possibly be involved in the room temperature decarbonylation; a reaction not observed by O'Donnell or Holloway under the anhydrous conditions of their investigations, which were carried out over a period of several days.  $\text{Re}(\text{CO})_5\text{F}$  has also been prepared by the cleavage, by  $\text{MeCN}$ , of  $[\text{Re}_2(\mu\text{-F})(\text{CO})_{10}]^+$ , which is obtained from the reaction of  $\text{Re}(\text{CO})_5(\text{CH}_3)$  with  $\text{HPF}_6$  or  $[\text{CPh}_3][\text{PF}_6]^{48}$ .

## 1.5

### Complexes of the General Formula $\text{ReF}(\text{CO})_3\text{L}_2$

Carbonyl fluoro-complexes of the type  $\text{ReF}(\text{CO})_3\text{L}_2$ , where  $\text{L} = \text{SbPh}_3$  or  $\text{L}_2 = \text{tmeda}$ , bipy or dppe, have been obtained in good yield from the bromide abstraction of the corresponding bromo-analogue with silver bifluoride<sup>49</sup>. The use of plastic vessels is important in these reactions, since the solvated HF in  $\text{AgF}_2\text{H}$  results in etching of glassware and the isolation of complexes containing the trifluoroborate anion,  $\text{BF}_3\text{OH}^-$ . The  $\text{AgF}_2\text{H}$  was used instead of the more commonly utilised  $\text{AgF}$  as it enables the formation of pure metal fluoride complexes via halide abstraction. Silver fluoride derived from aqueous solutions always contains some water even when dried over  $\text{P}_2\text{O}_5$ <sup>49</sup>. Previously Horn and Snow observed that the use of this hydrated reagent can result in the isolation of aqua complexes e.g.  $[\text{Re}(\text{CO})_3\text{F}]_4 \cdot 4\text{H}_2\text{O}$ <sup>47</sup>. The role of HF in  $\text{AgF}_2\text{H}$  is therefore important in solvating the  $\text{AgF}$  and thus preventing water solvation. Hence:-



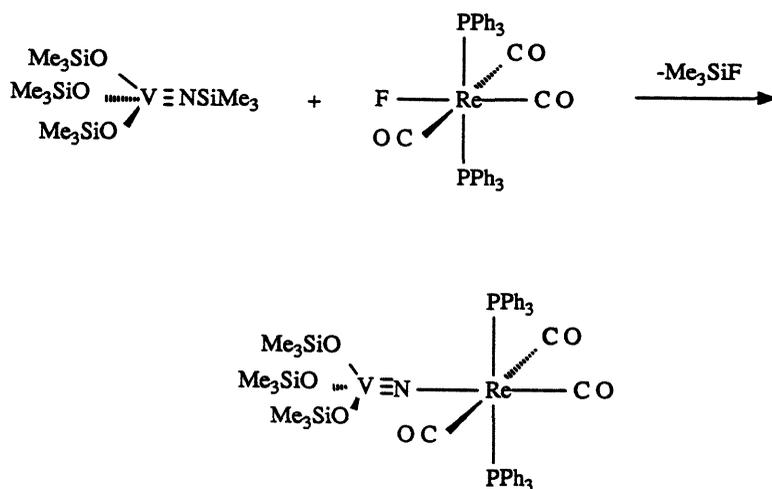
The crystal structure of  $\text{Re}(\text{CO})_3(\text{tmeda})\text{F}$  has been determined, and confirmed an octahedral geometry around the central rhenium atom with facial carbonyls. The molecules within the lattice were observed as discrete entities separated by a minimum distance of 3.196Å.

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The  $\text{PPh}_3$  phosphine analogue of  $\text{ReF}(\text{CO})_3\text{L}_2$  has only recently been reported<sup>50</sup>. Addition of silver triflate ( $\text{AgSO}_3\text{CF}_3$ ) to  $\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2$  results in the almost quantitative formation of  $\text{Re}(\text{CO})_3(\text{PPh}_3)_2(\text{SO}_3\text{CF}_3) \cdot 2\text{H}_2\text{O}$ . The weakly coordinating anion  $\text{SO}_3\text{CF}_3^-$  can be readily replaced by  $\text{F}^-$  derived from bis(triphenylphosphine)nitrogen fluoride,  $(\text{PPN})\text{F}$ , yielding *trans*- $\text{Re}(\text{CO})_3\text{F}(\text{PPh}_3)_2$  in a 90% yield. A  $^{13}\text{C}$  NMR study indicated a *trans*- phosphine rather than facial carbonyl arrangement. As the two carbonyl resonances exhibited only doublet couplings they were interpreted as resulting from  $^2\text{J}(\text{FC})$ . Hence the absence of observable  $^2\text{J}(\text{CP})$  implied a geometric arrangement where the carbonyl ligands were *cis*- to the phosphines i.e. mutually *trans*-phosphines.

An interesting characteristic of this fluoro-complex is its greater reactivity relative to the comparable chloro-species. When reacted with  $R_3VNSiMe_3$  ( $R=Me_3SiO$ ), it affords a nitride-bridged complex, whereas the chloride is unreactive even at elevated temperatures. The strengths of the resulting Si-X bonds ( $X= F$  or  $Cl$ ) is suggested as the governing factor in the reaction.

Fig 1.6



Similar chemistry is observed for rhodium and iridium  $MX(CO)(PPh_3)_2$  derivatives where, for a series of anions ( $X$ ), only the fluoro-, methoxy- and acetato-derivatives form sufficiently strong Si-X bonds to drive the reaction to  $(R_3SiO)_3V(\mu-N)-M(CO)(PPh_3)_2$ .

## 1.6

### Rhenium Nitrosyl Carbonyl Fluorides

Fluoro-complexes of rhenium are also known in nitrosyl chemistry. From the reaction of  $\text{ReH}_2(\text{NO})(\text{PPh}_3)_3$  with  $\text{HBF}_4$  under a CO atmosphere, the novel fluoro-complex,  $[\text{ReF}(\text{CO})(\text{NO})(\text{PPh}_3)_3]^+$ , was isolated<sup>51</sup>. Since the phosphine ligands are labile, this complex is a useful precursor for neutral species of the type  $\text{ReF}(\text{X})(\text{CO})(\text{NO})(\text{PPh}_3)_2$  where X=H,  $\text{OCH}_3$  or F, which can be readily synthesised by the addition of the appropriate anion. For the hydride complex,  $\text{NaBH}_4$  was used. The stereochemistry of this species was probed by IR and NMR spectroscopy, from which an arrangement of trans-phosphines with the hydride cis- to the fluoride but trans- to the nitrosyl ligand was established. This was confirmed, as the stability of the perchlorate salt of  $[\text{ReF}(\text{CO})(\text{NO})(\text{PPh}_3)_3]^+$  permitted a structural determination to be carried out, confirming the direct coordination of F- to the metal centre at a bond length of 1.97Å. This is consistent with low-valent transition metal fluoro-complexes<sup>4</sup>.

Later, in 1989, a successful attempt to extend this area of chemistry resulted from the preparation of  $[\text{ReH}(\text{MeOH})(\text{NO})(\text{PPh}_3)_3]\text{ClO}_4$ <sup>52</sup>, which exhibited useful lability of both a phosphine ligand and the solvate under different conditions. Hence, the addition of neutral ligands results in phosphine substitution, whereas if an anion is added replacement of the methanol solvate occurs. By this

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latter method the complexes  $[\text{ReHX}(\text{NO})(\text{PPh}_3)_3]\text{ClO}_4$ , where X = F, Cl, Br,  $\text{N}_3$  and NCO, were obtained. For the fluoro-complex,  $\text{KF}\cdot 2\text{H}_2\text{O}$  is the source of the fluoride ion. Subsequent substitution of the labile phosphine with CO resulted in the previously isolated species,  $\text{ReHF}(\text{CO})(\text{NO})(\text{PPh}_3)_2$ . However, from this alternative reaction scheme, obviously involving a different mechanism, the F *trans*-NO stereochemistry is obtained.

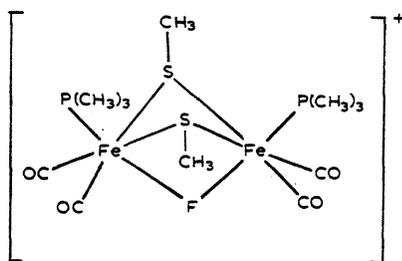
## 1.7

### Complexes of Iron

Ion cyclotron resonance spectroscopy (ICR) was used to investigate the interaction of  $F^-$  (produced by dissociative electron capture from  $NF_3$ ) with  $Fe(CO)_5$ <sup>53</sup>. The anion,  $[FeF(CO)_3]^-$ , is reported to be the product of this reaction. The species,  $CpFeF(CO)_2$ , has also been isolated, in high yield, from the reaction of  $CpFe(CO)_2(SiMe_2CH=CH_2)$  with  $HF$ <sup>54</sup>. Formation of this same material via  $F^-$  metathesis with  $CpFe(CO)_2Cl$  in acetone has also been attempted. However, definitive characterisation of the product was not possible as the species readily decomposes in acetone<sup>55</sup>. However,  $CpFeF(CO)_2$  in DMSO revealed a  $^{19}F$  NMR resonance at  $\delta$ -148.3 and displayed a parent ion in the mass spectrum consistent with  $[CpFeF(CO)_2]^+$ . The decarbonylation of  $CpFe(CO)_2F$  by  $Rh(PPh_3)_3Cl$  is reported to afford the carbonyl substituted derivative,  $CpFeF(CO)PPh_3$ , in trace amounts. (The source of  $CpFeF(CO)_2$  is not reported)<sup>56</sup>.

The chemical oxidation of  $[\text{FeSMe}(\text{CO})_2(\text{PMe}_3)]_2$  with  $\text{AgF}$  affords  $[\text{Fe}_2\text{F}(\text{SMe})_2(\text{CO})_4(\text{PMe}_3)_2]\text{PF}_6$  in a 50% yield<sup>57</sup>. This material was characterised by elemental analysis, including analysis for fluorine, and by IR and  $^1\text{H}$  NMR spectroscopies. The data was assigned to the iron (II) dimer containing a fluoride bridge and two methylthiolato bridges.

Fig 1.7 View of  $[\text{Fe}_2\text{F}(\text{SMe})_2(\text{CO})_4(\text{PMe}_3)_2]^+$



### 1.8

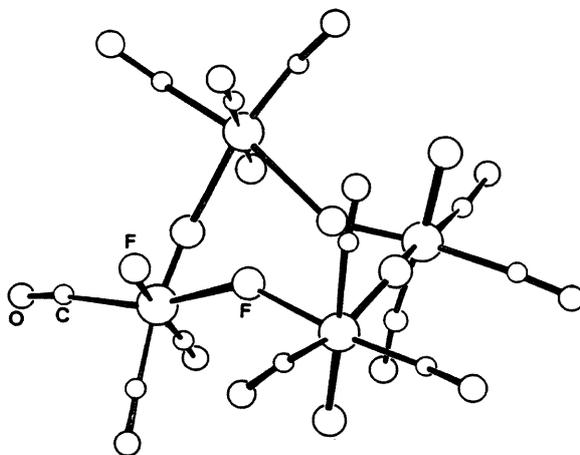
#### Complexes of Ruthenium

The carbonyl fluoride chemistry of ruthenium has received significantly less attention than that of rhenium, the majority of the work arising from a single group. The ruthenium carbonyl fluoride  $[\text{Ru}(\text{CO})_3\text{F}_2]_4$  has been observed in the high pressure, high temperature carbonylation of  $[\text{RuF}_5]_4$ , and also from the fluorination of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{XeF}_2$  in either HF or the fluorocarbon, Genetron 113

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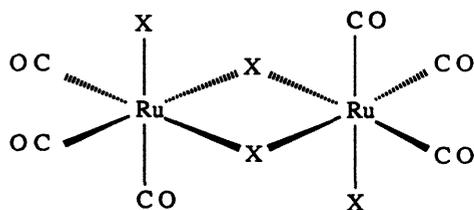
( $\text{CF}_2\text{ClCFCl}_2$ )<sup>58</sup>. The structure of the complex was determined by X-ray crystallography, which revealed a tetrameric ring with fluorine bridges<sup>59</sup>, similar to that of  $[\text{RuF}_5]_4$ <sup>60</sup>.

Fig 1.8 View of  $[\text{Ru}(\text{CO})_3\text{F}_2]_4$



To date, there have only been three crystal structures of complexes stabilised solely by carbonyl and fluoride ligands, and it is worth noting that all of these contain fluoride bridges ( $\text{Re}(\text{CO})_5(\mu\text{-F})\text{ReF}_5$ ,  $[\text{Re}(\mu\text{-F})(\text{CO})_3]_4$  and  $[\text{Ru}(\text{CO})_3\text{F}_2]_4$ ). For  $[\text{Ru}(\text{CO})_3\text{F}_2]_4$  the tetrameric structure is anomalous compared to the related chloro-, bromo- and iodo-complexes  $\text{Ru}(\text{CO})_3\text{X}_2$ . Although these species contain bridging halide ligands, they are dimeric species.

Fig 1.9 View of  $[\text{Ru}(\text{CO})_3\text{X}_2]_2$  X=Cl, Br, I



X= Cl, Br and I

Investigations of less-forcing carbonylation of  $[\text{RuF}_5]_4$  produced a yellow-brown, moisture sensitive complex with the empirical formula  $\text{Ru}(\text{CO})\text{F}_{3.5}$ . This was originally postulated to be  $[\text{Ru}(\text{CO})_2\text{F}][\text{RuF}_6]$ , or a related structure involving fluorine bridges, on the basis of an analysis of the IR spectrum which suggested the presence of an octahedral  $[\text{RuF}_6]^-$  unit<sup>61</sup>. However, in a later study, a more detailed analysis of the IR spectrum prompted reassignment to  $[\text{Ru}(\text{CO})_3\text{F}_2 \cdot \text{RuF}_5]_2$ <sup>58</sup>, with a structure similar to that of  $[\text{RuF}_5]_4$  and  $[\text{Ru}(\text{CO})_3\text{F}_2]_4$  containing alternating " $\text{Ru}(\text{CO})_3\text{F}_2$ " and " $\text{RuF}_5$ " units. The mixed valence of this product [Ru(II) and Ru(V)] accounted for its bulk magnetic susceptibility. This material was also prepared by the thermal (100°C) reaction of  $\text{Ru}_3(\text{CO})_{12}$  with an excess of  $\text{XeF}_2$  in Genetron 113. However the room temperature reaction with excess  $\text{XeF}_2$  results in the isolation of a third ruthenium carbonyl-fluoride, which was characterised as  $\text{Ru}(\text{CO})_3\text{F}_3$ . This formulisation was supported by analytical, e.s.r. and

magnetic-susceptibility data, and also IR spectroscopy. The number and position of the VCO bands are consistent with facial carbonyls, as observed for  $[\text{Ru}(\text{CO})_3\text{F}_2]_4$ . The magnetic moment of 1.92 BM, (at 298K), expected for a ruthenium (III) species, was interpreted as resulting from one unpaired electron. Although the e.s.r. spectrum of this material, in ANF at 77K, did not reveal hyperfine coupling to fluorine nuclei, this does not rule out assignment of the physical and spectroscopic data to the *fac* isomer.

To date the only other isolable organometallic fluoride of ruthenium is  $[\text{Ru}(\text{CO})(\text{dppe})_2\text{F}]^{+62}$ . This species was observed in a series of investigations where the workers were attempting to prepare  $[\text{Ru}(\text{CO})_2(\text{L-L})_2]\text{X}_2$  from the reaction of  $[\text{RuCl}_2(\text{L-L})_2]$  with silver salts of "non coordinating" anions ( $\text{X}^-$ ) under a pressure of carbon monoxide. When  $(\text{L-L}) = (\text{dppe})$ , however, the interaction with  $\text{AgBF}_4$  not only resulted in the desired  $[\text{Ru}(\text{CO})_2(\text{dppe})_2][\text{BF}_4]_2$ , but also caused fluoride ion abstraction from the  $\text{BF}_4^-$ . This afforded  $[\text{RuF}(\text{CO})_2(\text{dppe})_2]\text{BF}_4$ , which was separated by recrystallisation. The spectroscopic confirmation of the identity of this fluoro-monocation complex was made by  $^{31}\text{P}$  and  $^{19}\text{F}$  NMR spectroscopy. The  $^{31}\text{P}$  NMR spectrum comprised a doublet resonance at  $\delta$ -42.7 and the  $^{19}\text{F}$  NMR spectrum exhibited a related quintet at  $\delta$ -400. This data is assignable to an octahedral ruthenium(II) complex with four equivalent phosphines. Similar fluoro-complexes were

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observed in the analogous reaction with  $\text{AgPF}_6$  after prolonged reaction times or when the chelating phosphine was  $\text{dppm}$ . These were only present in trace amounts. However, their assignment was made on the basis of VCO IR stretching frequencies.

### 1.9

#### Complexes of Osmium

To date there has been only one reported example of an organometallic fluoro-complex of osmium. As part of a extensive investigation of  $\text{X}^-$  interaction with the 5-coordinate cation,  $[\text{Os}(\text{CO})_2(\text{NNPh})(\text{PPh}_3)_2]^+$ , the addition of  $[\text{NEt}_4][\text{F}]\cdot\text{H}_2\text{O}$  afforded the neutral octahedral complex  $\text{OsF}(\text{CO})_2(\text{NNPh})(\text{PPh}_3)_2$ <sup>63</sup>. This assignment is based on elemental analysis and IR spectroscopy. Surprisingly, in this study although  $^{31}\text{P}$  NMR spectroscopy was applied to the chloro-analogue to determine a *cis*- or a *trans*- geometry of the phosphines, no such investigation was extended to the fluoro species. The anticipated coupling to the fluoride would have confirmed Os-F bond formation, which at present is only inferred. The ruthenium analogue  $[\text{Ru}(\text{CO})_2(\text{NNPh})(\text{PPh}_3)_2]^+$  is unreactive towards  $\text{F}^-$ . An account of preliminary studies on the reaction of  $\text{Os}_3(\text{CO})_{12}$  and  $\text{XeF}_2$  is available in the PhD thesis<sup>64</sup> of A.Hewitt where the product is tentatively assigned to the tetrameric  $[\text{Os}(\text{CO})_3\text{F}_2]_4$  (c.f.  $[\text{Ru}(\text{CO})_3\text{F}_2]_4$ ). This work is discussed later in Chapter Three.

**Table 1.4**

Product	Reagent	Refs
[CpFe(CO) <sub>2</sub> F]	[CpFe(CO) <sub>2</sub> (SiMe <sub>2</sub> CH=CH <sub>2</sub> )] + HF	54
[Fe <sub>2</sub> F(SMe) <sub>2</sub> (CO) <sub>4</sub> (PMe <sub>3</sub> ) <sub>2</sub> PF <sub>6</sub>	[Fe <sub>2</sub> (SMe) <sub>2</sub> (CO) <sub>4</sub> (PMe <sub>3</sub> ) <sub>2</sub> ] + AgF	57
[Ru(CO) <sub>3</sub> F <sub>2</sub> ] <sub>4</sub>	[Ru <sub>3</sub> (CO) <sub>12</sub> ] + XeF <sub>2</sub>	58
[Ru(CO) <sub>3</sub> F <sub>2</sub> :RuF <sub>5</sub> ] <sub>2</sub>	[RuF <sub>5</sub> ] <sub>4</sub> + CO 200atm;200°C	58
	[Ru <sub>3</sub> (CO) <sub>12</sub> ] + XeF <sub>2</sub> 100°C	58
[Ru(CO) <sub>3</sub> F <sub>3</sub> ]	[Ru <sub>3</sub> (CO) <sub>12</sub> ] + XeF <sub>2</sub> 25°C	58
[Ru(CO)(L-L) <sub>2</sub> F] <sup>+</sup>	[Ru(CO) <sub>2</sub> (L-L) <sub>2</sub> ] <sup>2+</sup> + AgX	62
(L-L) = dppe, dppm	X = BF <sub>4</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>	
[OsF(CO) <sub>2</sub> (NNPh)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	[Os(CO) <sub>2</sub> (NNPh)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>2+</sup> + NEt <sub>4</sub> F	63

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### 1.10

#### Complexes of Cobalt

The only reported example of a carbonyl fluoro-complex of cobalt is that of the unstable  $[\text{CpCo}(\text{CO})\text{F}]^{-65}$ , formed from the gas-phase reaction of  $\text{CpCo}(\text{CO})_2$  and  $\text{F}^-$  and studied by ion cyclotron resonance spectroscopy. The source of  $\text{F}^-$  is from the dissociative attachment of electrons to  $\text{NF}_3$ . Neither  $\text{Cl}^-$  or  $\text{I}^-$  were reactive towards  $\text{CpCo}(\text{CO})_2$ , which was proposed as resulting from the much weaker gas-phase basicity of the heavier halides compared to  $\text{F}^-$ .

### 1.11

#### Complexes of Rhodium and Iridium

Rhodium and iridium have received by far the most attention in organometallic fluoride chemistry, particularly Vaska's derivatives. Since the preparation of  $\text{M}(\text{CO})\text{F}(\text{PPh}_3)_2$  ( $\text{M} = \text{Rh}$  or  $\text{Ir}$ ), these organometallic fluoro-complexes have been extensively studied. Initially they were obtained by the reaction of the chloride analogue with  $\text{AgF}$  in boiling acetone<sup>66</sup>. Later Vaska and Peone modified this synthetic route by the *in situ* formation of  $\text{AgF}$  from the reaction of  $\text{Ag}_2\text{CO}_3$  with  $\text{NH}_4\text{F}$  in methanol, increasing the yields of the fluoro-complexes to 90% for  $\text{Rh}$  and 80% for  $\text{Ir}$ <sup>67</sup>. The related tri-*p*-tolylphosphine<sup>68</sup>, alkyl-diphenylphosphine<sup>69</sup>,  $\text{AsPh}_3$ <sup>70, 71</sup> and  $\text{SbPh}_3$ <sup>70</sup> fluoro derivatives have also been reported.

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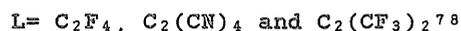
Forester reported that the halide preference for the  $d^8$  complexes, *trans*-  $M(CO)X(PPh_3)_2$  and *cis*-  $M(CO)_2X_2^-$  ( $M = Rh$  or  $Ir$ ), in aprotic media, followed the order  $X = Cl > Br > I$ <sup>72</sup>. From this trend, he suggested that, in rigorously aprotic solvents, fluoro derivatives may frequently be found to be the most stable halocarbonyl species. This prediction was substantiated, for  $Rh(CO)X(PPh_3)_2$   $X = F, Cl, Br$  or  $I$ , by Branan *et al*<sup>73</sup>, using equilibrium constants for the halide exchange of  $RhF(CO)(PPh_3)_2$  with  $(PPN)X$  ( $X = Cl, Br, \text{ or } I$ ). Earlier investigations revealed that  $PPN^+$  salts are strongly associated in  $CH_2Cl_2$  as ion pairs, with association constants independent of the nature of the anion<sup>74</sup>. Hence, there is little thermodynamic preference for  $(PPN)F$  formation over the other  $(PPN)X$  ion pairs. The equilibrium experiments were therefore interpreted as demonstrating the greater stability of the fluoro-complex relative to the heavier halo-complexes. The lability of the fluoride is greatly increased in the presence of polar molecules like water and methanol<sup>9</sup>. This was suggested to result from the high affinity of the uncomplexed fluoride for these species arising from strong hydrogen bonding to their hydroxyl groups. This phenomena was utilised by Vaska and Peone where a methanol solution of  $M(CO)F(PPh_3)_2$  allowed the convenient metathesis of the fluoride ligand with  $X^-$ , affording various derivatives of  $M(CO)X(PPh_3)_2$  ( $M = Rh$  or  $Ir$  and  $X = CN, NCS, NO_2, N(CN)_2, OClO_3, NCS, ONO_2, SePh, NCO, I, Br, Cl, N_3, SPh, O_2CH, O_2CPh, O_2CCH_3, OPh$  and  $OH$ )<sup>9</sup>.

The carbonyl IR stretching frequencies of  $\text{MX}(\text{CO})(\text{PPh}_3)_2$  ( $\text{M} = \text{Rh}, \text{Ir}$ ) have been shown to follow the order  $\text{X} = \text{F} < \text{Cl} < \text{Br} < \text{I}$ <sup>75</sup>, a trend consistent with the increasing  $\pi$ -acceptor strength of the halide. This trend would seem to imply that, although fluorine is the most electronegative element for this series, the fluoro-complex has the most electron rich metal centre. This trend is also observed for  $\text{RhX}(\text{CO})\text{L}_2$  ( $\text{L} = \text{AsPh}_3$  and  $\text{SbPh}_3$ )<sup>70</sup>, but McAuliffe and Pollock demonstrated that for  $\text{M} = \text{Ir}$  and  $\text{L} = \text{PMePh}_2$  and  $\text{PEtPh}_2$  the trend is not as clear<sup>76</sup>. For octahedral  $\text{Rh}(\text{III})$  complexes the halide trend for the  $\text{PPh}_3$  complexes,  $\text{RhXY}_2(\text{CO})(\text{PPh}_3)_2$ <sup>77</sup> ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$  or  $\text{I}$  and  $\text{Y}_2 = \text{Cl}_2, \text{Br}_2$  or  $\text{I}_2$ ), is reversed such that  $\text{RhF}_3(\text{CO})(\text{PPh}_3)_2$ , if it had been prepared, would be predicted to exhibit the highest  $\nu_{\text{CO}}$ . This investigation also revealed that  $\nu_{\text{CO}}$  is relatively insensitive to changes in the *trans*-halide in these complexes, which is in contrast to the square planar  $d^8$  derivatives.

The reaction between  $\text{O}_2$  and  $\text{Ir}(\text{CO})\text{X}(\text{L})_2$  is considered as an acid-base reaction, where the metal complex is acting as a Lewis base. Hence, factors increasing the electron density at the metal centre, in the absence of unfavourable steric effects, should enhance dioxygen addition. For this series where  $\text{L} = \text{PMePh}_2, \text{PEtPh}_2$  and  $\text{PPh}_3$ <sup>76</sup>, an increase in the basicity of the phosphine and a decrease in the electronegativity of the halogen, increased the rate of oxygenation. With a constant phosphine group, variation of

the halide enhanced the rate in the order  $F < Cl < Br < I$ . This experimental data was used to suggest the opposite trend for the electron density at the metal centre, previously derived from the VCO frequencies, and that the VCO frequencies did not follow a discernable trend for an extended series of phosphine and halide ligands.

The reactions with olefins similarly results in adduct formation.



When  $\text{L} = \text{C}_2\text{F}_4$ , the adduct is significantly more stable than the chloro analogue, which loses  $\text{C}_2\text{F}_4$  on crystallisation. The authors associated this with the relative  $\pi$ -bonding effects of the halide ligands, and also the closer approach of the unsaturated molecule to the metal atom which arises from the smaller size of the fluorine atom.

### 1.12

#### Complexes of Rhodium (III) and Iridium (III)

The oxidative addition of methyl fluorosulphates, such as  $\text{CH}_3\text{SO}_3\text{F}$  and  $\text{CH}_3\text{SO}_3\text{CF}_3$ , to  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ <sup>79</sup> yields  $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2(\text{CH}_3)\text{X}$  for  $\text{X} = \text{SO}_3\text{F}$  and  $\text{SO}_3\text{CF}_3$ . These weakly coordinating anions were found to be very labile in polar organic solvents, resulting in dissociation of the methyl fluorosulphate complex and thereby providing a new route to Ir(III) species, some of which are inaccessible by direct oxidative addition. The fluoro species,  $\text{IrF}(\text{CO})\text{Cl}(\text{PPh}_3)_2(\text{CH}_3)$ , is reportedly synthesised via this method,  $\text{NEt}_4\text{F}$  acting as the source of the  $\text{F}^-$ . Surprisingly, in the  $^1\text{H}$  NMR spectrum of this complex, the methyl resonance only exhibits coupling to the *trans*-phosphines. The further splitting by coupling to the fluoride ligand is not discussed.

The preparation of Rh(III) and Ir(III) fluoro-complexes is, however almost entirely dominated by the oxidative addition of a substrate A-B to Vaska's type derivatives  $\text{M}(\text{CO})\text{X}(\text{PR}_3)_2$  (where  $\text{M} = \text{Rh}$  or  $\text{Ir}$ ;  $\text{X} = \text{Cl}$ ,  $\text{Br}$  or  $\text{I}$  and A-B is a fluorinating agent); or alternatively by the reaction of A-B with  $\text{M}(\text{CO})\text{F}(\text{PPh}_3)_2$ . The complexes listed in Table 1.5 have been prepared via these reactions.

**Table 1.5**

<b>Organometallic Complexes of Rhodium (III) and Iridium (III)</b>		
Product	Reagent	Refs
[RhFCI(COPh)(PPh <sub>3</sub> ) <sub>2</sub> ]	[RhCl(PPh <sub>3</sub> ) <sub>3</sub> ] + PhCOF	87
[RhFX <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ] (X = Cl, Br, I)	[RhCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + X <sub>2</sub>	77
[IrFClH(CO)L <sub>2</sub> ] (L = PMe <sub>3</sub> , PPh <sub>3</sub> )	[IrCl(CO)L <sub>2</sub> ] + HCOF	88
[IrFHX(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] (X = Cl, Br, I)	[IrX(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + HF	89
[IrFH(SiR <sub>3</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] (SiR <sub>3</sub> = SiPh <sub>3</sub> , SiMeCl <sub>2</sub> Si(OEt) <sub>3</sub> and SiF <sub>3</sub> )	[IrF(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + HSiR <sub>3</sub>	90
[IrFH <sub>2</sub> (CN-p-tol)(AsPh <sub>3</sub> ) <sub>2</sub> ]	[IrH <sub>3</sub> (CN-p-tol)(AsPh <sub>3</sub> ) <sub>2</sub> ] + HF	91
[IrFCIMe(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	[IrCl(OTf)Me(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + NEt <sub>4</sub> F	79
[IrFIMe(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	[IrF(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + MeI	92
[IrF(O <sub>2</sub> )(CO)L <sub>2</sub> ] (L = PMePh <sub>2</sub> , PEtPh <sub>2</sub> , PPh <sub>3</sub> )	[IrF(CO)L] + O <sub>2</sub>	93, 76
[IrF(1,2-O <sub>2</sub> C <sub>6</sub> Cl <sub>4</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	[IrF(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + 1,2-O <sub>2</sub> C <sub>6</sub> Cl <sub>4</sub>	94
[IrFCl <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	[IrF(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + SF <sub>5</sub> Cl	95
[IrFI <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	[IrF(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + I <sub>2</sub>	93a),94
[IrFCl(SO <sub>2</sub> C <sub>10</sub> H <sub>7</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]	[IrCl(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + FSO <sub>2</sub> C <sub>10</sub> H <sub>7</sub>	96
[IrFX(SF <sub>3</sub> )(CO)(PEt <sub>3</sub> ) <sub>2</sub> ] (X = Cl, Br, I)	[IrX(CO)(PEt <sub>3</sub> ) <sub>2</sub> ] + SF <sub>4</sub>	83
[IrF(COF)(CO) <sub>2</sub> (L) <sub>2</sub> ] <sup>+</sup> (L = PEt <sub>3</sub> , PMe <sub>3</sub> , PMe <sub>2</sub> Ph PEt <sub>2</sub> Ph)	[Ir(CO) <sub>3</sub> (L) <sub>2</sub> ] <sup>+</sup> + XeF <sub>2</sub>	81, 82
[IrF(η <sup>2</sup> -NH=NC <sub>6</sub> H <sub>3</sub> -2-Br- (CO)(PPh <sub>3</sub> ) <sub>2</sub> ) <sup>+</sup>	[IrF(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + (2-BrC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> )BF <sub>4</sub>	97
[IrF(η <sup>2</sup> -NH=NC <sub>6</sub> H <sub>3</sub> X (CO)(PPh <sub>3</sub> ) <sub>2</sub> ) <sup>+</sup> (X = 2-F, 4-F, 2-CF <sub>3</sub> 4-Me, 2-NO <sub>2</sub> )	[IrH(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] + (XC <sub>6</sub> H <sub>4</sub> N <sub>2</sub> )BF <sub>4</sub> /air	85
[IrF(η <sup>2</sup> -NNC <sub>6</sub> H <sub>3</sub> -2-Br (CO)(PPh <sub>3</sub> ) <sub>2</sub> ) <sup>+</sup>	[IrF(η <sup>2</sup> -NH=NC <sub>6</sub> H <sub>3</sub> X)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> + NEt <sub>3</sub> or NaOH or NaOAc	97

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Recently a concerted effort to synthesis complexes containing a terminal fluoride led Cockman *et al* to investigate the fluorinating properties of SF<sub>4</sub> and XeF<sub>2</sub>. Vaska's derivatives were the ideal candidates for this particular study, where the oxidative addition can be anticipated to afford the d<sup>6</sup> fluoro-complexes.

These reactions are of particular interest in demonstrating the usefulness of multinuclear NMR techniques in elucidating reaction products within a system. Prior to these studies and those presented in the following chapters, very little <sup>19</sup>F, <sup>31</sup>P and <sup>13</sup>C NMR data was available for transition-metal fluoro-complexes. This is somewhat surprising as a wealth of information can be derived from such investigations, especially concerning the stereochemistry.

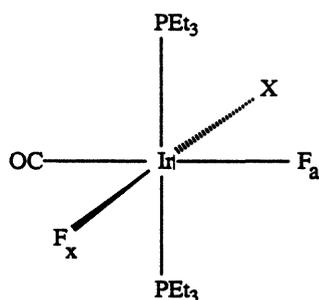
For the reaction between XeF<sub>2</sub> and M(CO)X(PEt<sub>3</sub>)<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub> (M= Rh and Ir and X= Cl, Br or I)<sup>80</sup>, the choice of the triethylphosphine increased the solubility of the complexes relative to the triphenylphosphine derivatives, which is an important criterion for NMR spectroscopy. Low temperature <sup>19</sup>F and <sup>31</sup>P NMR spectra revealed that, for iridium, reaction occurred at 233K affording, xenon and principally, the anticipated Ir(III) complex IrF<sub>2</sub>(CO)X(PEt<sub>3</sub>)<sub>2</sub>, in which the fluoride ligands adopt a *cis*-configuration. (The phosphines are always mutually *trans*-). The chloro-, bromo- and iodo-complexes are stable at room temperature. In each reaction, additional minor resonances

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were observed in both the  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra, representing less than 10% of the intensities of the major resonances. These correspond to the isomers of the mono- and trifluoro- derivatives, which were rationalised as the result of an intermolecular halogen rearrangement. The rhodium systems exhibited more complex reactions. The corresponding *cis*-fluorides,  $\text{RhF}_2(\text{CO})\text{X}(\text{PEt}_3)_2$  ( $\text{X} = \text{Cl}, \text{Br}$  and  $\text{I}$ ), displayed a thermal instability in the order  $\text{Cl} < \text{Br} < \text{I}$ . Ultimately,  $\text{F}_2\text{PEt}_3$  is the major fluorinated species produced at room temperature. Various isomers of the mono-, di- and tri-fluorinated species are observed, at low temperature in solution, resulting from intermolecular exchange and, in the case of  $\text{Br}$  and  $\text{I}$ , from the reaction with the solvent,  $\text{CD}_2\text{Cl}_2$ , which resulted in mixed chloro-halo-fluoro complexes.

These NMR analyses for an extensive series of related complexes enabled the establishment of various trends. The  $\text{Ir}(\text{III})$  products are more stable to halogen exchange than their rhodium ( $\text{III}$ ) analogues. In the rhodium system, reactivity towards halide exchange increases in the order  $\text{Cl} < \text{Br} < \text{I}$ . The most stable complexes in both the  $\text{Rh}$  and  $\text{Ir}$  systems are the trifluorides,  $\text{M}(\text{CO})\text{F}_3(\text{PEt}_3)_2$ . Certain trends were also observed in the NMR parameters.  $^2\text{J}(\text{PF}_a)$  is invariably larger than  $^2\text{J}(\text{PF}_x)$ , with only a minor dependency on  $\text{X}$ . Also  $^2\text{J}(\text{F}_a\text{F}_x)$  is dependent on both  $\text{X}$  and the metal, ranging from 89Hz for  $\text{X}=\text{F}$  and  $\text{M}=\text{Rh}$ , to 143Hz for  $\text{X}=\text{I}$  and  $\text{M}=\text{Ir}$ . Two distinct ranges for the  $^{19}\text{F}$  chemical shifts were

also observed in the  $^{19}\text{F}$  NMR spectra, the chemical shift of both lying to very low frequency when compared to organic fluorines and high-valent metal fluorides. Signals in the region between  $\delta$ -270 and  $\delta$ -390 are assignable to F *trans*- to a carbonyl ligand, whereas those below  $\delta$ -400 indicate fluorine *trans*- to a halide.



(X= Cl, Br and I)

The reactions of 5-coordinated Ir(I) complexes of the type  $[\text{Ir}(\text{CO})_3\text{L}_2]^+$ ,  $\text{L}=\text{PEt}_3$ ,  $\text{PMe}_3$ ,  $\text{PMe}_2\text{Ph}$ ,  $\text{PEt}_2\text{Ph}$  and  $\text{PEtPh}_2$ , with  $\text{XeF}_2$  in  $\text{CD}_2\text{Cl}_2$  results in the formation of a terminal metal-fluoride and the very unusual metal bound fluoroacyl ligand<sup>81,82</sup>. These reactions are discussed in detail in Chapter Four.

### 1.13

#### The Reaction of Vaska's Derivatives with the Chalcogenide Fluorides SF<sub>4</sub>, SeF<sub>4</sub> and TeF<sub>4</sub>

The use of low temperature NMR spectroscopy has also been applied to the study of the reactions of the chalcogenide fluorides, SF<sub>4</sub>, SeF<sub>4</sub> and TeF<sub>4</sub>, with IrX(CO)(PEt<sub>3</sub>)<sub>2</sub> (X= Cl, Br and I). With SF<sub>4</sub><sup>83</sup>, at very low temperatures (200K for X= Cl), complexes IrF(CO)X(PEt<sub>3</sub>)<sub>2</sub>(SF<sub>3</sub>) were identified by their <sup>19</sup>F and <sup>31</sup>P NMR spectra. As with the XeF<sub>2</sub> study (see above), <sup>19</sup>F NMR resonances assignable to metal-bound fluoride were observed at relatively low frequencies, and three resonances observed for the SF<sub>3</sub> ligand were attributable to the inequivalence of the fluorines due to the lone pair of the S(IV). Variable temperature NMR spectra revealed that at least two different exchange processes were occurring at higher temperatures. Analogous complexes of rhodium result from the reaction with SF<sub>4</sub><sup>84</sup>. These are however less stable and more isomeric products were identified. With SeF<sub>4</sub> and Rh(CO)X(PEt<sub>3</sub>)<sub>2</sub> (for X= Cl, Br, I, NCS and NCO)<sup>84</sup>, a low temperature reaction gave a mixture of complexes, the most abundant being RhX(CO)F(PEt<sub>3</sub>)<sub>2</sub>(SeF<sub>3</sub>), again identified by <sup>19</sup>F and <sup>31</sup>P NMR analysis. The minor resonances seen in the spectra were all associated with isomers or products of halide exchange. The major complexes were observed to be much less thermally

stable than their sulphur analogues.

With  $\text{TeF}_4$ , the reactions did not produce the expected analogous chemistry. The products of these reactions were the cationic 5-coordinate rhodium (III) complexes  $[\text{Rh}(\text{CO})\text{X}(\text{PEt}_3)_2(\text{TeF}_3)]^{+84,86}$ , with  $\text{TeF}_5^-$  as the counterion. The presence of  $\text{TeF}_5^-$  suggests that the six coordinate Rh(III) complex with a Rh-F bond was initially formed, but unreacted  $\text{TeF}_4$  is a Lewis acid of sufficient strength to remove the fluoride bound to the metal. Similar reactions between  $\text{Ir}(\text{CO})\text{X}(\text{PEt}_3)_2$ ,  $\text{SeF}_4$  and  $\text{TeF}_4$  have not been reported.

An alternative route to Ir(III) organometallic fluoro-derivatives has been reported to occur when the orthometallated hydrazido complex  $[(\text{PPh}_3)_2\text{Ir}(\text{CO})(\eta^2\text{NHNC}_6\text{H}_4\text{X})]^+$  ( $\text{X} = 2\text{-NO}_2$ ,  $2\text{-CF}_3$ ,  $2\text{-F}$  and  $4\text{-F}$ )<sup>85</sup>, abstracts fluoride from  $\text{BF}_4^-$ . These reactions were first observed as a result of air oxidation during work-up procedures. The metal complex least susceptible to this secondary reaction is the 2-nitro-derivative. However, the others in this series react quickly as air or oxygen dissolves into the solution yielding the aryldiazene complexes  $[\text{IrF}(\text{CO})(\text{PPh}_3)_2(\eta^2\text{NNC}_6\text{H}_4\text{X})]^+$  with Ir-F bond formation.

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#### 1.14 Summary

It may be seen from the literature, contrary to the predictions from hard/soft acid/base considerations, it is clear that there is no inherent instability in the metal-fluoride bond. For certain complexes fluoride has even been demonstrated to display the greatest stability within the halide series (see Rh and Ir). Therefore, the lack of study is probably the result of the anticipated practical problems of extending halogenation reactions to fluorine. Xenon difluoride has proven to be reasonably inert to a variety of common organic solvents, in which it displays reasonable solubility. The by-product of fluorination reactions, xenon gas, can easily be removed thus facilitating "clean" fluorinations. The work by Holloway *et al.*, and more recently Ebsworth *et al.*, demonstrates the effectiveness of  $\text{XeF}_2$  in overcoming the practical problems of fluorination.

Low-valent organometallic complexes are often stabilised by the carbonyl ligand due to its ability to remove electron density from electron rich metal centres, by  $\pi$ -back-bonding, therefore affording soft metal complexes. Hence, the study of low-valent organometallic fluoro-complexes presented in this thesis targeted the formation of carbonyl fluoro-complexes, chiefly concerned with the reaction of  $\text{XeF}_2$  with transition metal carbonyl or carbonyl-containing complexes. Other fluorinating agents are also discussed.

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## CHAPTER TWO

### Synthesis And Characterisation Of Fluoro-Complexes Of Iridium

## 2.1

### A Brief Synopsis of Iridium Carbonyl Halide Chemistry

Transition-metal carbonyl halides are well established for most of the transition-metals. In 1925 Manchot *et al.*<sup>1</sup> isolated small quantities of the first iridium carbonyl halo-complex,  $[\text{Ir}(\text{CO})_2\text{Cl}_2]_n$ , from the reaction of iridium (III) chloride with CO at atmospheric pressure and 150°C. Subsequent to this work in 1941, Hieber *et al.*<sup>2</sup> made a more detailed study of this type of reaction with  $\text{IrX}_3$  (X = Cl, Br or I) and revealed the presence of not only  $[\text{Ir}(\text{CO})_2\text{X}_2]_n$  complexes but also  $[\text{Ir}(\text{CO})_3\text{X}]_n$  and  $\text{Ir}_4(\text{CO})_{12}$ , however, no spectroscopic analysis was possible at this time. From this work it was concluded that the ease of halogen elimination from the halocarbonyl complexes by CO decreased in the order  $\text{Cl} > \text{Br} > \text{I}$ , suggesting a direct relationship with the ease of formation of the relevant carbonyl halides,  $\text{COX}_2$ .  $[\text{Ir}(\text{CO})_3\text{Br}]_n$  has also been observed as an impurity in the high-pressure carbonylation of  $\text{K}_2\text{IrBr}_6$  in the presence of a halide acceptor, provided reaction times were sufficiently long to afford decomposition of,  $\text{K}_2\text{Ir}_2(\text{CO})_4\text{Br}_5$  initially formed in the reaction<sup>3</sup>. The chloro analogue,  $\text{Ir}(\text{CO})_3\text{Cl}$ , was also prepared by Fischer *et al.*<sup>4</sup> and, in a later structural determination, was shown to exist as staggered planar  $\text{Ir}(\text{CO})_3\text{Cl}$  molecules joined by an Ir-Ir bond of 2.844Å.<sup>5</sup>

High pressure carbonylation of  $\text{IrI}_3$  was studied by Malatesta<sup>6</sup>, who observed that  $\text{Ir}(\text{CO})_3\text{I}_3$  and the dimer,

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$[\text{Ir}(\text{CO})_2\text{I}_3]_2$ , were formed. The former has also been obtained by the oxidative addition of iodine to the polymeric,  $\text{Ir}(\text{CO})_3\text{I}^7$ .

Thus, the only neutral iridium carbonyl halo complexes to be isolated to date are of the type  $[\text{Ir}(\text{CO})_2\text{X}_2]_n$ ,  $[\text{Ir}(\text{CO})_3\text{X}]_n$  where  $\text{X}=\text{Cl}$ ,  $\text{Br}$  or  $\text{I}$ , and  $\text{Ir}(\text{CO})_3\text{I}_3$ ,  $[\text{Ir}(\text{CO})_2\text{I}_3]_2$  and  $[\text{Ir}_2(\text{CO})_3\text{I}_6]$ , for which the chloro- and bromo-analogues have not yet been reported. The only iridium carbonyl fluorides to be reported to date are  $\text{Ir}(\text{CO})_3\text{F}_2^{15}$  and  $\text{Ir}(\text{CO})_2\text{F}_2^{15}$  which will be discussed later in more detail.

## 2.2

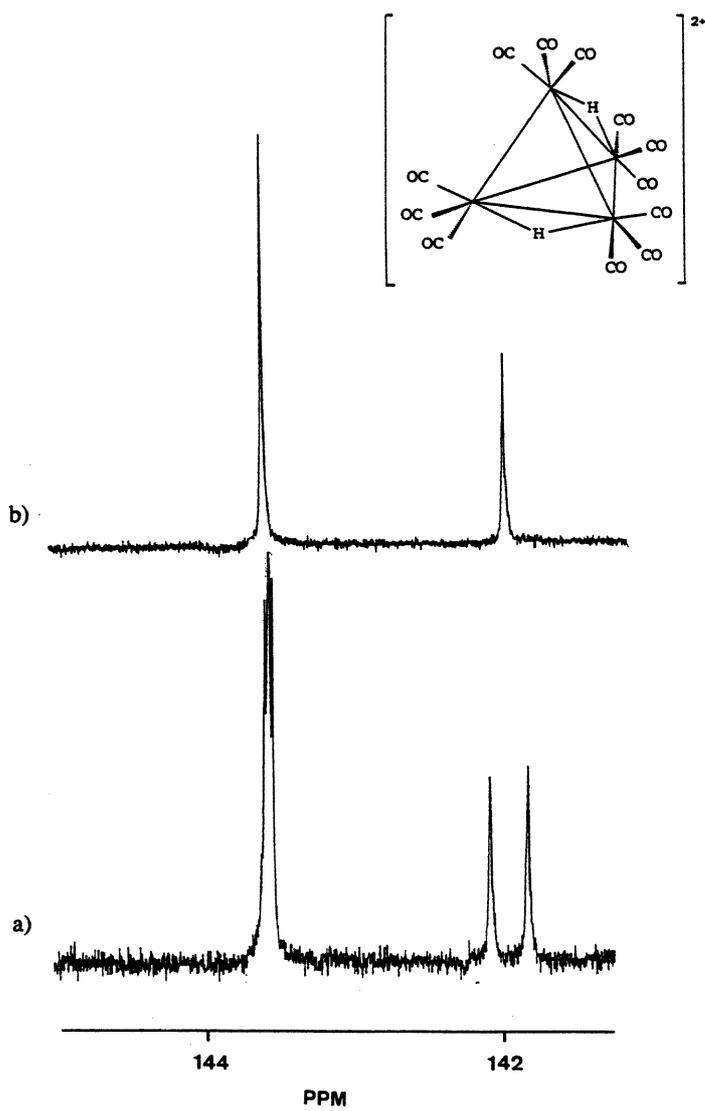
### The Reaction of $\text{Ir}_4(\text{CO})_{12}$ with AHF

Tetrairidium dodecacarbonyl was found to be insufficiently soluble in organic solvents to allow investigation of its fluorination by  $\text{XeF}_2$ . However, the reaction between  $\text{Ir}_4(\text{CO})_{12}$  and  $\text{XeF}_2$  was observed in anhydrous hydrogen fluoride (AHF) at ca.  $-40^\circ\text{C}$ , with the vigorous evolution of volatiles. The reaction also occurred in Genetron 113 ( $\text{CFCl}_2\text{CF}_2\text{Cl}$ ) if a trace amount of AHF was present, implying that the AHF was acting as a catalyst. Therefore, an attempt to elucidate the nature of the initial iridium carbonyl complex formed by the reaction of  $\text{Ir}_4(\text{CO})_{12}$  with AHF, which is readily fluorinated by  $\text{XeF}_2$ , was undertaken.

AHF was condensed on to a sample of yellow  $\text{Ir}_4(\text{CO})_{12}$ , in an FEP reactor. There was no immediate sign of reaction and the cluster appeared to be insoluble even at room temperature. However, with time, the colourless liquid above the solid began to develop a pale yellow tinge. After approximately 8hr. all of the solid had been consumed forming a yellow/green solution. The reaction time decreased with larger volumes of AHF or with agitation.

NMR spectroscopic data for the resulting complex in solution can convincingly be rationalised as arising from the diprotonated cluster,  $[\text{Ir}_4(\text{CO})_{12}\text{H}_2]^{2+}$ , in which the tetrahedral geometry of the  $\text{Ir}_4$  skeleton in  $\text{Ir}_4(\text{CO})_{12}$  has been retained (Fig.2.1). The three facial carbonyls on each

Fig 2.1  $^{13}\text{C}$  NMR Spectra of  $[\text{Ir}_4(\text{CO})_{12}\text{H}]^{2+}$   
a)  $^{13}\text{C}$  fully coupled b)  $^{13}\text{C}\{^1\text{H}\}$



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metal in such a structure are inequivalent, one being effectively *trans*- to a hydride, whereas the other two are *cis*-.  $^1\text{H}$  NMR spectroscopic analysis of the solution revealed a single hydride resonance at  $\delta$ -20.0 indicating protonation of the cluster.  $^{13}\text{C}$  NMR experiments on  $^{13}\text{CO}$  enriched samples showed two resonances at  $\delta$ 143.7 and 142.0, in an approximate 2:1 ratio. The resonance at  $\delta$ 143.7 resolved as a doublet of doublets exhibiting  $^2\text{J}(\text{CH})$  and  $^3\text{J}(\text{CH})$  coupling of approximately 2.2Hz from coupling to the adjacent hydride, and the hydride on the opposite edge of the tetrahedron. The similarity of these coupling constants, even though one is longer range, is presumably due to the geometry of the complex. Hence, the  $^3\text{J}(\text{CH})$  coupling arising from the interaction of a CO *trans*- to H is similar in magnitude to that of a *cis*-  $^2\text{J}(\text{CH})$ . The resonance at  $\delta$ 142.0 was observed as a large doublet, exhibiting  $^2\text{J}(\text{CH})$  of 21.2Hz. No  $^3\text{J}(\text{CH})$  was observed for this resonance as the carbonyl is effectively *cis*- to the hydride on the opposite side of the cluster and is therefore only expected to exhibit very small coupling, which was not resolved in this experiment. The non-fluxionality of the complex at room temperature is as expected for a third row transition-metal carbonyl complex of this type *c.f.*  $\text{Os}_3(\text{CO})_{12}$  and  $[\text{Os}_3(\text{CO})_{12}\text{H}]^{+8}$ .

Attempts to isolate the complex as a salt by the addition of either  $\text{BF}_3$ ,  $\text{PF}_5$ ,  $\text{AsF}_5$  or  $\text{SiF}_4$  resulted in the precipitation of solids. IR spectra of these showed a large

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number of terminal VCO bands consistent with a reduction in symmetry of the proposed structure. However, these salts decomposed to  $\text{Ir}_4(\text{CO})_{12}$ , HF and the appropriate gaseous Lewis acid with time as observed by IR spectroscopy, implying the greater thermodynamic stability of these species relative to that of  $[\text{Ir}_4(\text{CO})_{12}\text{H}]^{2+}$ .

The protonation of neutral carbonyls is not unexpected in strong acidic media and has previously been reported in similar investigations where concentrated  $\text{H}_2\text{SO}_4$  was used as the protonating agent<sup>9</sup>. Although HF is a fairly weak acid as a solute (e.g. aqueous HF), similar in strength to formic acid, its acidic strength increases dramatically as the HF is purified. Hence anhydrous HF is an extremely acidic solvent, comparable in acidity with anhydrous sulphuric acid, and both act as protonic solvents<sup>10</sup>.

In the  $\text{Ir}_4(\text{CO})_{12}/\text{H}_2\text{SO}_4$  reaction Knight and Mays<sup>9</sup> used accurate integrals, against a measured quantity of  $\text{Me}_2\text{SO}_4$ , on the hydride resonance, (also at  $\delta$ -20.0) to empirically interpret the product as  $[\text{Ir}_4(\text{CO})_{12}\text{H}_2]^{2+}$ . However, with the limited data available for the complex, which was only stable in solution, they were unable to make any predictions as to a possible geometry. Their attempt to isolate this complex by addition of  $\text{NH}_4\text{PF}_6$  resulted in the precipitation of  $\text{Ir}_4(\text{CO})_{12}$ . Hence, the addition of Lewis acids in this work has provided the only method of isolating this cationic species.

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The length of time needed for complete conversion of  $\text{Ir}_4(\text{CO})_{12}$  to  $[\text{Ir}_4(\text{CO})_{12}\text{H}_2]^{2+}$  implies that in the reaction of  $\text{Ir}_4(\text{CO})_{12}$  with  $\text{XeF}_2$  in  $\text{AHF}$ , which is a rapid process, the  $\text{HF}$  is acting catalytically. Hence, the subsequent rapid fluorination of  $[\text{Ir}_4(\text{CO})_{12}\text{H}_2]^{2+}$  "draws" the neutral carbonyl into solution such that all the  $\text{Ir}_4(\text{CO})_{12}$  reacts in a matter of minutes instead of hours. Of course, it is impossible to say unambiguously from this data that  $[\text{Ir}_4(\text{CO})_{12}\text{H}_2]^{2+}$  is the species which is reactive towards  $\text{XeF}_2$ . But the required presence of  $\text{HF}$  strongly implies that  $[\text{Ir}_4(\text{CO})_{12}\text{H}_2]^{2+}$ , or a related protonated species such as  $[\text{Ir}_4(\text{CO})_{12}\text{H}]^+$ , is necessary for reaction to take place.

### 2.3

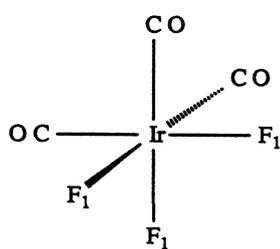
#### The Reaction of $\text{Ir}_4(\text{CO})_{12}$ with $\text{XeF}_2$ in AHF

Fluorination of  $\text{Ir}_4(\text{CO})_{12}/\text{AHF}$  by  $\text{XeF}_2$  was investigated between the molar ratios of 1:1 to 1:26. Below the ratio of 1:6, un-fluorinated  $[\text{Ir}_4(\text{CO})_{12}\text{H}_2]^{2+}$  was detected in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. New unassigned  $^{13}\text{C}$  NMR resonances which displayed coupling to either  $^1\text{H}$  or  $^{19}\text{F}$  nuclei, or both, were also observed, suggesting the presence of iridium carbonyl complexes containing both fluorine and hydrogen.

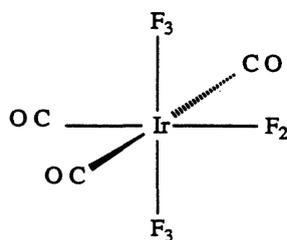
The ratio at which all the  $[\text{Ir}_4(\text{CO})_{12}\text{H}_2]^{2+}$  had been consumed was shown by NMR spectroscopy to be 1:6. In a typical reaction at this ratio, gas evolution occurred at ca.  $-40^\circ\text{C}$ , and the reaction was controlled by judicious cooling and venting. These volatiles were IR inactive, presumably Xe, implying that CO was not being released from the reaction. Once gas evolution had ceased, the resulting yellow solution was allowed to warm to room temperature overnight so that rearrangement to thermodynamically stable species could occur (see later). Room temperature  $^{19}\text{F}$  NMR spectroscopic analysis of the solutions showed three major resonances  $\text{F}_1$ ,  $\text{F}_2$  and  $\text{F}_3$ , at  $\delta$ -310,  $\delta$ -338 and  $\delta$ -476 respectively. These occur in the region of the  $^{19}\text{F}$  NMR spectrum characteristic of a fluoride ligand bound directly to a low-valent metal centre (see Section 1.12). At lower temperatures these broad resonances sharpened such that  $\text{F}_1$  was observed as a sharp singlet, and  $\text{F}_2$  and  $\text{F}_3$  as a triplet

and doublet respectively, in the ratio of 1:2, with a mutual coupling of 75Hz. (Fig.2.2.)

These M-F resonances fall into two very distinct regions. Those associated with  $F_1$  and  $F_2$  are characteristic of F *trans*-CO<sup>11</sup> whilst  $F_3$  occurs in the region expected for a F *trans*-F<sup>11</sup> environment (see Section 1.12). Hence the <sup>19</sup>F NMR data is readily assignable to the *fac*- and *mer*- isomers of the d<sup>6</sup> 18 electron complex Ir(CO)<sub>3</sub>F<sub>3</sub>.



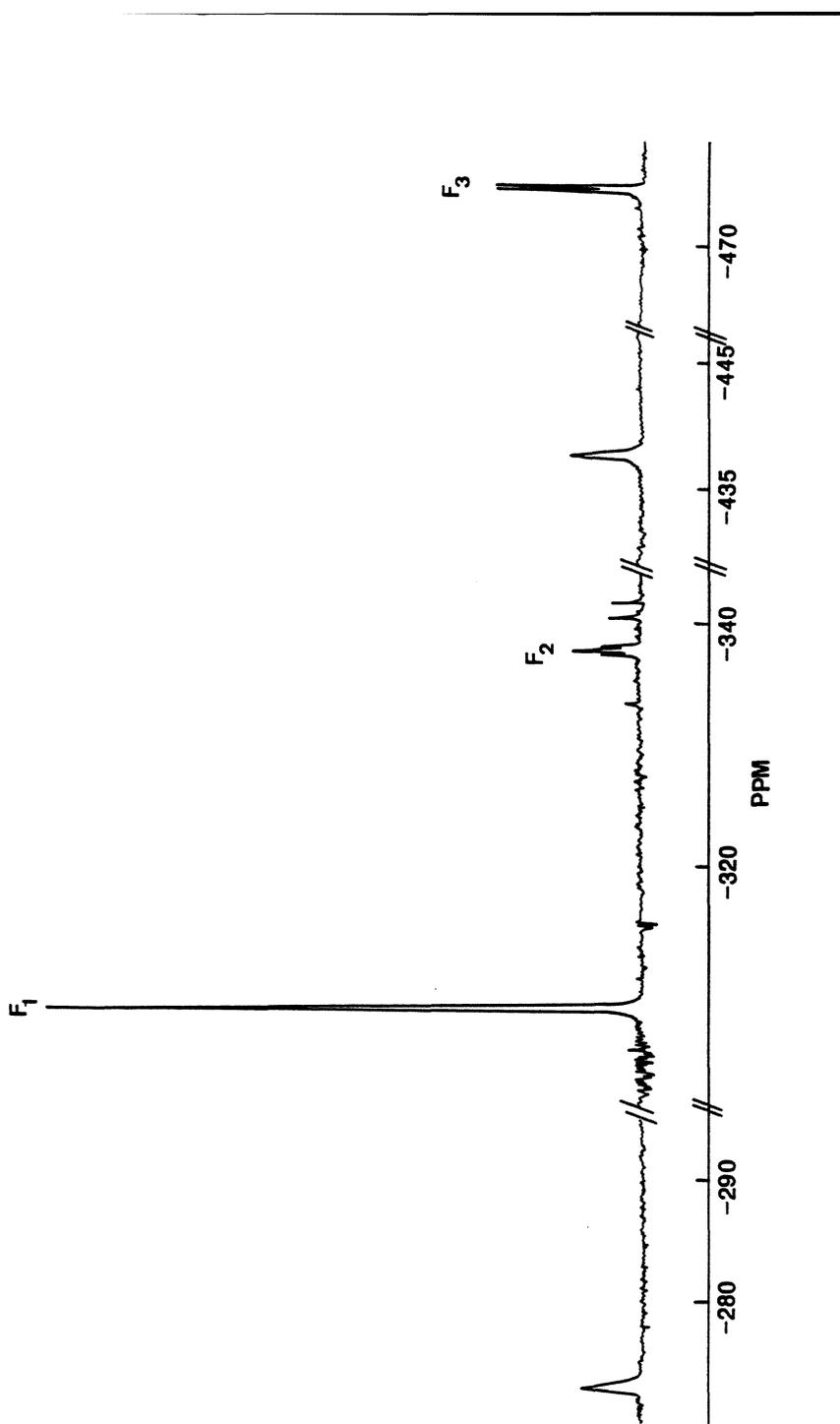
*Fac*-



*Mer*-

Undoubtedly the system undergoes slow exchange at room temperature but, for practical reasons, the coalescence point could not be obtained due to HF solvent leaching through the FEP NMR tubes at higher temperatures. The <sup>13</sup>C NMR spectra of the products from the reaction of XeF<sub>2</sub> with

**Fig 2.2**  $^{19}\text{F}$  NMR Spectrum of the Products from the Reaction Between  $\text{Ir}_4(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:6 Mole Ratio) at  $25^\circ\text{C}$  (Prior to the Removal of the Solvent)



$^{13}\text{C}$  enriched  $\text{Ir}_4(\text{CO})_{12}$  showed a broad second-order multiplet centred at  $\delta 131$ . Interpretation was greatly assisted by recording selective  $^{13}\text{C}\{^{19}\text{F}\}$  NMR spectra (Fig.2.3-2.5.) at the University of Edinburgh's Ultra high-frequency NMR service (600MHz). Irradiation at  $F_3$  ( $\delta$ -476) (b) only affected the resonances at  $\delta 130.7$  and  $\delta 141.6$ , removing the triplet couplings, whilst irradiation at the related  $F_2$  ( $\delta$ -338) (c) removed the doublet couplings on the same peaks. These resonances can therefore be assigned to CO trans- to F and CO trans- to CO in *mer*-  $\text{Ir}(\text{CO})_3\text{F}_3$ . Irradiation at  $F_1$  ( $\delta$ -310) (d) only affected the multiplet at ca.  $\delta 131$  which collapsed to a sharp singlet. Hence, this resonance can be assigned to the three equivalent carbonyls in *fac*-  $\text{Ir}(\text{CO})_3\text{F}_3$ . The fully coupled resonance can be successfully modelled as an  $\text{AXX}'_2$  system with the coupling constants given in Table 2.1.

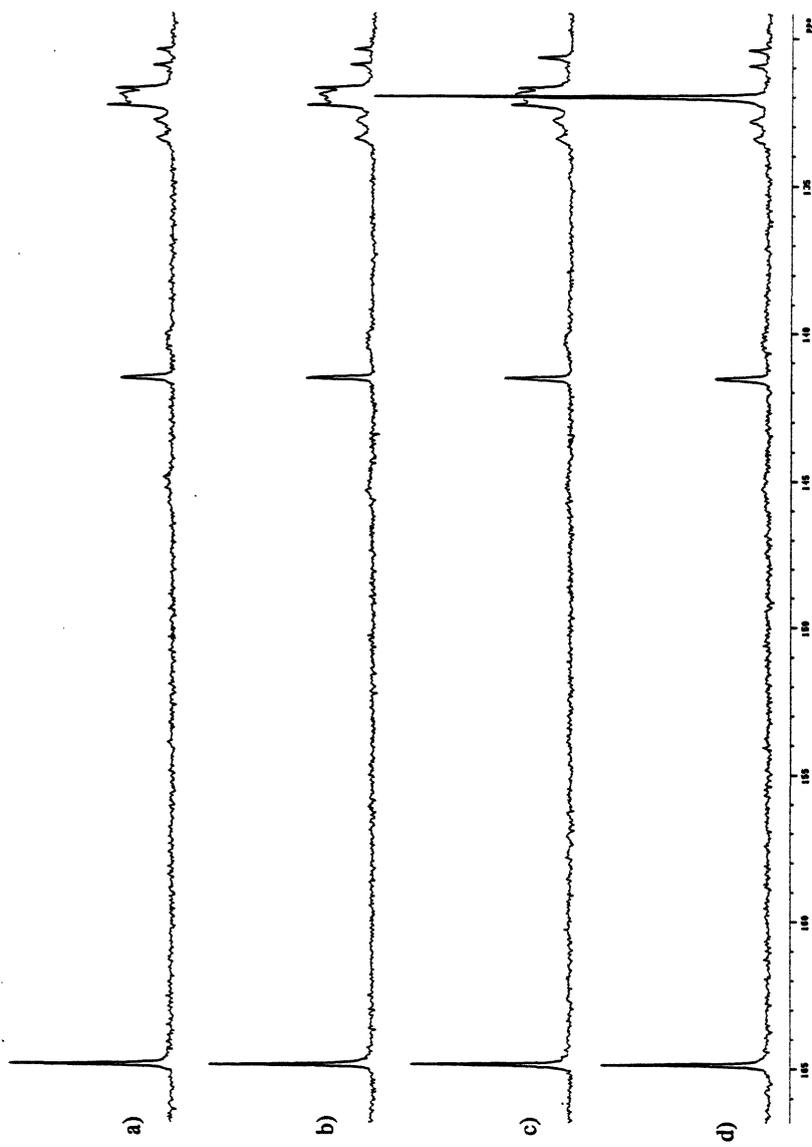
**Table 2.1**

$^{19}\text{F}$  and  $^{13}\text{C}$  NMR Parameters at 25°C

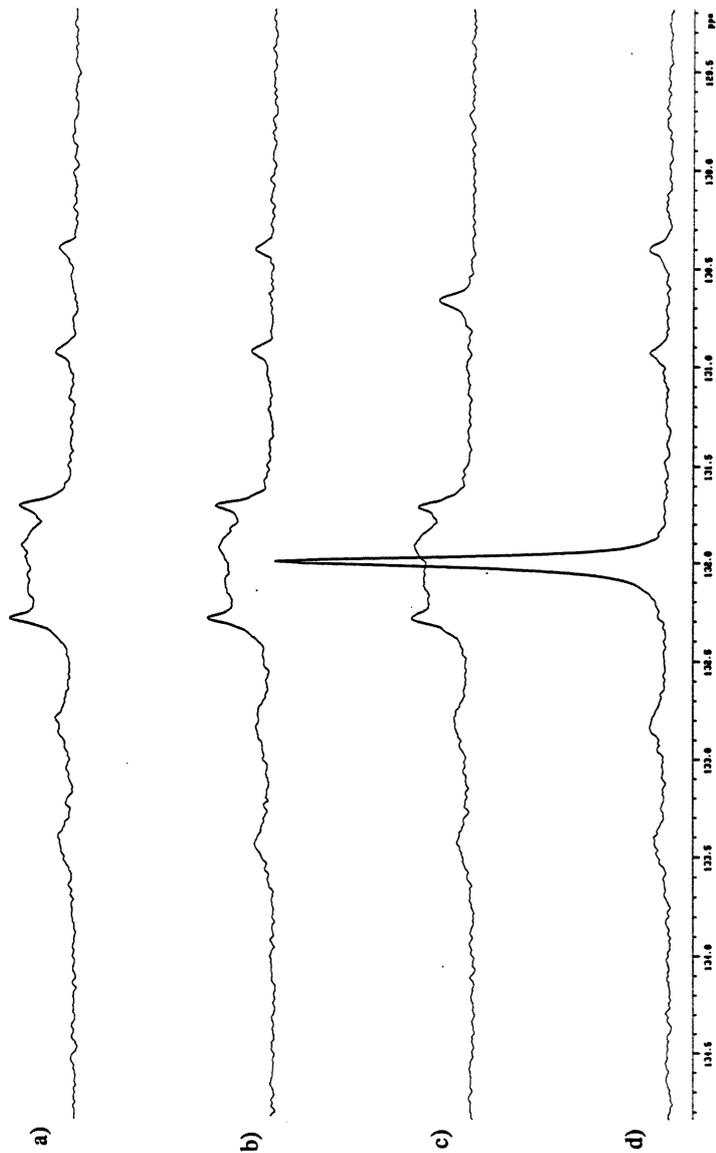
Complex	$^{19}\text{F}/\text{ppm}$	$^2J(\text{FF})/\text{Hz}$	$^{13}\text{C}/\text{ppm}$	$^2J(\text{FC})/\text{Hz}$
<i>fac</i> - [ $\text{Ir}(\text{CO})_3\text{F}_3$ ]	$F_1$ -310(s)	-	131.3 <sup>a</sup> CO(1)	.a
<i>mer</i> - [ $\text{Ir}(\text{CO})_3\text{F}_3$ ]	$F_2$ -338(t)	75	130.7(dt) CO(2)	79.2 <sup>b</sup> ,2 <sup>c</sup>
	$F_3$ -475(d)	75	141.6(dt) CO(3)	6.5,6.5

a,  $\text{AXX}'_2$  system, simulated with coupling constants of  $^2J(\text{F}_1\text{C})=84\text{Hz}$ ,  $^2J(\text{F}_2\text{C})=5\text{Hz}$  and  $^2J(\text{F}_3\text{C})=120\text{Hz}$ .  
b,  $^2J(\text{F}_2\text{C})$ .  
c,  $^2J(\text{F}_3\text{C})$ .

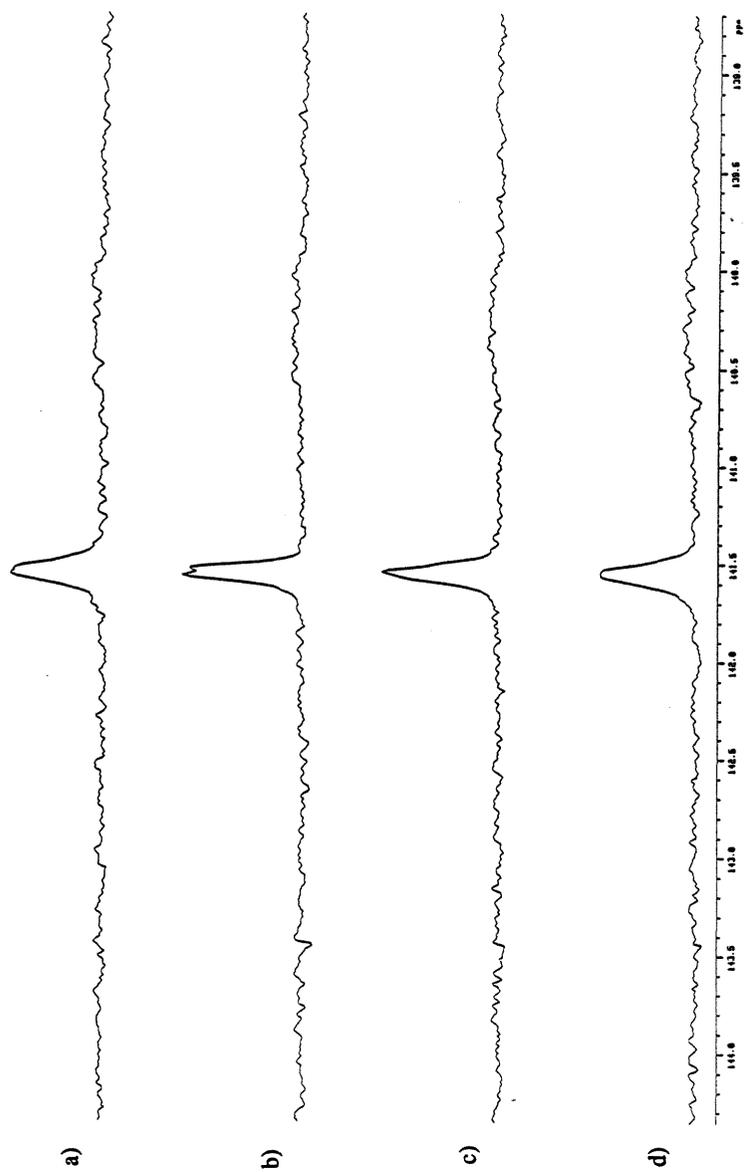
**Fig 2.3** Selective  $^{13}\text{C}\{^{19}\text{F}\}$  NMR Spectra of the Products from the Reaction Between  $\text{Ir}_4(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:6 Mole Ratio) at  $25^\circ\text{C}$  (Prior to the Removal of the Solvent)  
a)fully coupled b)decoupling  $\text{F}_3$  c)decoupling  $\text{F}_2$  d)decoupling  $\text{F}_1$



**Fig 2.4** Selective  $^{13}\text{C}\{^{19}\text{F}\}$  NMR Spectra of the Products from the Reaction Between  $\text{Ir}_4(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:6 Mole Ratio) at  $25^\circ\text{C}$  (Prior to the Removal of the Solvent)  
a)fully coupled b)decoupling F<sub>2</sub> c)decoupling F<sub>3</sub> d)decoupling F<sub>1</sub>



**Fig 2.5** Selective  $^{13}\text{C}(^{19}\text{F})$  NMR Spectra of the Products from the Reaction Between  $\text{Ir}_4(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:6 Mole Ratio) at  $25^\circ\text{C}$  (Prior to the Removal of the Solvent)  
a) fully coupled b) decoupling  $\text{F}_3$  c) decoupling  $\text{F}_2$  d) decoupling  $\text{F}_1$



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Removal of the solvent from the reaction mixture under high vacuum resulted in a yellow, very air-sensitive powder which, when redissolved in AHF, showed NMR spectra almost entirely attributable to *fac*-Ir(CO)<sub>3</sub>F<sub>3</sub> (>90%). Resonances assigned to *mer*-Ir(CO)<sub>3</sub>F<sub>3</sub> were absent. Attempts were made to find an alternative solvent for this complex, but, none were found to be suitable. The Ir(CO)<sub>3</sub>F<sub>3</sub> was insoluble in CH<sub>2</sub>Cl<sub>2</sub> and Genetron 113 and was reactive towards SO<sub>2</sub> and CH<sub>3</sub>CN, in the latter case with vigorous evolution of CO and the formation of a black solid.

As previously discussed, the solutions were allowed to remain at room temperature overnight as it was noted that NMR spectra recorded soon after reaction were relatively complicated, with resonances due to Ir(CO)<sub>3</sub>F<sub>3</sub> and uncharacterised intermediates. With time, rearrangement occurred so that Ir(CO)<sub>3</sub>F<sub>3</sub> represented approximately 75% of the products. The only other observable resonance in the <sup>13</sup>C NMR spectra was an apparent singlet at δ165, which will be discussed later, along with <sup>19</sup>F NMR resonances at δ-277 and -439.

A noteworthy observation from the <sup>13</sup>C NMR spectra recorded soon after reaction (~2hr.) is that the *mer*-isomer of Ir(CO)<sub>3</sub>F<sub>3</sub> is in greater relative abundance indicating that it is the more kinetically favoured isomer, whereas the *fac*-isomer is more thermodynamically stable as shown by the growth of its NMR signal with time. This is not unexpected, as bonding considerations suggest that CO

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*trans*- to F (or X<sup>-</sup>) is preferred to CO *trans*- to CO where two π-acidic ligands are competing for the same electron density on the central metal<sup>1,2</sup>.

Prior to this work, the only other halogen carbonyl of this type was Ir(CO)<sub>3</sub>I<sub>3</sub>, formed by the reaction of IrI<sub>3</sub> with CO under high temperature and pressure<sup>6</sup>. However, this complex readily loses CO even in the solid state to form the dimeric species, [Ir(CO)<sub>2</sub>I<sub>3</sub>]<sub>2</sub>. The analogous chloro- and bromo-species have not been reported to date. Hence, Ir(CO)<sub>3</sub>F<sub>3</sub> represents the first solid-state stable Ir(CO)<sub>3</sub>X<sub>3</sub>, X= halide, complex to be isolated.

As mentioned above, an apparent singlet at δ165 was observed in <sup>13</sup>C NMR spectra prior to the removal of the solvent. Variable temperature <sup>13</sup>C NMR experiments revealed that this apparent singlet was the fast exchange limit of a fluxional process. Unfortunately, because of the temperature range of the solvent employed, the limiting spectra could not be measured as this species was still fluxional at -80°C, only slightly above the freezing point of AHF. This high degree of fluxionality implies a coordinatively unsaturated complex, e.g. trigonal bipyramidal, where a low energy barrier for rearrangement would be expected.

Although the resonance is observed as a singlet at room temperature, the lack of coupling to fluorine is presumably either the result of the fluxional process (intermolecular exchange) or coupling which is small and

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not resolved in this experiment. It is likely, therefore, that this resonance is associated with at least one of the unassigned  $^{19}\text{F}$  NMR resonances at  $\delta$ -277 or -439. Unambiguous assignment of this species is only possible by reaching the low-temperature exchange limit. As the removal of the solvent appears to cause the decomposition of this species, this can only be obtained by depressing the freezing point of the AHF.

#### 2.4

##### The Reaction of $\text{Ir}_4(\text{CO})_{12}$ with $\text{XeF}_2$ in AHF (>1:6 Mole Ratio)

When the ratio of  $\text{Ir}_4(\text{CO})_{12}$  to  $\text{XeF}_2$  is increased above 1:6, a two-stage reaction is observed; an initial vigorous evolution of xenon gas as the solution is warmed to room temperature, followed by the much slower evolution of carbonyl fluoride ( $\text{COF}_2$ ), which was characterised by gas-phase IR spectroscopy. These solutions were left overnight with occasional venting so that the second phase of the reaction could reach completion. Solutions of 1:8 and 1:10 mole ratios showed both isomers of  $\text{Ir}(\text{CO})_3\text{F}_3$ , but, as the ratio was increased further, all the  $^{19}\text{F}$  NMR resonances due to metal fluorides disappeared.

A mole ratio of 1:26 was judged to be the end point of the reaction by the absence of any carbonyl bands in the IR spectrum of the yellow air-sensitive solid left after the removal of AHF. This solid was found to be  $[\text{XeF}][\text{IrF}_6]$ , by comparison of its IR and Raman spectral data with those

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in the literature<sup>13</sup>. The oxidation of Ir(0) to Ir(V) by XeF<sub>2</sub> has previously been reported by O'Donnell<sup>14</sup>, where iridium metal is oxidised to IrF<sub>5</sub> in anhydrous hydrogen fluoride. Presumably, the stoichiometry of the latter reaction precluded the formation of [XeF][IrF<sub>6</sub>].

## 2.5

### An Evaluation of the only Previous Report of a Iridium Carbonyl Fluoride Complex

The only previously reported example of an iridium complex stabilised solely by carbonyl and fluoride ligands is that by Misra<sup>15</sup> who, with only limited data, made questionable assignments. From the reaction of IrF<sub>5</sub> with carbon monoxide at atmospheric pressure, he isolated a complex which he suggested was Ir(CO)<sub>2.5</sub>F<sub>2</sub> on the basis of elemental analysis.

Subsequent "purification" by a high temperature and pressure carbonylation reaction produced two complexes assigned as Ir(CO)<sub>2</sub>F<sub>2</sub> and Ir(CO)<sub>3</sub>F<sub>2</sub>, although both of these materials appear to give essentially the same IR spectrum and have almost identical elemental analyses, consistent with "Ir(CO)<sub>3</sub>F<sub>2</sub>".

Comparison of the IR data in the νCO region of "Ir(CO)<sub>3</sub>F<sub>2</sub>"<sup>15</sup> with Ir(CO)<sub>3</sub>F<sub>3</sub> (this work) reveals a fairly good correlation of the strong, high frequency IR bands (Table 2.2) suggesting the reassignment of Misra's "Ir(CO)<sub>3</sub>F<sub>2</sub>" as Ir(CO)<sub>3</sub>F<sub>3</sub>. However, other data has to be considered before such a reassignment is made.

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Misra's elemental analysis is not consistent with an Ir:F ratio of 1:3, and his mass spectrum shows not only monomeric species but also dimeric and trimeric fragments. These observations could possibly be the result of polymeric impurities, explaining the extra bands observed as shoulders in the IR spectrum of "Ir(CO)<sub>3</sub>F<sub>2</sub>". However, reassignment, based purely on IR spectral data, can only be substantiated by repeating the original work and recording NMR spectra on the products.

**Table 2.2**

Comparison of  $\nu(\text{CO})$  IR Bands for "Ir(CO)<sub>3</sub>F<sub>2</sub>" and Ir(CO)<sub>3</sub>F<sub>3</sub>/cm<sup>-1</sup>

Ir(CO) <sub>3</sub> F <sub>2</sub>	Ir(CO) <sub>3</sub> F <sub>3</sub> (this work)
2210 s	2213 s
2170 s	2165 s
2155 sh	n/o
2085 sh	n/o

n/o not observed

## 2.6

### The EXAFS Analysis of Ir(CO)<sub>3</sub>F<sub>3</sub>

An inability to obtain suitable single crystals for X-ray crystallographic studies meant that structural information had to be obtained by an alternative technique. Recent work<sup>16,19</sup> has shown EXAFS to be a valuable tool for obtaining bond length data on compounds when other methods have failed or are inappropriate.

In a typical experiment, metal L<sub>III</sub>-edge EXAFS data were collected at the Daresbury Synchrotron Radiation Source on station 7.1 in transmission mode. Sample preparation was conveniently achieved by flattening a FEP NMR tube, so that solution EXAFS could be obtained on a sample of Ir(CO)<sub>3</sub>F<sub>3</sub> in AHF, once the <sup>19</sup>F and <sup>13</sup>C NMR spectra had been checked.

Initially the EXAFS data was modelled utilising EXCURVE90<sup>17</sup> and revealed the expected three shells of atoms around the central metal, consistent with Ir(CO)<sub>3</sub>F<sub>3</sub>. Subsequent calculations involving multiple scattering of the oxygen shell resulted in a final determination of the three shells as 3C's, 3F's, and 3O's at 1.93, 2.00 and 3.07Å respectively. However, two other obvious features were present at 3.54 and 4.87Å (Fig.2.6). Since the monomeric nature of the complex had already been unambiguously proven, these longer distance cannot be the result of any polymeric species. A possible explanation is the strong interaction of the solvent, HF, with Ir(CO)<sub>3</sub>F<sub>3</sub>.

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The data was successfully modelled with two additional shells of 5 and 2 fluorine atoms at 3.54 and 4.87Å respectively. The validity of this solvated model was subsequently tested with another monomeric complex, OsF<sub>6</sub>.

Osmium hexafluoride is known to dissolve in AHF to molar concentrations. Conductivity measurements indicate that there is only a very low level of ionisation, and Raman spectroscopic studies show that the octahedral geometry is unperturbed in solution<sup>18</sup>. Room temperature EXAFS experiments on OsF<sub>6</sub> in AHF, conducted in an identical manner to that for Ir(CO)<sub>3</sub>F<sub>3</sub>, revealed the expected six F's at 1.82Å, in very good agreement with that obtained for solid OsF<sub>6</sub> at 10K<sup>19</sup>. However, two additional, well defined features at 3.21 and 3.37Å modelled as 8 and 6 fluorines respectively, resulted in a significant reduction in the R-factor and fit index (Fig.2.7). These extra shells can only sensibly be rationalised as arising from solvent interaction, in agreement and therefore substantiating the Ir(CO)<sub>3</sub>F<sub>3</sub>/AHF model.

Comparison of the bond length data for Ir(CO)<sub>3</sub>F<sub>3</sub> with those of other fluoro-complexes of low-valent metals is hampered by the paucity of such structural information. The Ir-F distance of 2.00Å is consistent with that observed for other terminal fluoride ligands (Table 2.4). However, the Ir-C bond length, when compared with those in the same complexes, seems to be slightly longer than those reported for a carbonyl *trans*- to a fluoride ligand. Generally, for

Fig 2.6 The Background-Subtracted EXAFS ( $k^3$  weighted) and the Fourier Transform of  $\text{Ir}(\text{CO})_3\text{F}_3/\text{HF}$

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EO -5.77 VPI -1.36 AFAC 0.67
EMIN 52.44 EMAX 780.50 RMIN 0.10
RMAX 10.00 VIND 2.00 VP 0.10
EF -15.57 MPI 0.00

FT . 111111111 F1 0.00037 R 17.9799

N1 3.0 T1 3(C) R1 1.934 A1 -0.003
N2 3.0 T2 2(F) R2 1.999 A2 -0.002
N3 3.0 T3 4(O) R3 3.045 A3 0.008
N4 3.0 T4 2(F) R4 3.538 A4 0.027
N5 2.0 T5 2(F) R5 4.869 A5 0.003

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PARAMETERS Ir613.par92
PHASESHIFTS ex921r.ph
ex920a.ph
ex920a.ph
  
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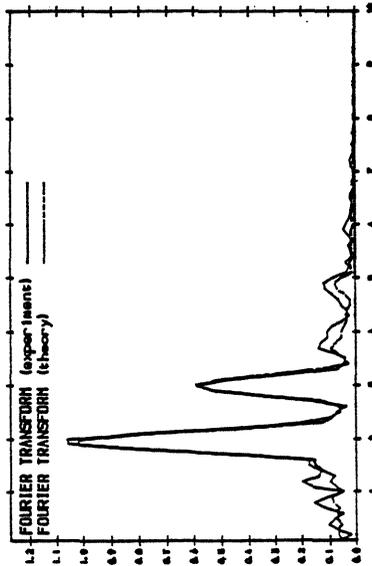
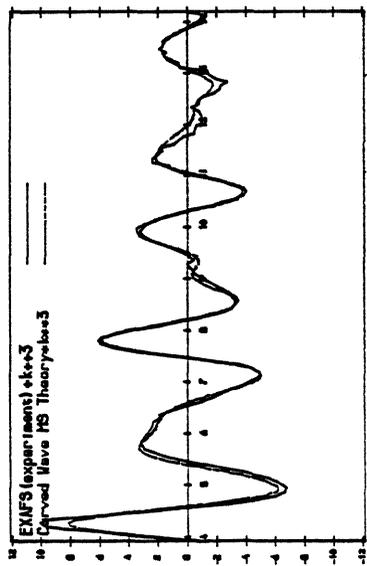
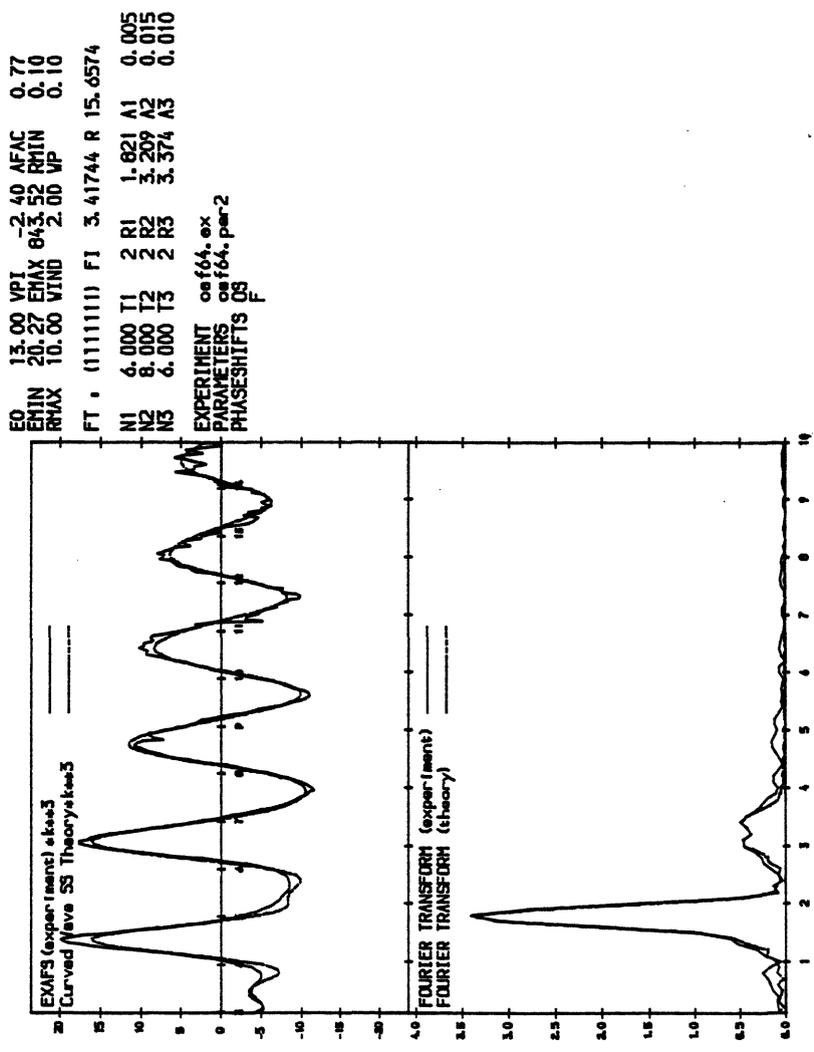


Fig 2.7 The Background-Subtracted EXAFS ( $k^3$  weighted) and the Fourier Transform EXAFS of OsF<sub>6</sub>/HF



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organometallic iridium carbonyl complexes, the range for the Ir-CO bond length is 1.898-1.839Å (av. 1.87)<sup>20</sup>. In considering the possible strength of the iridium-carbon bond in *fac*-Ir(CO)<sub>3</sub>F<sub>3</sub>, it is worth noting the IR spectrum of the solid. This molecule, with facial carbonyls and fluorides, possesses C<sub>3v</sub> symmetry and therefore from a group theory analysis is predicted to exhibit two IR active VCO bands (A<sub>1</sub> and E). However, these were observed at very high frequency, 2213 and 2170cm<sup>-1</sup>.

To a first approximation, since VCO occurs in a region of the IR spectrum significantly removed from other vibrations, C-O stretching frequencies can be regarded as being independent from other vibrations in the molecule<sup>21</sup>. Therefore a relationship between VCO frequencies and CO bond order can reasonably be established<sup>22</sup>. Generally<sup>22</sup>, the bonding between CO and a transition metal is described as involving the donation of electron density from the HOMO of CO (5σ\*) into an empty hybrid AO of the metal, in conjunction with the donation of electron density from the filled or partially filled AO of the metal to the LUMO of CO (2π\*); this latter interaction is termed back-bonding. The overall effect is a synergic type of bonding where the CO ligand is considered to act as both a σ-donor and π-acceptor. As the back-bonding from the metal to CO increases, the M-C bond should become stronger (shorter) and the C-O bond correspondingly weaker (longer). This increase in M-C bond order and, conversely, the decrease

for C-O, is manifested in the positions of the IR active bands of the resulting complexes, which usually show a shift to lower frequency on coordination to a metal (relative to free CO) in accordance with the bonding description described above<sup>23</sup>. However, for Ir(CO)<sub>3</sub>F<sub>3</sub>, the values of the IR bands are observed to be at higher frequency than for free CO.

Prior to this work there have been a few reports of such co-ordinated carbonyl complexes exhibiting IR frequencies higher than free carbon monoxide itself<sup>23</sup>.

**Table 2.3**

Comparison of the IR data of Ir(CO)<sub>3</sub>F<sub>3</sub>

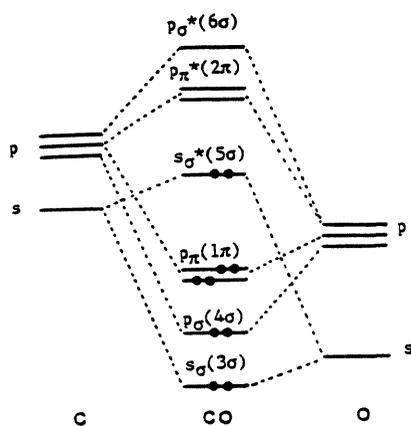
Complex	$\nu(\text{CO})/\text{cm}^{-1}$	Ref
Ir(CO) <sub>3</sub> F <sub>3</sub>	2213(s), 2165(s)	
Free CO <sup>a</sup>	2143	
NiF <sub>2</sub> (CO) <sup>b</sup>	2204	
Cu(CO) <sup>+c</sup>	2180	
Ag(CO) <sup>+c</sup>	2204	
Au(CO) <sup>+c</sup>	2198	

a. gas-phase; b matrix; c Nujol mull

DeKock *et al.*<sup>24</sup> interpreted the very high  $\nu\text{CO}$  IR frequency in NiF<sub>2</sub>(CO) as being a feature of a complex in which the carbonyl was entirely  $\sigma$ -bonded. Later, in 1979, Desjardins *et al.*<sup>25</sup> explained the increase in the IR frequency of Cu(CO)<sup>+</sup> relative to that of free CO, as being

attributable to  $\sigma$ -donation from the slightly antibonding  $5\sigma$  lone pair<sup>26</sup> of CO (Fig 2.8) towards the cuprous ion, increasing the positive charge on carbon and therefore the CO bond order. They also suggested that there was, presumably, only weak  $\pi$ -back donation. More recently, Willner and Aubke<sup>27</sup> substantiated this interpretation with a report of an  $\nu_{CO}$  IR band for  $\text{Au}(\text{CO})^+$ , at  $2198 \text{ cm}^{-1}$ , from which they suggested that the acceptor ability of a metal is increased by weakly electrophilic anionic ligands, in this case  $\text{AsF}_6^-$  and  $\text{SO}_3\text{F}^-$ , and that there would appear to be little or no  $\pi$ -back donation from the metal to the carbonyl. The phenomenon of CO acting solely as a  $\sigma$ -donor is probably best described for the adduct  $\text{BH}_3\text{CO}$ <sup>28</sup>; the central atom, boron, being devoid of the ability to  $\pi$ -back donate. For this adduct  $\nu_{CO}$  is observed at  $2164 \text{ cm}^{-1}$ .

Fig 2.8 Molecular Orbital Diagram of Carbon Monoxide



Comparison of these results with those obtained for  $\text{Ir}(\text{CO})_3\text{F}_3$  implies that the carbonyls are bonded in a similar manner, where there is little or no  $\pi$ -back donation which would be expected to shorten the Ir-C bond. Presumably, in a similar way to that reported by Willner and Aubke, the electron withdrawing fluoride ligands are effectively removing the electron density from the  $d^6$  Ir(III) metal centre, increasing the  $\sigma$ -acceptor ability of the metal.

**Table 2.4**

Selected Bond Length Data for Various Fluoro-Complexes (Å)

Complex	(C-O) <i>trans</i> -F	(C-O) <i>trans</i> -CO	M-CO <i>trans</i> -CO	M-CO <i>trans</i> -F	M-F (terminal)	M-F (bridging)	Ref <sup>a</sup>
$\text{Ir}(\text{CO})_3\text{F}_3$	1.13			1.934(4)	1.999(2)		-
$\text{F}_5\text{-Re-F-Re}(\text{CO})_5$	1.19(4)	Av.1.13	Av.1.99	1.89(3)	-	2.20(2)	41,42
$[\text{Re}(\text{CO})_6]^+$ $[\text{Re}_2\text{F}_{11}]^-$	-	Av.1.13	Av.2.01		Av. 1.84(2)	2.009(2)	41,42
$[\text{Re}(\text{CO})_3\text{F}]_4 \cdot 4\text{H}_2\text{O}$	Av. 1.153(10)			Av. 1.893(7)		Av. 2.200(5)	47
$\text{ReF}(\text{CO})_3(\text{tmeda})$	1.146(9)			1.913(6)	2.039(4)		49
$[\text{Ru}(\text{CO})_3\text{F}_2]_4$	1.18(7) 1.20(7)			1.90(7) 1.84(7)	1.99(7)	2.04(7)	59
$[\text{IrF}(\text{CO})\text{L}(\text{PPh}_3)_2]^{\text{+b}}$						2.21(4)	85
$[\text{IrF}(\text{CO})_2(\text{COF})(\text{PEt}_3)_2]^{\text{+}}$			1.989(5) <i>trans</i> - to COF	1.883(5)	1.998(3)		81

a, References pertain to Chapter One

b, L=(NHN C<sub>6</sub>H<sub>3</sub>-2-CF<sub>3</sub>)

## 2.7

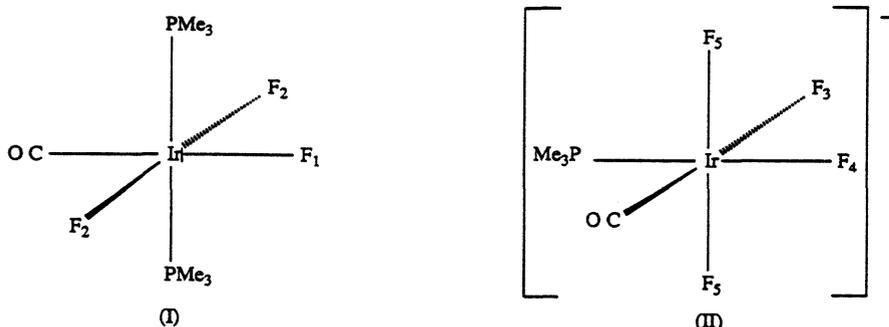
### Reaction of *fac*-Ir(CO)<sub>3</sub>F<sub>3</sub> with PMe<sub>3</sub>

Following the unambiguous characterisation of *fac*-Ir(CO)<sub>3</sub>F<sub>3</sub>, it was of interest to investigate the chemistry of this very reactive species. The substitution of carbonyls by various  $\pi$ -acceptor ligands such as phosphines, arsines, stibines, nitrous oxide and amines is well established in the literature<sup>29</sup>. Of these ligands, phosphines were targeted, because the 100% spin  $\frac{1}{2}$  <sup>31</sup>P nuclei provides another NMR handle which, in conjunction with <sup>19</sup>F NMR spectroscopy, should facilitate characterisation of the resulting complexes. Of the various phosphine ligands available, PMe<sub>3</sub> was used in the preliminary investigation since, being volatile, it could be easily manipulated in the vacuum line, essential for handling the very reactive Ir(CO)<sub>3</sub>F<sub>3</sub>.

*Fac*-Ir(CO)<sub>3</sub>F<sub>3</sub> was found to be insoluble in CD<sub>2</sub>Cl<sub>2</sub> at room temperature but, on addition of PMe<sub>3</sub>, vigorous evolution of CO occurred with the development of a yellow solution.

Combinations of <sup>19</sup>F, <sup>31</sup>P and <sup>13</sup>C NMR spectroscopic data revealed the presence of two major complexes in solution, (I) and (II), and <sup>13</sup>C and <sup>31</sup>P NMR data provided evidence of a third complex, (III), which did not contain

fluorine. All the NMR data (Table 2.6) described below are from mixtures of (I), (II) and (III).

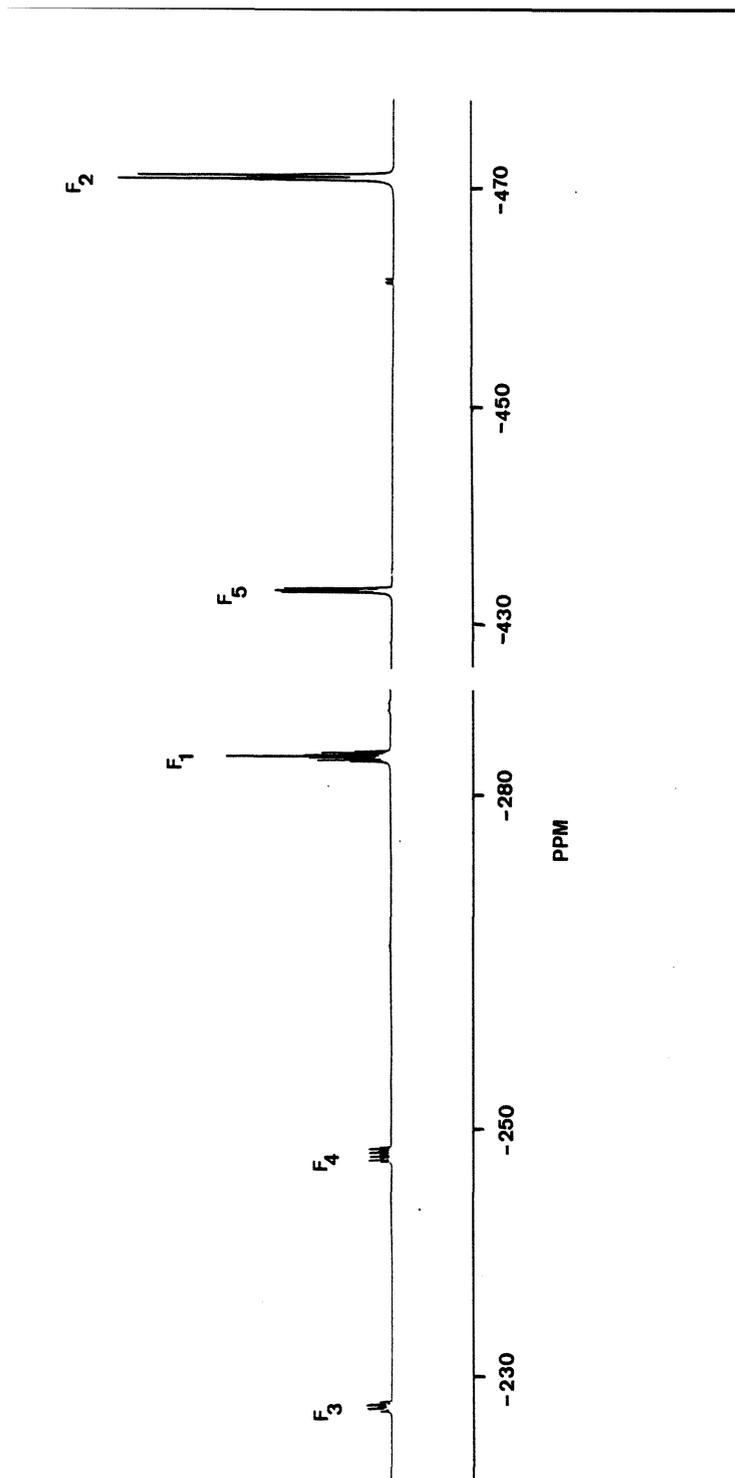


(III)

### 2.8 Discussion of the Data for $\text{IrF}_3(\text{CO})(\text{PMe}_3)_2$

The  $^{19}\text{F}$  NMR spectrum of complex (I) revealed two resonances at  $\delta$ -284.6 and  $\delta$ -470.6, due to  $\text{F}_1$  and  $\text{F}_2$ , (Fig.2.9 and 2.10) in a ratio of 1:2 respectively. That associated with  $\text{F}_1$  is observed as a triplet of triplets and that due to  $\text{F}_2$  as a doublet of triplets with mutual  $^2\text{J}(\text{FF})$  coupling of 97Hz for the triplet and doublet couplings respectively. The remaining triplet couplings on each resonance arise from *cis*- couplings of the fluorines to two equivalent *trans*- phosphine ligands, (Fig.2.10), consistent with the structure of (I), and confirmed by the observation of a doublet of triplets in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. The only discernible information from the  $^{13}\text{C}$  NMR spectrum, an expected 18 line pattern, was the large *trans*-

Fig 2.9  $^{19}\text{F}$  NMR Spectrum of the Reaction Between  $\text{Fac-Ir}(\text{CO})_3\text{F}_3$  and  $\text{PMe}_3$



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F coupling (see Table 2.6).

Fluoro-complexes of Ir(III) generally result from the oxidative addition of substrate A-B to various  $d^8$  Ir(I) starting materials, in one of two ways. Either the A-B substrate is added to a fluoro precursor, e.g.  $\text{Ir}(\text{CO})\text{F}(\text{PPh}_3)_2$ , or A-B is a fluorinating agent such as  $\text{SF}_4$ , where the oxidative addition of an S-F bond to  $\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2$  affords  $\text{IrF}(\text{CO})\text{Cl}(\text{SF}_3)(\text{PEt}_3)_2$  (see Chapter 1). As these two preparative procedures have only been carried out separately, only monofluoro carbonyl complexes of iridium were known.

Iridium(III) carbonyl phosphine halo-complexes of the type  $\text{Ir}(\text{CO})\text{XY}_2\text{L}_2$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$ ,  $\text{Y}_2 = \text{Cl}_2, \text{Br}_2, \text{or I}_2$  and  $\text{L} =$  various phosphine ligands) have been obtained by the oxidative addition of halogens  $\text{Y}_2$  to  $\text{Ir}(\text{CO})\text{XL}_2^{30}$ . Of these, the fluoro-complexes obtained result from the reaction of  $\text{Cl}_2, \text{Br}_2, \text{or I}_2$  with  $\text{Ir}(\text{CO})\text{F}(\text{PPh}_3)_2$ . There is no reported example of fluorine gas being used in a similar investigation, presumably for practical reasons.

Very recently Cockman *et al.*<sup>11</sup> successfully identified the first example of  $\text{F}_2$  addition, where the fluorinating agent  $\text{XeF}_2$  was allowed to react with  $\text{M}(\text{CO})\text{X}(\text{PEt}_3)_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ; and  $\text{M} = \text{Ir}, \text{Rh}$ ) in solution to give  $\text{M}(\text{CO})\text{F}_2\text{X}(\text{PEt}_3)_2$  and thus completing the series of  $\text{M}(\text{CO})\text{XY}_2(\text{PEt}_3)_2$  complexes ( $\text{X}$  and  $\text{Y} =$  halogen). Since  $\text{Ir}(\text{CO})\text{F}(\text{PEt}_3)_2$  has not been reported in the literature, the comparable reaction of this Ir(I) complex with  $\text{XeF}_2$  which should result in the

formation of the trifluoro Ir(III) derivative,  $\text{Ir}(\text{CO})\text{F}_3(\text{PEt}_3)_2$ , could not be undertaken. However, this Ir(III) complex was observed in the NMR analysis of the products of the reaction of  $\text{IrX}(\text{CO}(\text{PEt}_3)_2)$  with  $\text{XeF}_2$  from what was considered to be an intermolecular halogen rearrangement process. However, it only represented a minor component of the reaction mixture.

Comparison of the NMR data of  $\text{Ir}(\text{CO})\text{F}_3(\text{PEt}_3)_2$ <sup>11</sup> and  $\text{Ir}(\text{CO})\text{F}_3(\text{PMe}_3)_2$  (I) shows the relative insensitivity of <sup>19</sup>F NMR chemical shifts and coupling constants to changes in the phosphine ligand. In contrast, a marked difference in the <sup>31</sup>P chemical shifts associated with the  $\pi$ -acidity of the two phosphines was observed<sup>31</sup>.

**Table 2.5**

Comparison of NMR data.

Complex	$\delta\text{F}_1$	$\delta\text{F}_2$	$2\text{J}(\text{FF})$	$2\text{J}(\text{PF}_1)$	$2\text{J}(\text{PF}_2)$	$\delta^{31}\text{P}$
$[\text{Ir}(\text{CO})\text{F}_3(\text{PEt}_3)_2]$	-288.5	-470.6	96	31	18	6.9
$[\text{Ir}(\text{CO})\text{F}_3(\text{PMe}_3)_2]$	-284.6	-470.6	97	38	24	-14.2

Although (I) does not represent the first example of a trifluoro-iridium phosphine complex, it is the first report of an attempt to prepare such a species. It is also the first example of this type of complex being obtained in a significant yield.

Fig 2.10 Expansion of F<sub>1</sub> and F<sub>2</sub>

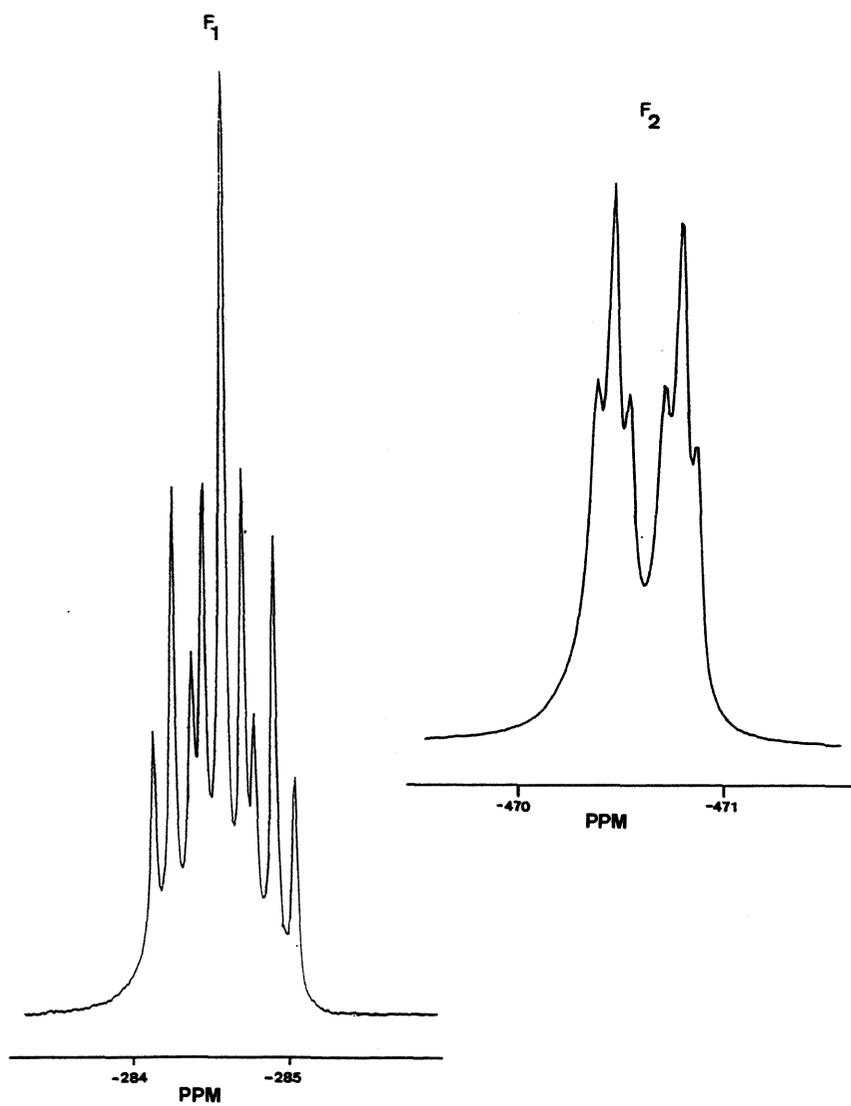
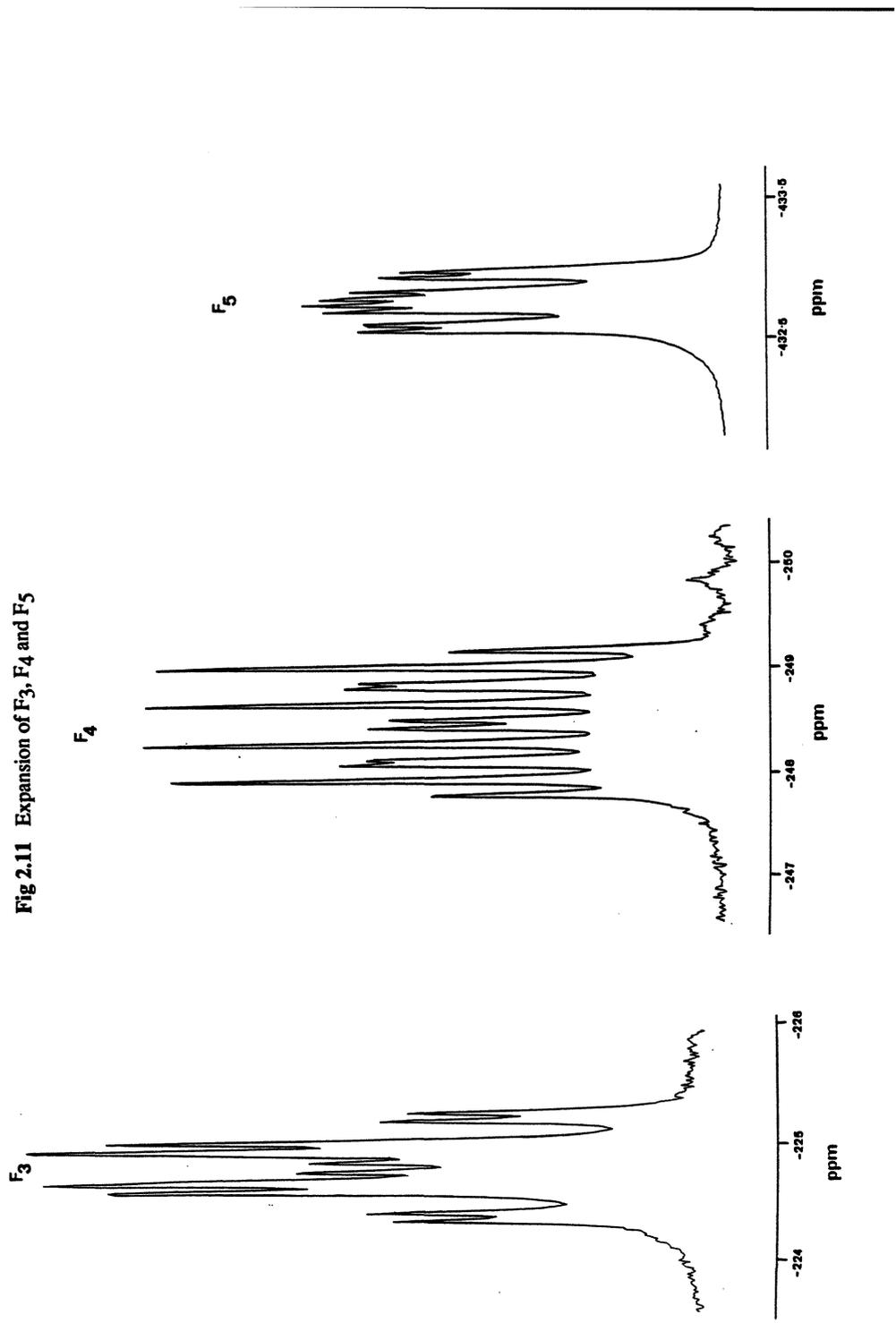


Fig 2.11 Expansion of F3, F4 and F5



### 2.9 Discussion of the Data for $[\text{IrF}_4(\text{CO})(\text{PMe}_3)]^-$

The  $^{19}\text{F}$  NMR spectrum of complex (II) revealed three resonances, at  $\delta$ -224.9, -248.5 and -432.8, associated with  $\text{F}_3$ ,  $\text{F}_4$  and  $\text{F}_5$ , respectively in a ratio of 1:1:2 see (Fig. 2.9 and 2.11).  $\text{F}_3$  was observed as a doublet ( $^2\text{J}(\text{F}_3\text{F}_4)=100\text{Hz}$ ) of triplets ( $^2\text{J}(\text{F}_3\text{F}_5)=70\text{Hz}$ ) of doublets ( $^2\text{J}(\text{F}_3\text{P})=19\text{Hz}$ ),  $\text{F}_4$  as a doublets ( $^2\text{J}(\text{F}_4\text{P})=208\text{Hz}$ ) of doublets ( $^2\text{J}(\text{F}_4\text{F}_3)=100\text{Hz}$ ) of triplets ( $^2\text{J}(\text{F}_4\text{F}_5)=43\text{Hz}$ ) and  $\text{F}_5$  as a doublet ( $^2\text{J}(\text{F}_5\text{F}_3)=70\text{Hz}$ ) of doublets ( $^2\text{J}(\text{F}_5\text{F}_4)=43\text{Hz}$ ) of doublets ( $^2\text{J}(\text{F}_5\text{P})=13\text{Hz}$ ), (Fig. 2.11). The couplings were consistent with the structure of (II), which was confirmed by observing a doublet of doublet of triplets in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at  $\delta$ -29.2. As with compound (I), the only discernible information from the  $^{13}\text{C}$  NMR spectrum was the large *trans*- F coupling.

The  $^{19}\text{F}$  chemical shifts for complex (II),  $([\text{Ir}(\text{CO})\text{F}_4(\text{PMe}_3)]^-)$ , although still within the expected regions for F *trans*- to F and F *trans*- to CO (and in this case F *trans*- to  $\pi$ -acceptor ligand) are observed at higher frequency than those of the neutral  $\text{Ir}(\text{CO})_3\text{F}_3$  and  $\text{Ir}(\text{CO})\text{F}_3(\text{PR}_3)_2$  complexes above. This is somewhat surprising as increasing negative ionic charge is usually associated with increase in the shielding of the NMR nucleus (see NMR discussion 3.3).

Complex (II) represents the first example of a transition metal carbonyl phosphine complex co-ordinated by four fluoride ligands, and is best regarded as an anionic

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18 electron Ir(III) species, analogous to carbonyl halide complexes of the type  $\text{Ir}(\text{CO})_2\text{X}_4^-$  where X= Cl, Br and  $\text{I}^{32}$ , and the phosphine carbonyl halide complexes of the type  $\text{Ir}(\text{PR}_3)_2\text{X}_4^-$  ( $\text{PR}_3 = \text{PEt}_3, \text{PEt}_2\text{Ph}$ )<sup>33</sup>. The former species are obtained from the halogenation of the respective  $\text{Ir}(\text{CO})_2\text{X}_2^-$  in poorly co-ordinating solvents, the carbonyl ligands being very labile and easily replaced.

#### 2.10 Discussion of the Data for $[\text{Ir}(\text{CO})(\text{PMe}_3)_4]^+$

The third major complex in solution, (III), was identified by comparison of its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum with that of  $[\text{Ir}(\text{CO})(\text{PMe}_3)_4]\text{Cl}$  prepared by the reaction of  $\text{Ir}(\text{CO})\text{Cl}(\text{PEt}_3)_2$  and  $\text{PMe}_3$ . The  $^{13}\text{C}$  NMR spectrum of (III) was observed as a quintet due to coupling to four equivalent phosphorus ligands presumably resulting from a complex which is fluxional on the NMR timescale. As coupling is observed to all the phosphorus ligands, even in the presence of excess  $\text{PMe}_3$ , the fluxional process must be intramolecular. Complex (III) is presumably acting as the counter-ion in solution to  $[\text{Ir}(\text{CO})(\text{PMe}_3)_4\text{F}_4]^-$  (II). The overall reaction represents a preliminary study and, to date, no attempt has been made to isolate the individual complexes. However, the differing charge on these species suggests that such a separation could be possible from the addition of various salts to the solution. It would also be of interest to investigate the initial products from reaction. The reaction described above represents the

thermodynamically favoured species in the presence of excess  $\text{PMe}_3$ . The resulting solution from the reaction was also allowed to stand, at room temperature, for ~10 hours. This reaction of  $\text{Ir}(\text{CO})_3\text{F}_3$  with  $\text{PMe}_3$  exhibits the possible usefulness of this iridium carbonyl fluoride as a precursor to many different complexes derived from similar substitution reactions.

**Table 2.6**

NMR Data for Complexes (I) and (II) at 25°C

$\text{IrF}_3(\text{CO})(\text{PMe}_3)_2$	$\delta$	$^2J(\text{F}_1\text{F}_2)/\text{Hz}$	$^2J(\text{PF})/\text{Hz}$	$^2J(\text{F}_1\text{C})/\text{Hz}$
$\text{F}_1$ (tt)	-284.6	97	38	-
$\text{F}_2$ (dt)	-470.6	97	23	-
$^{31}\text{P}$ (dt)	-14.2	-	38,23	-
$^{13}\text{CO}$	159.1	-	-	86

$[\text{IrF}_4(\text{CO})(\text{PMe}_3)]^-$	$\delta$	$^2J(\text{F}_3\text{F})/\text{Hz}$	$^2J(\text{F}_4\text{F})/\text{Hz}$	$^2J(\text{F}_5\text{F})/\text{Hz}$	$^2J(\text{PF})/\text{Hz}$	$^2J(\text{F}_3\text{C})/\text{Hz}$
$\text{F}_3$ (tdd)	-224.9	-	100	70	19	-
$\text{F}_4$ (ddt)	-248.5	100	-	43	208	-
$\text{F}_5$ (ddd)	-432.8	70	43	-	13	-
$^{31}\text{P}$ (ddt)	-29.2	-	-	-	208,19,13	-
$^{13}\text{CO}$	157.5	-	-	-	-	100

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## CHAPTER THREE

### Synthesis And Characterisation Of Fluoro-Complexes Of Osmium

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Carbonyl halide complexes of osmium have been extensively studied for the heavier halogens Cl, Br and I, and the preparations and formulation of these species have been reviewed<sup>1</sup>. Generally they either result from a high pressure, high temperature carbonylation reaction of the metal halide, or by the halogenation of the metal carbonyl. However, to date there is only one preliminary report of an osmium complex stabilised solely by carbonyl and fluoride ligands<sup>2</sup>, "[Os(CO)<sub>3</sub>F<sub>2</sub>]<sub>4</sub>", which is discussed later. In fact the only other reported example of an organometallic carbonyl fluoro-complex of osmium is OsF(CO)<sub>2</sub>(NNPh)(PPh<sub>3</sub>)<sub>2</sub> (see Section 1.9).

### 3.1 Reaction between M<sub>3</sub>(CO)<sub>12</sub> (M=Ru and Os) and AHF

The reaction between Os<sub>3</sub>(CO)<sub>12</sub> and XeF<sub>2</sub> was carried out in AHF, since these reagents were previously shown by Hewitt<sup>2</sup> to be unreactive in common organic solvents. Therefore it was of interest to investigate the interaction, if any, of Os<sub>3</sub>(CO)<sub>12</sub> with AHF. This study was extended to the Ru<sub>3</sub>(CO)<sub>12</sub>/AHF system for comparison.

Ru<sub>3</sub>(CO)<sub>12</sub> and Os<sub>3</sub>(CO)<sub>12</sub> were found to react with AHF, in FEP reaction tubes, in a similar manner to that previously described for Ir<sub>4</sub>(CO)<sub>12</sub>, forming orange and yellow solutions respectively. The <sup>1</sup>H and <sup>13</sup>C NMR spectra revealed the presence of more than one protonated species in both cases. Thus, as with Ir<sub>4</sub>(CO)<sub>12</sub>, the reactions closely parallel the analogous protonation by *conc.* H<sub>2</sub>SO<sub>4</sub>. The

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similarity of the two acids is outlined in Section 2.2.

A significant amount of work has been carried out on protonation reactions of transition metal carbonyls with sulphuric acid. J.Knight *et al.*<sup>3</sup> have investigated the protonation of  $M_3(CO)_{12}$ , where  $M = Fe, Ru$  and  $Os$ . The iron carbonyl,  $Fe_3(CO)_{12}$ , decomposed rapidly in a 98% sulphuric acid solution, but ruthenium and osmium analogues dissolved only slowly at room temperature to give solutions which were air-stable for many days. The presence of a hydride ligand was confirmed by  $^1H$  NMR spectroscopic studies, and an accurate integral against weighed amounts of  $Me_2SO_4$  suggested the formula  $[M_3(CO)_{12}H]^+$  for both the ruthenium and osmium species. This was further substantiated by carbon and phosphorus chemical analysis of  $PF_6^-$  salts obtained by the addition of the respective acid solutions to aqueous  $NH_4PF_6$ . By analogy to the isoelectronic hydrido complexes of rhenium<sup>4</sup>,  $[Re_3(CO)_{12}H_2]^-$  and  $[Re_3(CO)_{12}H]^{2-}$ , where it has been postulated that the hydrogen atoms adopt edge bridging sites from X-ray diffraction studies, it was suggested that the  $[M_3(CO)_{12}H]^+$  have similar structures.

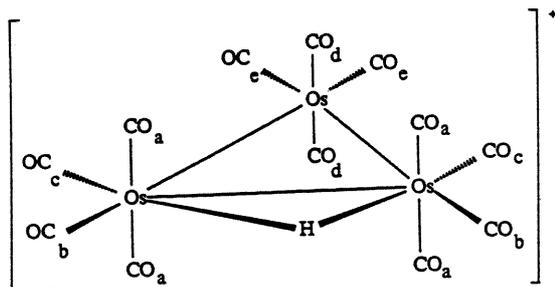
A second species was also observed in the reaction of  $Os_3(CO)_{12}$  with *conc.*  $H_2SO_4$ , which exhibited a resonance at  $\delta$ -20.2 in the  $^1H$  NMR spectrum, typical of a bridging hydride. The intensity of this resonance increased on heating the solution to  $100^\circ C$ . However,  $[Ru_3(CO)_{12}H]^+$  decomposed at higher temperatures without the formation of any new hydride complex.

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In an independent study Deeming *et al.*<sup>5</sup> also reported the protonation of  $\text{Os}_3(\text{CO})_{12}$  and substituted derivatives by *conc.*  $\text{H}_2\text{SO}_4$ . For  $\text{Os}_3(\text{CO})_{12}$ ,  $[\text{Os}_3(\text{CO})_{12}\text{H}]^+$  was the first species observed at  $20^\circ\text{C}$  followed by an intermediate hydride complex after 1hr at  $100^\circ\text{C}$ , which gave rise to a  $^1\text{H}$  NMR resonance at  $\delta$ -20.3. This is in agreement with that reported by Knight *et al.*<sup>3</sup>. However, no assignment of this complex was made by either group. In the latter study a third species was observed at  $\delta$ -8.2 after heating at  $100^\circ\text{C}$  for 6hr, and assigned to the monomeric cation,  $[\text{Os}(\text{CO})_5\text{H}]^+$ . This formulation was confirmed by allowing  $\text{Os}(\text{CO})_5$  to react with sulphuric acid, and observing a  $^1\text{H}$  NMR resonance at the same chemical shift. The overall stoichiometry for the reaction of  $\text{Os}_3(\text{CO})_{12}$  with *conc.*  $\text{H}_2\text{SO}_4$  in yielding  $[\text{Os}(\text{CO})_5\text{H}]^+$  could not be ascertained, however it was concluded that "the cleavage of the metal-metal bonds is associated with the transfer of a carbonyl from one osmium atom to another."

The structure postulated for  $[\text{Os}_3(\text{CO})_{12}\text{H}]^+$  was later confirmed by Koridze *et al.*<sup>6</sup> using  $^{13}\text{C}$  NMR spectroscopy. The proton decoupled spectrum showed five resonances of relative intensity 1:2:1:1:1 at  $\delta$ 177.6, 177.1, 166.7, 161.4 and 160.8. The two highest-field resonances exhibit  $^2\text{J}(\text{CH})$  of 3.7 and 6.6Hz respectively in the fully coupled spectrum. This data was assigned to structure (I), the axial and equatorial carbonyl groups D and E being differentiated by measuring  $^1\text{J}(^{187}\text{Os}-^{13}\text{C})$ , the latter exhibiting larger coupling. This was established from a series of osmium

cluster complexes. Assignment of B and C was made on the assumption that *trans*-H-C coupling is greater than *cis*-H-C coupling.



$[\text{Ru}(\text{CO})_5\text{H}]^+$ , prepared in an analogous manner to  $[\text{Os}(\text{CO})_5\text{H}]^+$ , was also characterised by NMR spectroscopy<sup>5,7</sup>. The  $^1\text{H}$  NMR spectrum displayed a singlet at  $\delta$ -7.23, while a  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a sample prepared from 40%  $^{13}\text{C}$  enriched  $\text{Ru}(\text{CO})_5$  showed two singlets at 6180.5 and 178.5 in an approximate 4:1 ratio<sup>7</sup>. These resonances exhibited  $^2\text{J}(\text{CH})$  of  $<4$  and 24Hz in the fully coupled spectrum and were thus assigned to CO *cis*- and CO *trans*-H respectively. This is consistent with  $[\text{Ru}(\text{CO})_5\text{H}]^+$  being an octahedral ion which is stereochemically rigid on the NMR timescale.

As already stated, both  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$  dissolve in AHF yielding the same protonated species described for the  $\text{H}_2\text{SO}_4$  dissolutions. The only difference between these two protonating agents was the temperature at which reaction takes place. With AHF,  $[\text{Os}(\text{CO})_5\text{H}]^+$  and  $[\text{Ru}(\text{CO})_5\text{H}]^+$  are observed at room temperature, whereas in

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H<sub>2</sub>SO<sub>4</sub> high temperatures are required. According to the Hammett acidity function, which is a widely used means for gauging acidity of non-aqueous media in high concentration, liquid H<sub>2</sub>SO<sub>4</sub> is a stronger acidic solvent than liquid HF<sup>8</sup>. Hence, the difference between these two solvents in their reactions with metal carbonyls appears to be independent of their relative acidities. An alternative reason for the difference in the reactivities could possibly be attributed to the respective anions HF<sub>2</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup>, where HF<sub>2</sub><sup>-</sup> promotes the subsequent reaction of [M<sub>3</sub>(CO)<sub>12</sub>H]<sup>+</sup>. For ruthenium the monomeric complex [Ru(CO<sub>5</sub>H)]<sup>+</sup> was observed in greater abundance when compared with the osmium case, this is consistent with the stronger M-M bonds<sup>9</sup> for osmium relative to ruthenium. However, [M<sub>3</sub>(CO)<sub>12</sub>H]<sup>+</sup> is still the major product from each reaction.

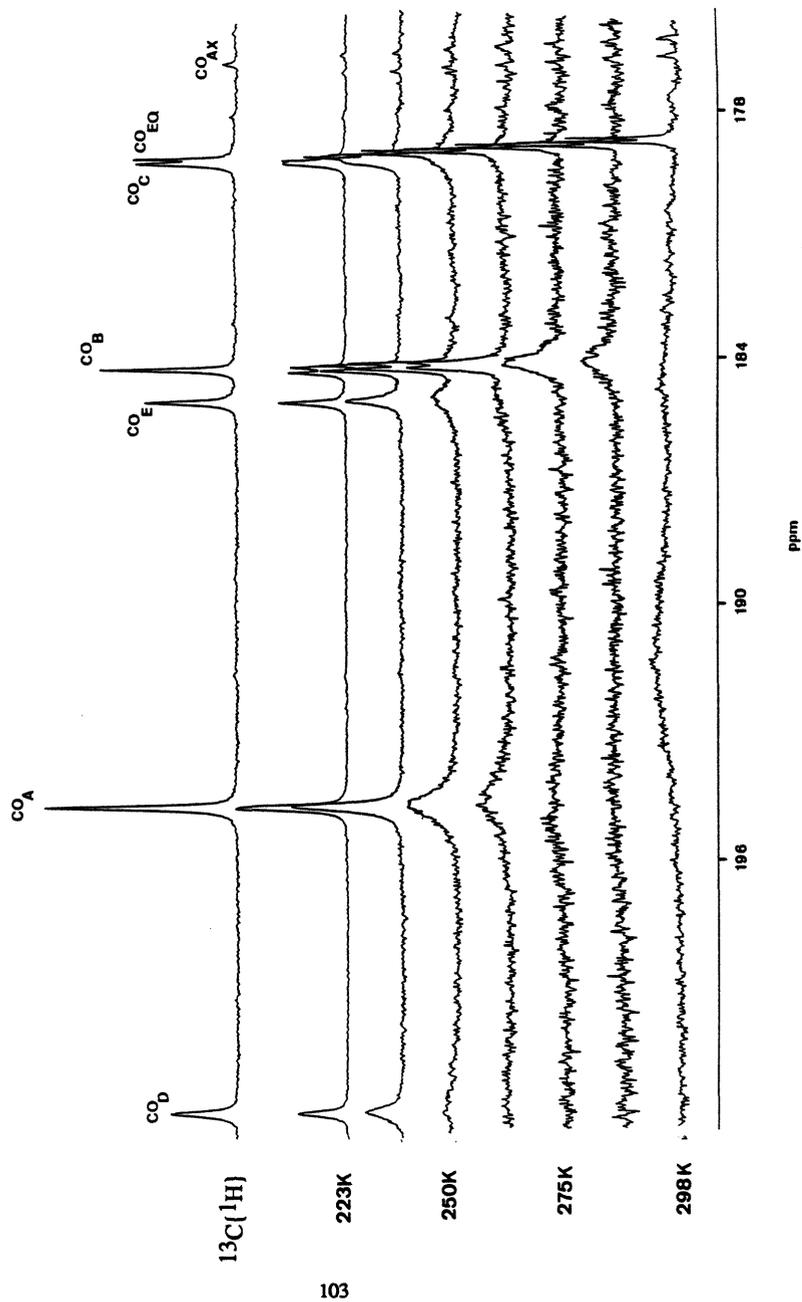
The <sup>1</sup>H NMR resonance observed at δ -20.2 when Os<sub>3</sub>(CO)<sub>12</sub> is dissolved in H<sub>2</sub>SO<sub>4</sub> was also apparent at δ -20.7 in the room temperature reaction with AHF. This indicated the presence of another complex containing a hydride in a bridging environment. The resonance was of a similar intensity to that observed for [Os<sub>3</sub>(CO)<sub>12</sub>H]<sup>+</sup>. However, the <sup>13</sup>C NMR spectrum suggested that [Os<sub>3</sub>(CO)<sub>12</sub>H]<sup>+</sup> is the major species (~75%). Thus the proton resonance at δ -20.7 (in AHF) must result from a hydride carbonyl cluster with more than one hydride ligand, which must be equivalent. The <sup>13</sup>C NMR spectrum for this species showed one major resonance at δ 159.4 exhibiting proton coupling, but assignment of this

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resonance and an indication of its multiplicity was not possible due to an overlap of the resonance with that of CO<sub>(c)</sub> for [Os<sub>3</sub>(CO)<sub>12</sub>H]<sup>+</sup>. Three other, as yet unassigned minor <sup>13</sup>C carbonyl resonances were also observed at δ 158.2, 157 and 150. These appeared to be unaffected in decoupling experiments and it is not evident, therefore, whether they are associated with the complex discussed above or another carbonyl containing cluster. From the data available it is reasonable to suggest that the unassigned hydrido-cluster has a Os:CO ratio less than 1:4, in view of the observed formation of [Os(CO)<sub>5</sub>H]<sup>+</sup> which, with a Os:CO ratio of 1:5, is greater than that of the starting material.

<sup>13</sup>C and <sup>1</sup>H NMR data for both the AHF and H<sub>2</sub>SO<sub>4</sub> dissolutions are correlated in Table 3.1. The data is reasonably consistent, slight variations in chemical shifts resulting presumably from the different solvents employed. Prior to this work only the <sup>1</sup>H NMR spectrum had been reported for [Ru<sub>3</sub>(CO)<sub>12</sub>H]<sup>+</sup>. This established the bridging hydride environment<sup>3,5</sup>. Variable-temperature <sup>13</sup>C NMR spectra has now revealed that this complex is fluxional on the NMR timescale, being at coalescence at room temperature (Fig 3.1). On cooling to -60°C the five resonances expected for the stereochemically rigid [Ru<sub>3</sub>(CO)<sub>12</sub>H]<sup>+</sup> were observed and assigned in accordance with the [Os<sub>3</sub>(CO)<sub>12</sub>H]<sup>+</sup> species. The fluxionality of this cluster at room temperature is not unexpected and is directly analogous to that observed for the parent carbonyl<sup>10</sup>. Unfortunately, the fast exchange

Fig 3.1 Variable Temperature  $^{13}\text{C}$  NMR Spectra of  $[\text{Ru}_3(\text{CO})_{12}\text{H}]^+$  and  $[\text{Ru}(\text{CO})_5\text{H}]^+$



limit of this cluster was unobtainable for practical reasons (FEP is porous to AHF at higher temperatures), so a prediction of the possible mechanism of exchange, i.e scrambling via CO bridges or localised interconversion of CO<sub>ax</sub> to CO<sub>eq</sub>, is not possible. The former of these two mechanisms is more likely and has previously been reported as the method of exchange for Os<sub>3</sub>(CO)<sub>12</sub> at 150°C<sup>6</sup>.

**Table 3.1**

NMR Data for Hydrido-Complexes.<sup>a</sup>

Complex	<sup>1</sup> H/ppm	<sup>13</sup> C/ppm	Relative Intensity	<sup>2</sup> J(CH)/Hz	Assignment
[Ru(CO) <sub>5</sub> H] <sup>+</sup> at 25°C	-7.9(-7.23 <sup>b</sup> )	179.0(180.5 <sup>b</sup> ) 176.9(178.2 <sup>b</sup> )	4 1	6.6(<4 <sup>b</sup> ) 30.7 (24 <sup>b</sup> )	(CO) <sub>eq</sub> (CO) <sub>ax</sub>
[Ru <sub>3</sub> (CO) <sub>12</sub> H] <sup>+</sup> at -60°C	-19.4	201.8 194.5 184.9 184.1 179.1	1 2 1 1 1	n.o 2 n.o. 9.4 2	(CO) <sub>d</sub> (CO) <sub>a</sub> (CO) <sub>e</sub> (CO) <sub>b</sub> (CO) <sub>c</sub>
[Os(CO) <sub>5</sub> H] <sup>+</sup> at 25°C	-8.5(-8.2 <sup>c</sup> )	159 n.o	- -	3 n.o	(CO) <sub>eq</sub> CO) <sub>ax</sub>
[Os <sub>3</sub> (CO) <sub>12</sub> H] <sup>+</sup> at 25°C	-20.3(-19.2 <sup>c</sup> )	176.4(177.6 <sup>d</sup> ) 169.8(171.1 <sup>d</sup> ) 165.1(166.7 <sup>d</sup> ) 167.0(161.4 <sup>d</sup> ) 159.5(160.8 <sup>d</sup> )	1 2 1 1 1	-(n.o <sup>d</sup> ) 2.9(n.o <sup>d</sup> ) -(n.o <sup>d</sup> ) 2(3.7 <sup>d</sup> ) 7(6.6 <sup>d</sup> )	(CO) <sub>d</sub> (CO) <sub>a</sub> (CO) <sub>e</sub> (CO) <sub>b</sub> (CO) <sub>c</sub>
[Ir <sub>4</sub> (CO) <sub>12</sub> H <sub>2</sub> ] <sup>2+</sup> at 25°C <sup>e</sup>	-20.0(20.0) <sup>e</sup>	143.7 142.0	2 1	2.2, 2.2 21.2	f

a, Literature data within parentheses

b, Ref. 5 and 7

c, Ref. 3 and 5

d, Ref. 6

e, Ref. 3

f, See Fig 2.1

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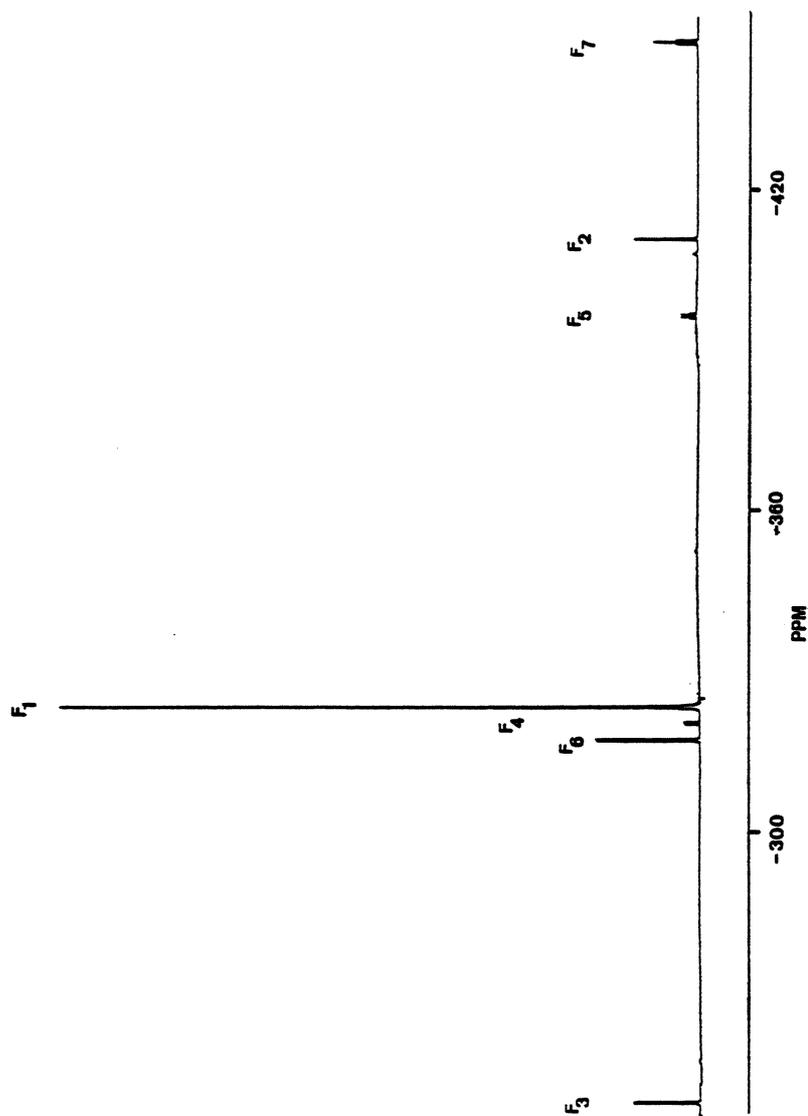
### 3.2 Reaction of Os<sub>3</sub>(CO)<sub>12</sub> with XeF<sub>2</sub> in AHF

Triosmium dodecacarbonyl was observed to be unreactive towards XeF<sub>2</sub> in common organic solvents. However, a vigorous reaction occurred in AHF suggesting a similar solvent dependency to that described for the Ir<sub>4</sub>(CO)<sub>12</sub>/XeF<sub>2</sub> system where the formation of the protonated species discussed above catalyses the subsequent rapid fluorination (see Section 2.2).

The fluorination of Os<sub>3</sub>(CO)<sub>12</sub> in AHF was studied in the molar ratios Os<sub>3</sub>(CO)<sub>12</sub>: XeF<sub>2</sub> from 1:1 to 1:5. Unreacted XeF<sub>2</sub>, evidenced by the <sup>19</sup>F NMR spectrum<sup>11,12</sup>, was apparent in reactions of molar ratios >1:3, whereas, for lower ratios, <sup>1</sup>H NMR spectroscopy revealed the presence of unreacted [Os(CO)<sub>5</sub>H]<sup>+</sup> and [Os<sub>3</sub>(CO)<sub>12</sub>H]<sup>+</sup> due to incomplete fluorination.

At the 1:3 molar ratio neither XeF<sub>2</sub> nor starting material were observed. Further addition of XeF<sub>2</sub> had no effect on the species present. The room-temperature <sup>19</sup>F NMR spectrum (Fig 3.2) at this ratio revealed a large singlet at δ-342 and six smaller resonances of similar integral intensity: a singlet at δ-433, three doublets at δ-266, -335 and -340, a triplet at δ-465, and a doublet of triplets at δ-412.5 (Table 3.2). These resonances, highly shielded from the usual chemical shift region for the <sup>19</sup>F NMR nucleus<sup>12</sup>, are characteristic of a fluoride ligand coordinated directly to a low-valent transition-metal centre<sup>13,14</sup>. All seven resonances were found to be

Fig 3.2 The  $^{19}\text{F}$  NMR Spectrum of the Products from the Reaction of  $[\text{Os}_3(\text{CO})_{12}]$  and  $\text{XeF}_2$  (1:3 Mole Ratio) at  $-60^\circ\text{C}$



temperature independent, sharpening only at lower temperatures. This facilitated the assignment. The  $^{13}\text{C}$  NMR spectra for samples at the 1:3 molar ratio with ca. 15%  $^{13}\text{C}$  enrichment showed, both at room temperature and at  $-60^\circ\text{C}$ , a large number of signals, the assignment of which was only possible by recording selective  $^{13}\text{C}\{^{19}\text{F}\}$  NMR spectra.

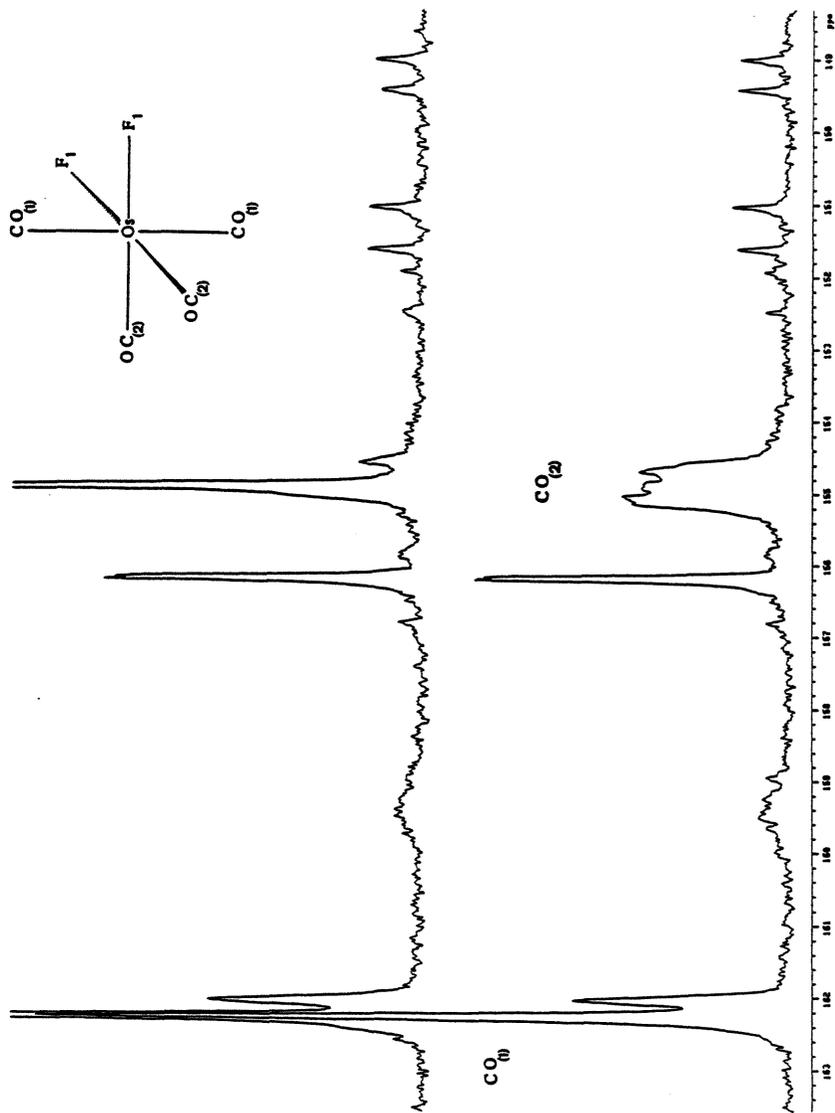
**Table 3.2**

$^{19}\text{F}$  NMR Parameters at  $25^\circ\text{C}$

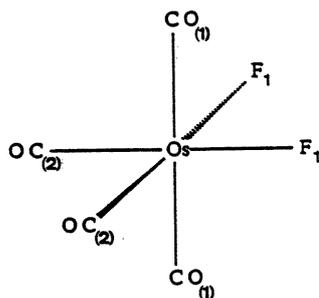
Complex	$^{19}\text{F}/\text{ppm}$	Assignment	$^2\text{J}(\text{FF})/\text{Hz}$
$[\text{Os}(\text{CO})_4\text{F}_2]$ (1)	-342.5(s)	F <sub>1</sub>	-
$[\text{Os}(\text{CO})_5\text{F}]^+$ (2)	-433(s)	F <sub>2</sub>	-
$[\text{Os}_2(\text{CO})_7\text{F}_4]$ (3)	-266(d)	F <sub>3</sub>	86.4
	-340(d)	F <sub>4</sub>	117
	-412.5(dt)	F <sub>5</sub>	86.4, 117
$[\text{Os}_2(\text{CO})_8\text{F}_3]^+$ (4)	-336(d)	F <sub>6</sub>	112
	-465(t)	F <sub>7</sub>	112

Irradiation at the sharp singlet in the  $^{19}\text{F}$  NMR spectrum at  $\delta$ -342, F<sub>1</sub>, characteristic of F *trans*-CO<sup>14</sup>, sharpened the apparent singlet at  $\delta$ 162.4, CO<sub>(1)</sub>, and collapsed most of the multiplet at  $\delta$ 154.8, CO<sub>(2)</sub>, to a singlet (Fig 3.3). This multiplet represents a number of resonances of which the major contribution is from the decoupled singlet at  $\delta$ 154.8. The sharpening of CO<sub>(1)</sub> implies the removal of a small fluorine-carbon coupling  $<2$  Hz, characteristic of *cis*- $^2\text{J}(\text{FC})$ <sup>15</sup>, while the much larger

Fig 3.3 Selective  $^{13}\text{C}\{^{19}\text{F}\}$  NMR Spectra of the Products from the Reaction Between  $\text{Os}_3(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:3 Mole Ratio) at  $25^\circ\text{C}$  Decoupling at the  $^{19}\text{F}$  NMR Resonance  $F_1$



coupling in the multiplet  $\text{CO}_{(2)}$  is typical of *trans*- ${}^2\text{J}(\text{FC})^{15}$ . These two  ${}^{13}\text{C}$  resonances can therefore be unambiguously assigned as resulting from *cis*- $\text{Os}(\text{CO})_4\text{F}_2$  (1).

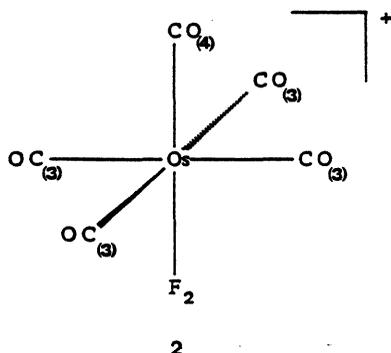


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The positions of the resonances are in agreement with those in previous findings, particularly for  $\text{Os}(\text{CO})_4\text{I}_2$ , where in the majority of cases the  ${}^{13}\text{C}$  resonances of a carbonyl *trans*- to a one-electron donor are at higher field than those resulting from a *cis*- geometry<sup>16</sup>. The observation of  $\text{Os}(\text{CO})_4\text{F}_2$  completes the series  $\text{Os}(\text{CO})_4\text{X}_2$ ,  $\text{X}=\text{Cl}$ ,  $\text{Br}$  and  $\text{I}$ . For the heavier halogens there are numerous preparative routes to their formation<sup>1,17</sup>. Generally, they have been isolated as the *cis*- isomers. However, for  $\text{Os}(\text{CO})_4\text{Cl}_2$  and  $\text{Os}(\text{CO})_4\text{I}_2$ , the *trans*- isomers have also been observed and characterised by vibrational spectroscopy<sup>18,19</sup>. The syntheses of these isomers require stringent control of the reaction conditions and the chloro- species is only obtained from the reaction of *trans*- $\text{Os}(\text{CO})_4(\text{SnPPh}_3)_2$  with  $\text{Cl}_2$  at room temperature<sup>18</sup>. For  $\text{Os}(\text{CO})_4\text{I}_2$  *trans*- to *cis*- isomerisation is

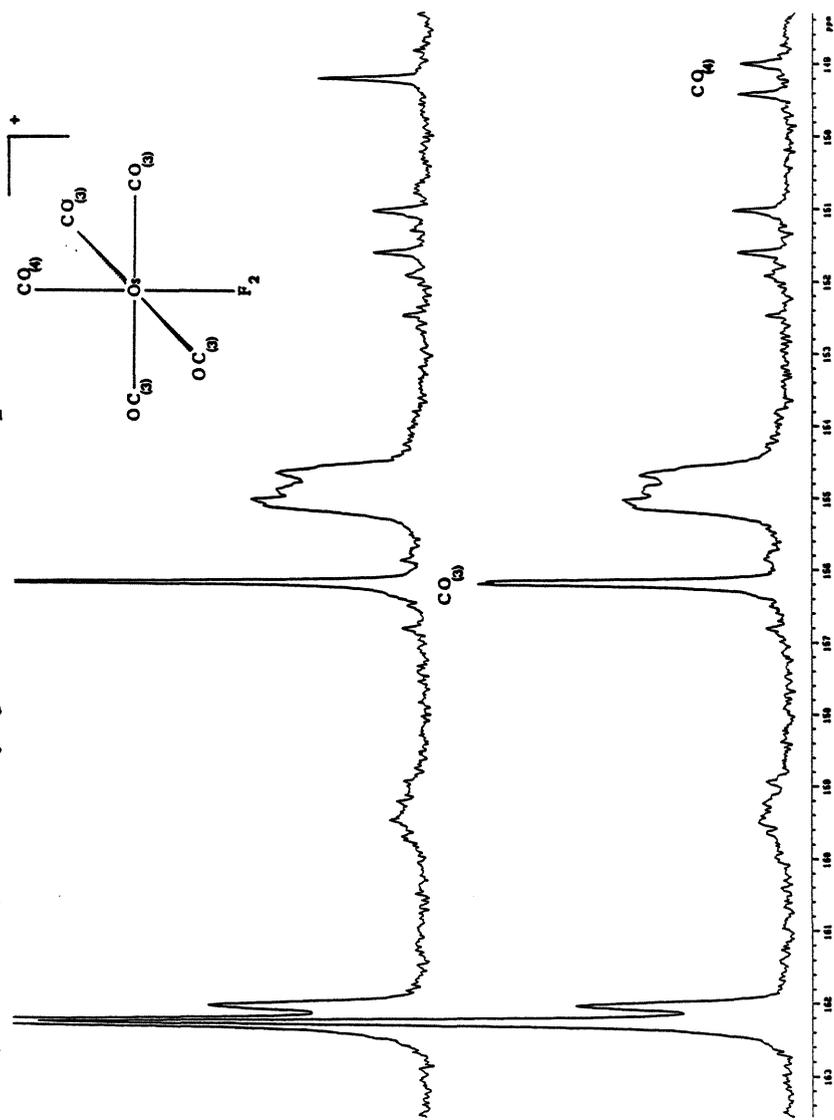
observed as a result of heating or photolysis<sup>19</sup>.

Irradiation at the second sharp singlet in the  $^{19}\text{F}$  NMR spectrum at  $\delta$ -433,  $\text{F}_2$ , removed the small (*cis*-) doublet coupling at 6156.3,  $\text{CO}_{(3)}$ , and the large (*trans*-) doublet coupling at 6149.2,  $\text{CO}_{(4)}$ , in the  $^{13}\text{C}$  NMR spectrum (Fig 3.4). This indicates that the complex contains a single fluoride ligand and has two non-equivalent carbonyl sites. The two CO resonances are in an approximate 4:1 ratio,  $\text{CO}_{(3)}:\text{CO}_{(4)}$ , and were therefore assigned to the equatorial and axial CO's of  $[\text{Os}(\text{CO})_5\text{F}]^+$ , (2). This species is isoelectronic and isostructural with  $[\text{W}(\text{CO})_5\text{F}]^-$  and  $\text{Re}(\text{CO})_5\text{F}$  (see Chapter 1). The counter ion in the complex is presumably  $[\text{HF}_2]^-$ . Again, the high-field resonance is typical of the CO *trans*- to a one electron donor<sup>16</sup>.



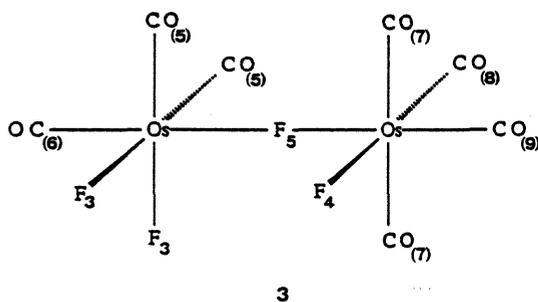
To date, only the chloro- congener has been reported in this class of compounds<sup>20</sup>. It was obtained, in a quantitative yield, from the reaction of  $\text{Cl}_2$  with a solution of  $\text{Os}(\text{CO})_5$  at  $-78^\circ\text{C}$ . Elemental analysis and IR data for this complex

Fig 3.4 Selective  $^{13}\text{C}\{^{19}\text{F}\}$  NMR Spectra of the Products from the Reaction Between  $\text{Os}_3(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:3 Mole Ratio) at  $25^\circ\text{C}$  Decoupling at the  $^{19}\text{F}$  NMR Resonance  $\text{F}_2$



are consistent with the ionic formulation,  $[\text{Os}(\text{CO})_5\text{Cl}]\text{Cl}$ . This species is stable at room temperature but dimerises to  $[\text{Os}(\text{CO})_3\text{Cl}_2]_2$  when refluxed in hexane. This compares with  $\text{Os}(\text{CO})_4\text{Cl}_2$ , which also dimerises under similar conditions<sup>21</sup>.

Analysis of coupling constants for the multiplets observed in the  $^{19}\text{F}$  NMR spectrum revealed that the doublets at  $\delta$ -266,  $F_3$ , and  $\delta$ -340,  $F_4$  are related to the doublet of triplets at  $\delta$ -412.5,  $F_5$ , by couplings of 86 and 117Hz respectively, and in a ratio of 2:1:1. These couplings are typical of  $^2J(\text{FF})$ <sup>14</sup>. The absence of coupling between the two doublets implies the presence of a dimer, the unusually high field  $^{19}\text{F}$  NMR resonance resulting from a bridging fluoride. Complex (3),  $\text{Os}(\text{CO})_3\text{F}_2(\mu\text{-F})\text{Os}(\text{CO})_4\text{F}$ , satisfies this  $^{19}\text{F}$  NMR data, an assignment which is substantiated by its  $^{13}\text{C}\{^{19}\text{F}\}$  NMR spectrum (Fig 3.5-3.7).



Irradiation at  $F_3$  removed a large coupling to the  $^{13}\text{C}$  resonance at  $\delta$ 159.7,  $\text{CO}_{(5)}$ , whilst irradiation at  $F_4$  removed

**Fig 3.5** Selective  $^{13}\text{C}$  ( $^{19}\text{F}$ ) NMR Spectra of the Products from the Reaction Between  $\text{Os}_3(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:3 Mole Ratio) at  $25^\circ\text{C}$  Decoupling at the  $^{19}\text{F}$  NMR Resonance  $\text{F}_3$

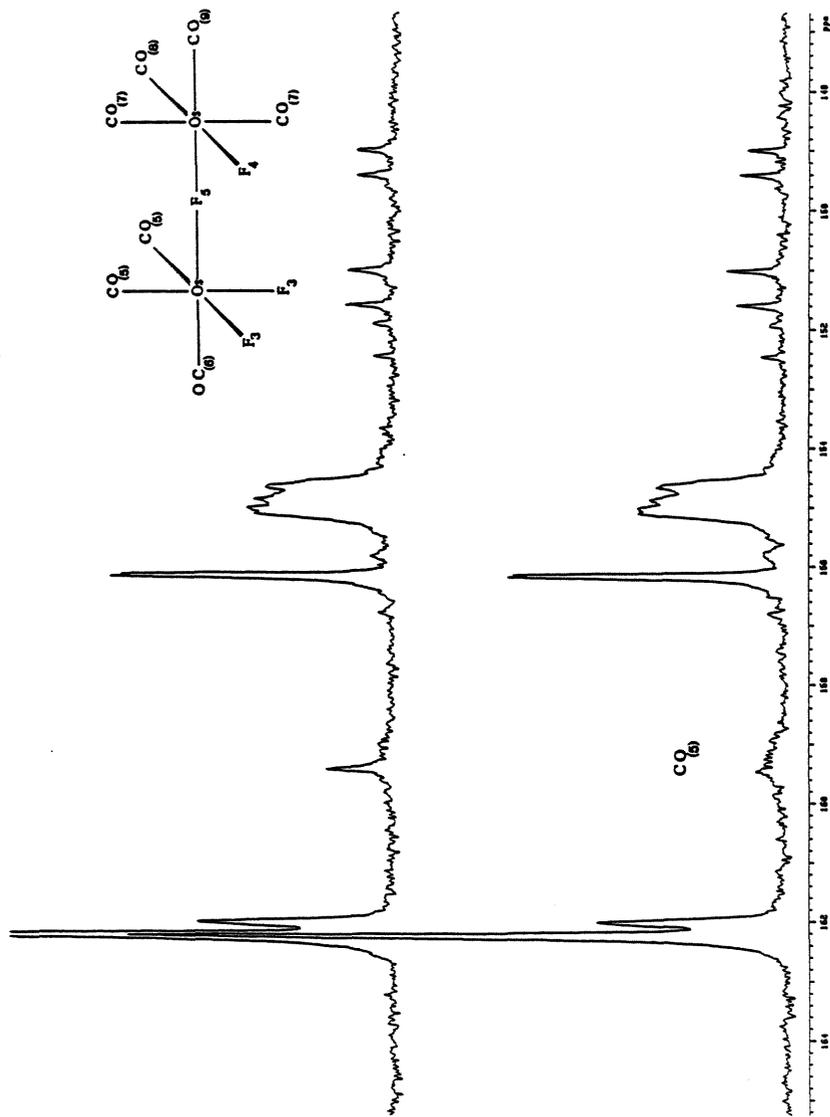
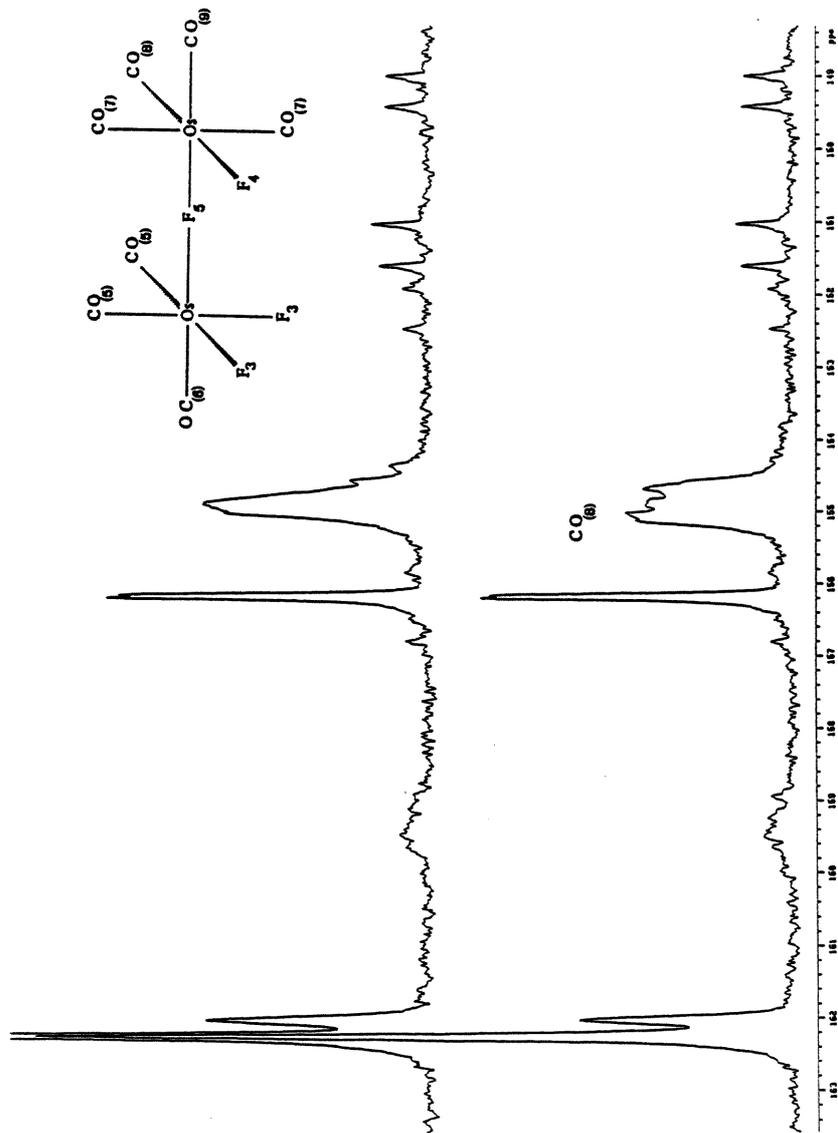
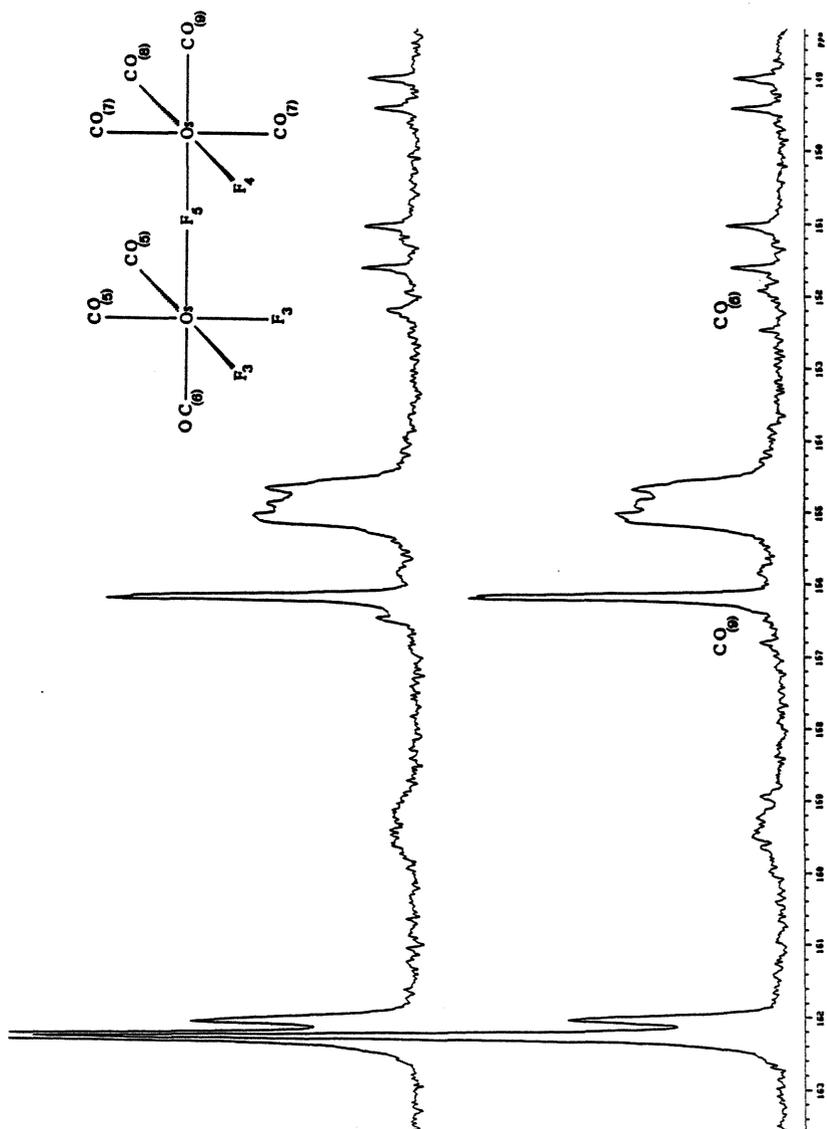


Fig 3.6 Selective  $^{13}\text{C}\{^{19}\text{F}\}$  NMR Spectra of the Products from the Reaction Between  $\text{Os}_3(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:3 Mole Ratio) at  $25^\circ\text{C}$  Decoupling at the  $^{19}\text{F}$  NMR Resonance  $\text{F}_4$



**Fig 3.7** Selective  $^{13}\text{C}\{^{19}\text{F}\}$  NMR Spectra of the Products from the Reaction Between  $\text{Os}_3(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:3 Mole Ratio) at  $25^\circ\text{C}$  Decoupling at the  $^{19}\text{F}$  NMR Resonance  $\text{F}_5$

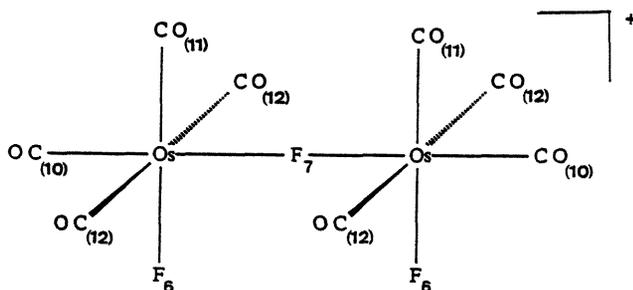


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coupling to CO<sub>(8)</sub> at  $\delta$ 155. As expected, when the bridging <sup>19</sup>F NMR resonance F<sub>5</sub> was irradiated, two resonances CO<sub>(6)</sub> and CO<sub>(9)</sub> at  $\delta$ 152.2 and 156.5, were strongly affected. Since no *cis*- fluorine-carbon coupling was observed on either resonance, no firm assignment as to which resonance is CO<sub>(6)</sub> or CO<sub>(9)</sub> can be made. Unfortunately, the <sup>13</sup>CO resonance labelled CO<sub>(7)</sub> was not observed in the spectra, presumably because it is obscured by other resonances. The only coupling that this resonance would exhibit is a small *cis*- fluorine-carbon coupling, so the decoupled spectrum is not likely to be significantly different.

The other two resonances in the <sup>19</sup>F NMR spectra were the doublet and triplet at  $\delta$  -336, F<sub>6</sub>, and -465, F<sub>7</sub>, which exhibit mutual coupling of 112Hz and are in a ratio of 1:2 respectively. Irradiation at F<sub>7</sub> in the <sup>13</sup>C{<sup>19</sup>F} experiment removes the large (*trans*-) doublet coupling on the peak at  $\delta$ 151.4, CO<sub>(10)</sub>, and causes minor variations in both the singlet at  $\delta$ 161.6, CO<sub>(12)</sub>, and the broad resonance at *ca.*  $\delta$ 155, CO<sub>(11)</sub> (Fig 3.8). Irradiation at F<sub>6</sub> sharpens CO<sub>(12)</sub> and removes a large (*trans*-) coupling in CO<sub>(11)</sub> (Fig 3.9), but has little effect on CO<sub>(10)</sub>. This species, therefore, contains three carbonyl environments as well as two fluorine environments (in a 2:1 ratio), both of which must be *trans*-CO. The fluorine-bridged cationic dimer, [Os<sub>2</sub>(CO)<sub>8</sub>F<sub>3</sub>]<sup>+</sup>, (4),

readily accounts for all of the NMR data, and is a further example of the class of fluorine-bridged transition-metal carbonyl fluorides<sup>22</sup>.



These NMR experiments indicate that there are four AHF stable osmium carbonyl fluorides formed in the reaction of  $\text{Os}_3(\text{CO})_{12}$  with  $\text{XeF}_2$ . These are the first examples of osmium complexes stabilised solely by carbonyl and fluoride ligands. The experiment was found to be reproducible with only minor variations in the product ratios, suggesting that these are the thermodynamically favoured species. In all of the complexes there are no examples of species containing F *trans*-F. This correlates with the fluorination of  $\text{Ir}_4(\text{CO})_{12}$  (see Chapter 2), where *fac*- $\text{Ir}(\text{CO})_3\text{F}_3$  is thermodynamically favoured over *mer*- $\text{Ir}(\text{CO})_3\text{F}_3$ . In contrast to the iridium system, however, the osmium carbonyl fluorides are stable to

Fig 3.8 Selective  $^{13}\text{C}\{^{19}\text{F}\}$  NMR Spectra of the Products from the Reaction Between  $\text{Os}_3(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:3 Mole Ratio) at 25°C Decoupling at the  $^{19}\text{F}$  NMR Resonance F7

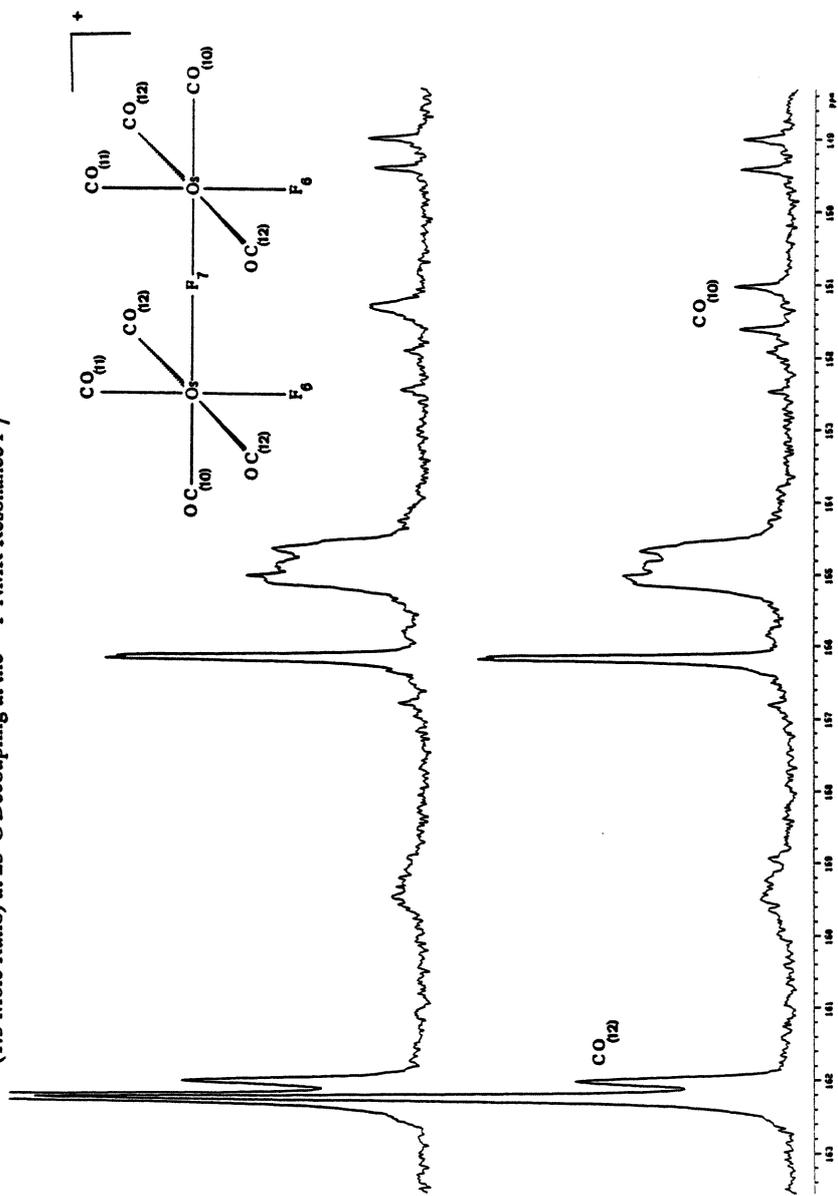
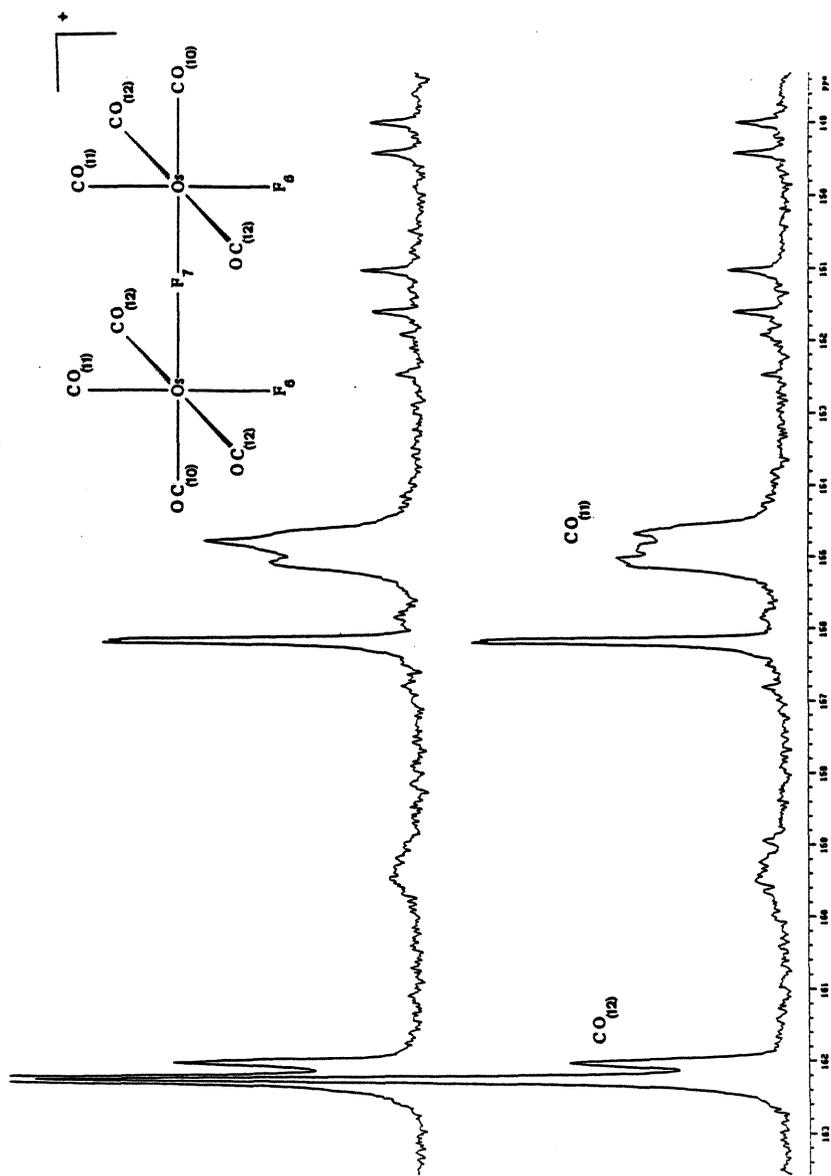


Fig 3.9 Selective  $^{13}\text{C}\{^{19}\text{F}\}$  NMR Spectra of the Products from the Reaction Between  $\text{Os}_3(\text{CO})_{12}$  and  $\text{XeF}_2$  (1:3 Mole Ratio) at  $25^\circ\text{C}$  Decoupling at the  $^{19}\text{F}$  NMR Resonance  $\text{F}_6$



further oxidation by XeF<sub>2</sub> and even elemental fluorine (see Section 3.6) which may be accounted for by the stronger M-CO bond for osmium relative to iridium in the respective compounds.

**Table 3.3**

<sup>13</sup>C NMR Parameters at 25°C

Complex	<sup>13</sup> C/ppm	<sup>2</sup> J(FC)/Hz <sup>a</sup>
[Os(CO) <sub>4</sub> F <sub>2</sub> ] (1)	CO(1) 162.4	<2 <sup>b</sup> (F <sub>1</sub> )
	CO(2) 154.8	65 (F <sub>1</sub> )
[Os(CO) <sub>5</sub> F] <sup>+</sup> (2)	CO(3) 156.3	6.5 <sup>b</sup> (F <sub>2</sub> )
	CO(4) 149.2	62.1 (F <sub>2</sub> )
[Os <sub>2</sub> (CO) <sub>7</sub> F <sub>4</sub> ] (3)	CO(5) 159.7	86 (F <sub>3</sub> )
	CO(9) 156.5	
	CO(8) -155	34 (F <sub>4</sub> )
	CO(6) 152.2	-
	CO(7) n.o	83.1 (F <sub>6</sub> )
[Os <sub>2</sub> (CO) <sub>8</sub> F <sub>3</sub> ] <sup>+</sup> (4)	CO(12) 162	<2 <sup>b</sup>
	CO(11) 154.6	-35 (F <sub>6</sub> )
	CO(10) 151.4	87.5 (F <sub>7</sub> )

a, <sup>19</sup>F resonance, involved in coupling, in parenthesis (generally these are <sup>2</sup>J(F<sup>trans</sup>CO), as <sup>2</sup>J(F<sup>cis</sup>CO) were <3Hz.  
b, <sup>2</sup>J(F<sup>cis</sup>CO)

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### 3.3 Discussion of the NMR Data

The regions of the  $^{19}\text{F}$  NMR spectrum associated with a terminal fluoride ligand *trans-* to either a carbonyl or halide has already been established for rhodium and iridium organometallic complexes (see Section 1.12) The data presented within this thesis substantiates this and also extends the trends to osmium and ruthenium chemistry. However, alternative environments for the fluoride ligand have also been established warranting further discussion. For neutral complexes the  $^{19}\text{F}$  NMR resonances for F *trans*-CO and F *trans*-F fall within the expected regions for the terminal ligand. However, for cationic complexes, these regions overlap such that for,  $[\text{Os}(\text{CO})_5\text{F}]^+$ , the  $^{19}\text{F}$  NMR signal for the fluoride *trans-* to a carbonyl group is observed to occur within the region associated with F *trans*-F (similar results are obtained for cationic phosphine fluoro-complexes see Chapter Four). For anionic complexes this situation is reversed, the  $^{19}\text{F}$  NMR resonances being deshielded relative to their neutral analogues. This is opposite to the expected trend in NMR spectroscopy where an increase in negative charge is usually accompanied by an increase in the shielding of the NMR nucleus<sup>23</sup>. Recently<sup>24</sup> similar observations have been reported for  $[\text{XeF}_5]^-$  where although the  $^{129}\text{Xe}$  chemical shift for this species is significantly shielded relative to  $\text{XeF}_4$ , the  $^{19}\text{F}$  chemical shift of  $[\text{XeF}_5]^-$  is deshielded relative to  $\text{XeF}_4$ . At present the reason for this phenomenon is unclear.

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The reaction between  $\text{Os}_3(\text{CO})_{12}$  and  $\text{XeF}_2$  also revealed the possibility of a fluoride ligand adopting a bridging environment between metal centres. For these species, the  $^{19}\text{F}$  NMR resonances of bridging fluorides, although being *trans-* to carbonyl groups, can be observed at lower frequencies than the comparable resonances due to the terminal ligands, overlapping with the F *trans-F* region, e.g.  $\text{F}_5(\delta-412.5)$ . This situation is similar to that observed for  $^1\text{H}$  NMR where terminal hydride ligand resonances occur at higher frequency than those of bridging hydrides, see Table 3.1.

Hence, although  $^{19}\text{F}$  NMR spectroscopy provides a useful tool for interpreting reaction products and proposing their geometries, care must be taken if relying solely on chemical shift values, especially where ionic complexes may result from the reaction. For carbonyl containing complexes this situation can be overcome by recording  $^{13}\text{C}$  NMR spectra, where the magnitude of the coupling between  $^{19}\text{F}$  and  $^{13}\text{C}$  nuclei clearly distinguishes between *cis-* and *trans-* geometries of the fluoride and carbonyl ligands. Thus, from a combination of the NMR data unambiguous assignment is possible. The reliance on  $^{13}\text{C}$  NMR data is not as important for complexes containing other spin active nuclei e.g.  $^{31}\text{P}$ .

### 3.4 Discussion on the Fluorination of Osmium Carbonyl

In the reaction of  $\text{Os}_3(\text{CO})_{12}$  with  $\text{XeF}_2$  in  $\text{AHF}$  the formation of  $[\text{Os}(\text{CO})_5\text{F}]^+$ , with a carbonyl to osmium ratio higher than that of the starting material means that carbonyl scrambling must have occurred. The analogous hydride,  $[\text{Os}(\text{CO})_5\text{H}]^+$ , discussed above, was also obtained from cleavage of the trinuclear cluster  $\text{Os}_3(\text{CO})_{12}$ . From this it was suggested that metal-metal bond cleavage is associated with carbonyl scrambling around the cluster<sup>5</sup>. A similar process occurring during the fluorination of  $\text{Os}_3(\text{CO})_{12}$  can be envisaged. However, the dependence on the presence of metal-metal bonds for the formation of  $[\text{Os}(\text{CO})_5\text{F}]^+$  in this reaction is only speculative. An alternative carbonyl scrambling mechanism could occur from an intermolecular process after fragmentation of the cluster.

In a parallel investigation, an attempt to prepare  $\text{Os}(\text{CO})_4\text{F}_2$  via an alternative route was undertaken. The complex,  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$ , was found to react with  $\text{AHF}$  evolving methane gas. (The full reaction is discussed in Section 3.7). The  $^{19}\text{F}$  NMR spectrum of the resulting solution established the presence of  $\text{Os}(\text{CO})_4\text{F}_2$  (1) and  $[\text{OsF}(\text{CO})_4(\mu\text{-F})\text{OsF}(\text{CO})_4]^+$  (4). However, in this reaction  $[\text{Os}(\text{CO})_5\text{F}]^+$  (2) and  $\text{Os}(\text{CO})_3\text{F}_2(\mu\text{-F})\text{Os}(\text{CO})_4\text{F}$  (3), which are observed from the reaction of  $\text{Os}_3(\text{CO})_{12}$  with  $\text{XeF}_2$  or  $\text{F}_2$  gas (see Section 3.6), were absent. Since  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$  is monomeric, the absence of (2) and (3) strongly implies that their formation in the

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$\text{Os}_3(\text{CO})_{12}/\text{XeF}_2$  system is associated with carbonyl scrambling resulting from metal-metal bond cleavage, as described for  $[\text{Os}(\text{CO})_5\text{H}]^{+5}$ . Another implication of the  $^{19}\text{F}$  NMR data from the  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$  reaction is that, although complex (1) is the dominant species in solution, the fact that subsequent room temperature reaction over several days yielded complex (4) implies dimerisation of (1) with loss of CO. This suggests a greater thermodynamic stability for fluorine bridging species, relative to those containing terminal fluorides. This is also strongly supported by the polymerisation of  $\text{Os}(\text{CO})_4\text{F}_2$  in the solid state (discussed below).

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### 3.5 Polymerisation of the Complexes (1) (2) (3) and (4) on Removal of the Solvent

For the  $\text{Os}_3(\text{CO})_{12}/\text{XeF}_2$  system the removal of solvent from reaction mixtures of >1:3 mole ratio resulted in the formation of an air-sensitive off-white solid, the IR spectrum of which showed two broad absorptions assignable to terminal VCO at 2130 and 2025 $\text{cm}^{-1}$ . However, when these samples were redissolved in AHF the  $^{19}\text{F}$  NMR spectrum reveals a dramatic difference in the solution species. A previous investigation by Hewitt<sup>2</sup> on the solid product from the reaction using X-ray powder diffraction studies gave similar, but not identical results to those on  $[\text{Ru}(\text{CO})_3\text{F}_2]_4$ . This had been prepared by the analogous reaction of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{XeF}_2$  and also by the reaction of  $[\text{RuF}_5]_4$  with CO at high temperature and pressure<sup>25</sup>. The X-ray crystal structure of this complex<sup>26</sup> reveals a structure which closely resembles that of  $[\text{RuF}_5]_4$ , where the ruthenium atoms are in a tetrameric ring with bent fluorine bridges<sup>27</sup>. From this data Hewitt concluded that the solid obtained from the osmium system was  $[\text{Os}(\text{CO})_3\text{F}_2]_4$ .

The  $^{19}\text{F}$  NMR spectrum of this complex redissolved in AHF establishes that the previously described fluoro-complexes, (1), (2), (3) and (4) are still present. However there are a number of new resonances, the multiplicity of which indicates products of a polymeric nature. The polymerisation was time dependent such that samples held under dynamic vacuum for about two hours exhibited  $^{19}\text{F}$  NMR spectra showing

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the growth of these polymeric species. These NMR data suggest that the tetramer does not exist in AHF solution; the predicted first order  $^{19}\text{F}$  NMR spectrum for  $[\text{Os}(\text{CO})_3\text{F}_2]_4$ , two triplet resonances of equal intensity exhibiting mutual coupling, is not observed.

If the tetramer is not stable to AHF dissolution fragmentation may result. The oxide fluoride,  $[\text{WOF}_4]_4$ , which has a similar tetrameric structure to that of  $[\text{Ru}(\text{CO})_3\text{F}_2]_4$ , is known to be unstable on dissolution in AHF or MeCN<sup>28</sup>, with fragmentation to  $[\text{WOF}_5]^-$ ,  $[\text{W}_2\text{O}_2\text{F}_9]^-$  and  $[\text{W}_3\text{O}_3\text{F}_{13}]^-$ . The absence of NMR data assignable to  $[\text{Os}(\text{CO})_3\text{F}_2]_4$  in this present investigation is therefore not surprising. For  $[\text{Os}(\text{CO})_3\text{F}_2]_4$  in AHF possible fragmentation products include *mer-* or *fac-*  $[\text{Os}(\text{CO})_3\text{F}_3]^-$ , analogous and isoelectronic with  $\text{Ir}(\text{CO})_3\text{F}_3$ ; and  $[\text{Os}_2(\text{CO})_6\text{F}_5]^-$  (*c.f.*  $[\text{W}_2\text{O}_2\text{F}_9]^-$ ) for which there are 6 possible isomers, without considering the possibility of ligand scrambling. The  $^{19}\text{F}$  NMR spectra of these molecules are likely to be complicated, especially if  $^4\text{J}(\text{FF})$  coupling is large enough to be resolved.

The complexity of the NMR data means that any assignment can only be regarded as tentative, so an attempt to find a solvent which is less likely to be destructive to a polymeric material was undertaken. Tungsten oxide tetrafluoride retains its tetrameric structure in toluene<sup>29</sup>, a less coordinating solvent than AHF, but, unfortunately,  $[\text{Os}(\text{CO})_3\text{F}_2]_4$  is insoluble in this and other non-coordinating solvents. It was, however, found to be soluble in MeCN, a

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potential coordinating solvent, and the  $^{19}\text{F}$  NMR spectrum of this solution exhibits one M-F resonance at  $\delta$ -305. The assignment of this resonance is complicated by the lack of available NMR data for F *trans*-coordinated MeCN. The  $^{19}\text{F}$  NMR resonance of such a fluoride environment is expected to occur in a similar region to that of F *trans*- to CO since CO and NCMe are both  $\pi$ -acidic ligands. However, it seems reasonable to suggest that carbonyl substitution has occurred with the formation of a solvated complex e.g.  $\text{Os}(\text{CO})_2(\text{NCMe})_2\text{F}_2$ . The fluoride ligands are found to be unreactive in substitution reactions (see Section 3.7). Removal of the solvent at this stage resulted in the precipitation of an intractable white solid which would not redissolve in MeCN. Presumably, the removal of the solvent results in the loss of the coordinated MeCN and polymerisation of the solid.

Unfortunately, although this NMR analysis proved to be ineffective in confirming the proposed solid state structure of  $[\text{Os}(\text{CO})_3\text{F}_2]_4$ , the data does give evidence of polymerisation of the solution intermediates. Samples held under dynamic vacuum for about two hours exhibit  $^{19}\text{F}$  NMR spectra showing the growth of polymeric materials. This phenomenon is not surprising and directly parallels previous observations for other transition metal carbonyl fluorides. Structurally characterised complexes of this type have, in all cases, revealed fluorine-bridges where the fluoride occupies bridging sites between 2 or 3 metal centres (see

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Section 1.8). For complexes where X-ray structures are unavailable, there is also a predominance of formulations with fluoride-bridges. This indicates a thermodynamic preference for polymerisation.

The polymerisation of the major species,  $\text{Os}(\text{CO})_4\text{F}_2$ , on removal of the solvent, is anomalous when compared with related complexes containing the heavier halogens,  $\text{Os}(\text{CO})_4\text{X}_2$   $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ , which can all be isolated in the solid state<sup>1,17</sup>. For these complexes, polymerisation to the halide bridged dimers,  $[\text{Os}(\text{CO})_3\text{X}_2]_2$ , is only observed to occur at elevated temperatures in various solvents<sup>30</sup>. This suggests a greater carbonyl lability for fluoro-complexes when compared to their halo-analogues, a situation which is also paralleled in the rhenium system,  $\text{Re}(\text{CO})_5\text{X}$   $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$ .

From an IR analysis,  $\text{Re}(\text{CO})_5\text{F}$  has been proposed as a solution intermediate from the reaction of  $\text{Re}(\text{CO})_5\text{Br}$  with  $\text{AgF}$ . However, this complex was found to polymerise to the structurally characterised tetramer  $[\text{Re}(\text{CO})_3\text{F}]_4$  in fluorobenzene at room temperature<sup>31</sup>. On the other hand for the rhenium carbonyl complexes of the heavier halides the isolation of the pentacarbonyl halides as solids is easily achieved<sup>32</sup>. Very recently, this greater lability of the CO ligands in fluoro-complexes relative to their halo-analogues has been quantitatively demonstrated for the  $\text{Re}(\text{CO})_3(\text{PPh}_3)_2\text{X}$  system<sup>15b</sup>. Using  $^{13}\text{C}$  NMR spectroscopy Hoffman *et al.* established an accelerated room temperature  $^{12}\text{CO}/^{13}\text{CO}$

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exchange at the rhenium centre, roughly 2 orders of magnitude greater at a carbonyl in the *cis*- position to the halide for the fluoro-complex relative to that in the chloro-complex. The phenomenon of increased *cis*-labilisation fits the series for the heavier halide ligands, previously shown to follow the order  $\text{Cl} > \text{Br} > \text{I}^{33}$ . A corresponding trend was also observed for the incorporation of the labelled CO *trans*- to the chloride ligand in,  $\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2$ , albeit at a significantly slower rate.

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### 3.6 Fluorination of Os<sub>3</sub>(CO)<sub>12</sub> by Fluorine gas

Reactions of metal carbonyls with halogens giving rise to the formation of halogencarbonylmetal derivatives have been reported for many of the transition metals<sup>34</sup>. For the iron triad the reaction between Fe<sub>3</sub>(CO)<sub>12</sub> and I<sub>2</sub> in THF results in the isolation of Fe<sub>2</sub>(CO)<sub>8</sub>I<sub>2</sub> in small yields<sup>35</sup>, whereas the halogenation of Ru<sub>3</sub>(CO)<sub>12</sub>, at low temperature<sup>36</sup> produces the monomeric *cis*- Ru(CO)<sub>4</sub>X<sub>2</sub>. For Os<sub>3</sub>(CO)<sub>12</sub>, halogenation proceeds slowly producing sequential cleavages of the osmium-osmium bonds allowing the isolation of intermediates in high yields<sup>34d</sup>. This behaviour contrasts with that of ruthenium, reflecting the increased stability of the metal-metal bonds to oxidation on descending a transition metal group<sup>9</sup>. This enhanced stability makes Os<sub>3</sub>(CO)<sub>12</sub> an ideal candidate for investigation of its reaction with fluorine gas. The reactivity of Ru<sub>3</sub>(CO)<sub>12</sub> with the heavier halogens has been demonstrated to decrease in the order Cl > Br > I<sup>34e</sup>, suggesting that any reaction with F<sub>2</sub> would be the most vigorous for any system. Traditionally, the fluorination of low-valent transition metals by F<sub>2</sub> gas has been avoided. This is, in part, because of practical limitations of manipulating the gas, but more importantly because of the powerful oxidising properties of the reagent. There is potential for uncontrollable reactions, such as that observed for Mo(CO)<sub>6</sub> which, although reported to produce an olive green compound below -75°C, can also result in detonation<sup>37</sup>. In this investigation a similar reaction

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was observed between  $F_2$  and solid  $Os_3(CO)_{12}$ , which resulted in combustion. Presumably, the formation of the thermodynamically favoured carbonyl fluoride,  $COF_2$ , is driving these reactions. However, probably the major reason for these vigorous reactions is the absence of suitable, inert solvent to mediate them. Investigation of the interaction of metal carbonyl clusters with AHF (see Sections 2.2 and 3.1) indicates that this solvent meets the necessary requirements envisaged for more controllable reactions. Hence, the reaction of  $Os_3(CO)_{12}$  with  $F_2$  in AHF was attempted.

Complete dissolution of  $Os_3(CO)_{12}$  in AHF was achieved by vigorous agitation of the solid with AHF at room temperature. The resulting yellow solution, containing mainly  $[Os_3(CO)_{12}H]^+$ , was then frozen to allow the addition of a stoichiometric amount of  $F_2$  gas. Subsequent warming of this reaction mixture produced no apparent sign of reaction. However, on standing, the upper portion of the yellow solution decolourised. On agitation, a rapid colour change occurred eventually resulting in a pale yellow green solution after ten minutes. Although  $Os_3(CO)_{12}$  in AHF appears yellow, the colour changes were obvious and at one point the reaction mixture appeared pink. To ensure complete reaction, the solution was agitated overnight. A  $^{19}F$  NMR analysis of a decanted sample of this solution revealed an analogous reaction scheme to that described from the fluorination by  $XeF_2$ , in which the spectrum was dominated

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(excluding the peak due to HF) by the Os-F resonance of *cis*-Os(CO)<sub>4</sub>F<sub>2</sub> at 6-342, other resonances assigned to (2), (3) and (4) were also observed. The further addition of F<sub>2</sub> above a 1:3 Os<sub>3</sub>(CO)<sub>12</sub>:F<sub>2</sub> ratio did not alter the overall scheme of the reaction but resulted in a change in the proportion of (2) when compared to the earlier spectrum, an observation similar to that described for Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> and AHF. The implication from these observations is that the complexes labelled (1) to (4) are unreactive to excess of F<sub>2</sub> as well as to XeF<sub>2</sub>. The relative growth of the complex (2) with time has already been discussed for the Os<sub>3</sub>(CO)<sub>12</sub>/XeF<sub>2</sub> system, and arises from the dimerisation of (1) to the more thermodynamically preferred complex, (2).

### 3.7 Osmium Phosphine Fluoro-Complexes

As mentioned above it was not possible to unambiguously confirm the nature of the solid state complex postulated by Hewitt<sup>2</sup> to be "[Os(CO)<sub>3</sub>F<sub>2</sub>]<sub>4</sub>". However, its reaction with acetonitrile was of interest in displaying the lability of the carbonyl groups in this complex. As discussed previously (see Section 2.7), substitution of carbonyls by other donor ligands, especially phosphines, is a well established area of chemistry.

For ruthenium and osmium carbonyl halides, substituted derivatives have been extensively studied and a wide range of complexes have been isolated for the heavier halides (Cl,

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Br, or I) with various phosphine ligands (L)<sup>1,17</sup>. The general formulae for these complexes are  $M(\text{CO})_3\text{LX}_2$ ,  $M(\text{CO})_2\text{L}_2\text{X}_2$ ,  $M(\text{CO})\text{L}_3\text{X}_2$  and the dimeric  $\text{M}_2(\text{CO})_4\text{L}_2\text{X}_4$  and they can be synthesised via three general procedures:-

- 1) Reaction of neutral and anionic carbonyl halides with L.
- 2) Carbonylation of the respective hydrated metal halides, halometallates or metal phosphine halides, with L in alcoholic media.
- 3) Halogenation of metal carbonyl phosphine complexes.

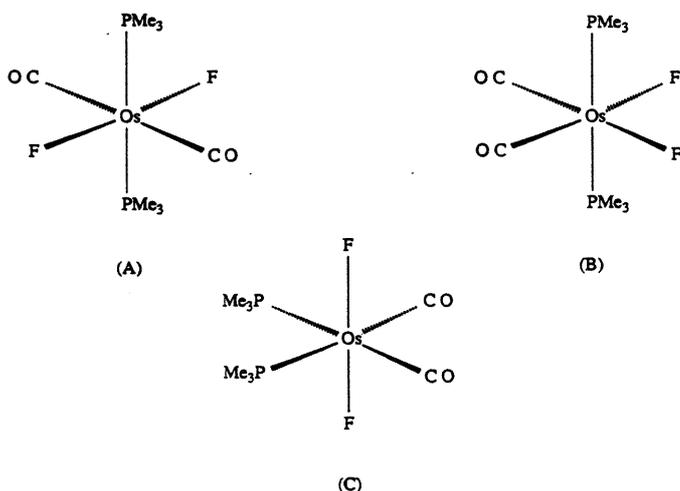
The absence of fluoro analogues to date is presumably due to the unsuitability of these preparative techniques for the formation of such complexes, in particular:-

- 1) No reported fluoro-precursors.
- 2) The fluoride ligand is very labile in polar solvents as observed for  $\text{IrF}(\text{CO})(\text{PPh}_3)_2$  in MeOH. Hence, the isolation of fluoro-complexes via this synthetic route is likely to be hampered by the formation of solvated complexes.
- 3) Fluorine is a very reactive gas requiring specialised equipment for its safe handling and is likely to be destructive (sometimes explosively) to oxidation-sensitive complexes.

The off-white solid " $[\text{Os}(\text{CO})_3\text{F}_2]_4$ " was found to be insoluble in  $\text{CD}_2\text{Cl}_2$  at room temperature but, on addition of

$\text{PMe}_3$ , vigorous evolution of CO occurred with the development of a colourless solution and a small amount of a fine white solid. By a combination of  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopy the soluble material from this reaction was identified as *cis*- $\text{Os}(\text{CO})_2\text{F}_2(\text{PMe}_3)_2$ , exhibiting triplets in both the  $^{19}\text{F}$  and the  $^{31}\text{P}$  NMR spectra at  $\delta$ -315.3 and  $\delta$ -15.2 respectively, with mutual coupling of 38Hz. This stoichiometry is in line with the initial Os:F ratio of 1:2 required for the formation of the precursor. Thus, in the removal of the solvent and subsequent reaction with  $\text{PMe}_3$  there is no loss of fluoride as  $\text{COF}_2$  or  $\text{F}_2\text{PMe}_3$  respectively, suggesting that the Os-F bond in these complexes is stable in both the solution and solid phases.

There are three possible geometric isomers of this complex, A, B and C, which would give rise to triplets in both the  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra. Structure C, as well as



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being an unlikely configuration for a soluble product of this type, can be discounted since  $^1\text{H}$  NMR spectra of the complex revealed a virtual triplet<sup>38</sup> for the methyl resonances consistent with mutually *trans*-phosphine ligands (a *cis*-configuration would give rise to a second order doublet). Differentiation between A and B is based on the observation of the  $^{19}\text{F}$  NMR resonance at  $\delta$ -315.3, which is characteristic of F *trans*-CO<sup>14</sup> as in B. This assignment is in agreement with the preference for CO ligands to adopt *cis*-configurations where competition for the available electron density on the metal is minimised<sup>39</sup>. The isolation of this complex via the substitution of carbonyls in a transition-metal carbonyl halide complex is not unexpected and directly parallels the chemistry for the heavier halogens Cl, Br and I, as outlined above. However, the only previously reported fluoro-complex of osmium containing carbonyl ligands is  $\text{OsF}(\text{CO})_2(\text{N}=\text{NPh})(\text{PPh}_3)_2$  (see Section 1.9).

As outlined above, an alternative preparation of substituted carbonyl halide complexes is by the halogenation (excluding  $\text{F}_2$ ) of osmium (or ruthenium) carbonyl phosphine compounds. Since fluorine gas is likely to be destructive to the phosphine ligand it was felt that  $\text{XeF}_2$  might be a more suitable fluorinating agent for some of these species.

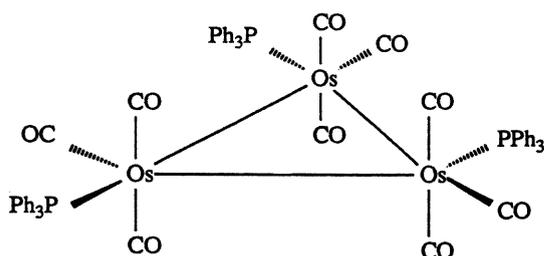
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### 3.8 Osmium Carbonyl Phosphines

This area of chemistry has been highlighted in various review articles and the synthesis of both mono- and trinuclear derivatives have been reported<sup>40</sup>. The former class,  $\text{Os}(\text{CO})_{5-n}\text{L}_n$  ( $n=1-3$ ), have been obtained via direct substitution reactions eliminating various ligands such as CO, NO, alkane or  $\text{H}^+$  from the appropriate precursor. The latter class of complexes have also been synthesised by substitution and for monodentate phosphine ligands have been isolated for  $\text{Os}_3(\text{CO})_{12-n}\text{L}_n$  ( $n=1-4$ ). For  $n=1$  or 2 these complexes can be obtained by allowing L to react with  $\text{Os}_3(\text{CO})_{11}(\text{NCMe})$  and  $\text{Os}_3(\text{CO})_{12}(\text{NCMe})_2$  respectively. Alternatively, for  $n=1-3$  these complexes can be prepared from the reaction of L with  $\text{Os}_3(\text{CO})_{12}$  under thermal or photochemical conditions, and then separated chromatographically.

The reaction of mononuclear  $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$  with  $\text{XeF}_2$  is discussed in Chapter Four along with the analogous reaction with  $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ . The trinuclear derivative,  $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$ , was chosen for the investigation of its

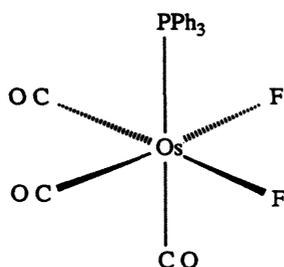
reaction with  $\text{XeF}_2$ . The  $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$  has been analysed crystallographically<sup>41</sup>, showing that the three tertiary phosphine ligands occupy equatorial sites, one per osmium atom and so arranged to minimise steric crowding.



Hence, the expected cleavage of the osmium-osmium metal bonds due to reaction with  $\text{XeF}_2$  should result in retention of a phosphine ligand on each osmium. For the mono- and di-substituted complexes, although their reaction would be of interest, a similar cleavage would be expected to result in a mixture of products. The greater solubility of  $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$  in organic solvents with respect to the parent carbonyl,  $\text{Os}_3(\text{CO})_{12}$ , permits its fluorination by  $\text{XeF}_2$  to be investigated in dichloromethane.

The reaction occurred vigorously on warming from  $-100^\circ\text{C}$  to room temperature. Subsequent NMR analysis revealed that the expected product, *cis*- $\text{OsF}_2(\text{CO})_3(\text{PPh}_3)$ , was obtained in significantly higher yields if the reaction was controlled thermally. Hence, in a typical reaction the dichloromethane solution was gradually allowed to warm to room temperature

overnight. The resulting solution exhibited a doublet and a triplet resonance in the  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra at  $\delta$ -328.0 and  $\delta$ 1.9 respectively, with mutual coupling of 26Hz. This is consistent with structure below.



Although the related isomer with mutually *trans*-fluorines would also give rise to resonances of the same multiplicity, the  $^{19}\text{F}$  NMR resonance is within the region consistent with a F *trans*- to CO environment and not F *trans*- to  $\text{F}^{14}$ , the complex is, therefore, assigned as shown.

The formation of this complex now completes the series for the tricarbonyl halides,  $\text{OsX}_2(\text{CO})_3(\text{PPh}_3)_2$  X= F, Cl, Br or I, which for the heavier halides are obtained by the oxidative cleavage of  $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$  with halogens<sup>42</sup>.

The complex represents the major product in solution (~85%). A second minor product exhibits an unresolved  $^{19}\text{F}$  NMR resonance at  $\delta$ -328.8. Unfortunately, the absence of a comparable  $^{31}\text{P}$  spectrum precluded assignment. The  $^{19}\text{F}$  NMR resonance was in the region of the spectrum associated with F *trans*- CO or P, and is therefore unlikely to be due to the *trans*- isomer of  $\text{Os}(\text{CO})_3\text{F}_2(\text{PPh}_3)$ .

### 3.9 An Alternative Formation of Fluoro-complexes

Alkyl-transition metal carbonyl complexes have proved useful in the synthesis of novel transition metal compounds. Protons react readily with such complexes with the elimination of the appropriate alkane. This synthetic procedure has recently been demonstrated for the formation of the first low-valent transition-metal carbonyl teflate ( $-\text{OTeF}_5$ ) complex;



$\text{CpFe}(\text{CO})_2(\text{OTeF}_5)$  and  $\text{Re}(\text{CO})_5(\text{OTeF}_5)$  were also prepared from the corresponding methyl derivatives<sup>43</sup>.

Cleavage of a rhenium-methyl bond by protic electrophiles has also been demonstrated by the formation of  $\text{CpRe}(\text{NO})(\text{PPH}_3)\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ )<sup>44</sup> and  $[\text{LRe}(\text{NO})(\text{CO})\text{X}]^+$  ( $\text{L} = 1,4,7\text{-Triazacyclononane}$  and  $\text{X} = \text{F}, \text{Cl}, \text{Br}$ , or  $\text{NO}_2$ )<sup>45</sup>. For the latter series of complexes it is noteworthy that aqueous HF resulted in the isolation of the fluoro-complex. In both of the above classes of compounds, retention of configuration was observed although different mechanisms are proposed. Very recently, Cotton *et al.*<sup>46</sup> reported the isolation of  $\text{Mo}_2\text{F}_4(\text{PR}_3)_4$  from the reaction of the alkyl precursor  $\text{Mo}_2(\text{CH}_3)_4(\text{PR}_3)_4$  with Olah's reagent (pyridine/HF 30:70% solution). This reaction highlights the importance of this route where the desired product is unobtainable via a simple fluorine metathesis reaction with the chloro-analogue.

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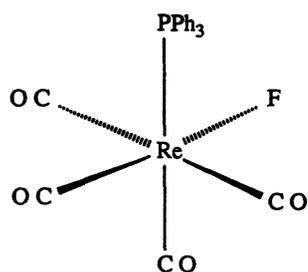
The formation of  $\text{LReF(NO)(CO)}$  by methane elimination demonstrates the usefulness of this little-used synthetic procedure in the preparation of the fluoro-complexes. To date, the only other reported examples of this reaction scheme being employed is the reaction of  $\text{Re(CO)}_5\text{CH}_3$  with  $\text{HPF}_6$  or  $[\text{CPh}_3]\text{PF}_6$ , which results in the formation of  $[\text{Re(CO)}_5(\mu\text{-F)Re(CO)}_5]^{+47}$ .

A number of alkyl derivatives of transition metals are available and it is anticipated that they will undergo similar reactions to those described above. In the present investigation the demethylations of  $\text{Re(CO)}_4(\text{PPh}_3)\text{CH}_3$  and  $\text{Os(CO)}_4(\text{CH}_3)_2$  were attempted.

The reaction of  $\text{Re(CO)}_4(\text{PPh}_3)(\text{CH}_3)$  with  $\text{AHF}$  was undertaken in  $\text{CD}_2\text{Cl}_2$ . On addition of  $\text{AHF}$  and subsequent warming to room temperature methane gas was evolved (characterised by IR), and the solution developed a yellow colour. The resulting complex, formed in a quantitative yield, was characterised by  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopy as *cis*- $\text{ReF(CO)}_4(\text{PPh}_3)$ . The  $^{19}\text{F}$  and  $^{31}\text{P}$  spectra exhibit doublet resonances at  $\delta$ -374.9 and  $\delta$ 10.8 respectively, with mutual coupling of 34Hz. These NMR data are consistent with the *cis*- configuration and are directly analogous to  $\text{ReF(CO)}_3(\text{PPh}_3)_2$ , (see Table 3.5) where assignment of F *cis*- to mutually *trans*- phosphines is proposed.

Also tabulated for comparison are the IR active  $\nu\text{CO}$  bands for  $\text{ReF(CO)}_4(\text{PPh}_3)$  and those of the corresponding halide analogues. The data is consistent with terminal

carbonyls in a molecule of  $C_s$  symmetry (*cis*- isomer) where all four modes of the CO stretching vibration are IR active.



(For the *trans*- geometry,  $C_{4v}$ , 2 bands are predicted). The absence of the corresponding  $\nu_{CO}$  at  $\sim 2018\text{cm}^{-1}$  (observed as a shoulder for the iodo-complex) is presumably the result of the broad absorption at  $1995\text{cm}^{-1}$  obscuring this band. A noteworthy observation from this reaction is the solid-state stability of the complex. Differences in the stability of  $\text{ReF}(\text{CO})_5$  and  $\text{ReF}(\text{CO})_3(\text{PPh}_3)_2$  have already been mentioned (see Section 3.5). For the former complex, room temperature decarbonylation occurred in solution with the formation of the tetramer,  $[\text{Re}(\text{CO})_3\text{F}]_4$ , whilst, for the phosphine substituted derivative, the monomeric species is stable as both a solid and in solution. Hence, from comparison of the observations for  $\text{ReF}(\text{CO})_4\text{PPh}_3$  (this work) and  $\text{ReF}(\text{CO})_3(\text{PPh}_3)_2$  with  $\text{Re}(\text{CO})_5\text{F}$ , the greater basicity of the phosphine ligand compared to that of carbon monoxide would appear to account for the stability of these phosphines towards decarbonylation.

**Table 3.4**Comparison of IR and NMR Data for  $\text{ReF}(\text{CO})_4(\text{PPh}_3)$ 

Complex	$\delta$ $^{31}\text{P}$	$\delta$ $^{19}\text{F}$	$\nu_{\text{CO}}/\text{cm}^{-1}$
$\text{ReF}(\text{CO})_3(\text{PPh}_3)_2^{\text{a}}$	10.3 (35) <sup>a</sup>	not reported	2039(w) 1939(0.27) 1890(0.11)
$\text{ReF}(\text{CO})_4(\text{PPh}_3)$	10.8 (34)	-374.9	2107(s) * 1995(s,br) 1933(br)
$\text{ReCl}(\text{CO})_4(\text{PPh}_3)^{\text{b}}$	4.4	-	2105(0.24) 2018(0.71) 2002(1.00) 1945(0.56)
$\text{ReBr}(\text{CO})_4(\text{PPh}_3)^{\text{b}}$	-	-	2100(s) 2015(s) 1998(vs) 1940(s)
$\text{ReI}(\text{CO})_4(\text{PPh}_3)^{\text{b}}$	-	-	2103(m) 2018(sh) 2001(s) 1949(m)

a, Reference 15b).

b, Reference 50.

\*, Not observed see text

Dimethylsmium tetracarbonyl was found to react with the protic solvent anhydrous hydrogen fluoride at approximately  $-40^\circ\text{C}$ , with the vigorous evolution of methane gas (characterised by gas phase IR). At room temperature all of the solid starting material was consumed and gas evolution appeared to have ceased. A room temperature  $^{19}\text{F}$  NMR spectrum of the colourless solution revealed the presence of two M-F resonances at  $\delta$ -342.8 and  $\delta$ -358.4. With

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time (days) in a closed system, at room temperature, further reaction was observed so that the  $^{19}\text{F}$  NMR resonance at  $\delta$ -342.8 dominated the spectrum. This resonance was attributed to *cis*- $\text{Os}(\text{CO})_4\text{F}_2$  (1) by comparison of the  $^{19}\text{F}$  NMR data with that previously obtained from the  $\text{Os}_3(\text{CO})_{12}/\text{XeF}_2$  system. The resonance at  $\delta$ -358.4 had disappeared at this stage whilst a new resonance at  $\delta$ -361.2 representing 19% of the fluorine-containing species, was evident. The only other resonances in this spectrum are assignable to  $[\text{FOs}(\text{CO})_4(\mu\text{-F})\text{Os}(\text{CO})_4\text{F}]^+$  (4) and result from the dimerisation of  $\text{Os}(\text{CO})_4\text{F}_2$  (*c.f.* the  $\text{Os}_3(\text{CO})_{12}/\text{XeF}_2$  system). A  $^{13}\text{C}$  NMR spectrum of this sample confirmed the assignment of the major species as *cis*- $\text{Os}(\text{CO})_4\text{F}_2$ . However, two new resonances not attributable to  $[\text{FOs}(\text{CO})_4(\mu\text{-F})\text{Os}(\text{CO})_4\text{F}]^+$  were observed at  $\delta$ 161.5 and 154.5. These are presumably associated with the  $^{19}\text{F}$  NMR resonance at  $\delta$ -361.2, although assignment is not possible at this stage.

In another experiment  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$  was allowed to react with  $\text{AHF}$  at  $-40^\circ\text{C}$ . After the initial gas evolution had ceased, the reaction mixture was briefly warmed to room temperature to ensure completion of this initial evolution of volatiles, and then a low temperature ( $-50^\circ\text{C}$ )  $^{19}\text{F}$  NMR spectrum was recorded. The spectrum was dominated by a M-F resonance at  $\delta$ -354.8 (the temperature shifted resonance,  $\delta$ -358.4), which was resolved as a quartet ( $^2J(\text{FH})=13\text{Hz}$ ) exhibiting coupling to three equivalent protons (in the  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum,  $\delta$ -354.8 was observed as a singlet).

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The  $^1\text{H}$  NMR spectrum revealed the corresponding doublet resonance at  $\delta$  0.2 ( $^2\text{J}(\text{FH}) = 13\text{Hz}$ ). These data are assignable to *cis*- or *trans*-  $\text{Os}(\text{CO})_4(\text{CH}_3)\text{F}$  where cleavage of only one  $\text{Os}-\text{CH}_3$  bond has occurred. The  $^1\text{H}$  NMR spectrum of this sample also revealed the presence of a second resonance at  $\delta$  0.1 ( $-50^\circ\text{C}$ ) in an approximate ratio of 2:1 relative to that of the  $-\text{CH}_3$  resonance of  $\text{Os}(\text{CO})_4(\text{CH}_3)\text{F}$ . A possible assignment of this resonance is to dissolved  $\text{CH}_4$ , liberated from the reaction ( $\text{CH}_4$  was reported by F.L'Eplattenier at  $\delta$  0.18 in THF)<sup>48</sup>. However, a low temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the initial reaction products revealed 5 resonances, 3 singlets assignable to terminal CO's at  $\delta$  170.5, 167.2 and 163.3, and 2 C-H resonances at  $\delta$ -23.0 (singlet) and  $\delta$ -19.3 (doublet 9Hz). The doublet in this  $^{13}\text{C}\{^1\text{H}\}$  spectrum is undoubtedly due to  $^{19}\text{F}$  coupling, in agreement with the assignment of  $\text{Os}(\text{CO})_4(\text{CH}_3)\text{F}$ . For the *trans*- isomer of this species one carbonyl resonance would be expected, whereas the *cis*- isomer has three carbonyl environments. Although three  $^{13}\text{C}$  carbonyl resonances were observed, for the *cis*- isomer one should exhibit a large *trans*- F coupling ( $\sim 80\text{Hz}$ ), whereas the other two  $^{13}\text{CO}$  resonances should display relatively smaller CO *cis*- F ( $\sim 2\text{Hz}$ ) and therefore may be unresolved at this resolution. Hence, the data is not unambiguously assignable to either *cis*- or *trans*-  $\text{Os}(\text{CO})_4(\text{CH}_3)\text{F}$ . It appears from the  $^{19}\text{F}$  NMR that there is only one fluorinated complex, but the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicate that two species exist in solution. One possible

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interpretation of these results is that the initial reaction has not reached completion, resulting in the presence of *trans*- Os(CO)<sub>4</sub>(CH<sub>3</sub>)F together with unreacted *cis*- Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub>. This would account for the unassigned methyl resonance in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. Comparison of <sup>13</sup>C chemical shifts data for *cis*- Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> with those from the literature is hampered by differing solvents. However, the <sup>13</sup>CO resonances at δ 167.2 and 163.3 and the methyl resonance at δ-23 appear to be consistent with this assignment. For *cis*- Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> two <sup>13</sup>CO resonances, δ 177.7 and 170.6, are observed at 30°C in the <sup>13</sup>C NMR spectrum.

Obviously, the characterisation of species in this initial stage of the reaction is tentative and requires further investigation. However, it can be ascertained that the reaction of AHF with Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> initially yields Os(CO)<sub>4</sub>(CH<sub>3</sub>)F and then, more slowly, *cis*- Os(CO)<sub>4</sub>F<sub>2</sub>. The latter is observed to partially dimerise to [FOs(CO)<sub>4</sub>(μ-F)Os(CO)<sub>4</sub>F]<sup>+</sup>. The stability of the Os-CH<sub>3</sub> bond to electrophilic attack has also been demonstrated by F.L'Eplattancier *et al.*<sup>49</sup>, where the reaction of the Br<sub>2</sub> with *cis*-Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> similarly resulted in the cleavage of one Os-CH<sub>3</sub> bond to form *cis*-Os(CO)<sub>4</sub>(CH<sub>3</sub>)Br. The second Os-CH<sub>3</sub> bond was unreactive towards Br<sub>2</sub>. However, for the ethyl derivative, complete dealkylation was observed with the formation of *cis*-Os(CO)<sub>4</sub>Br<sub>2</sub>. Characterisation of the intermediates discussed above would be greatly aided by low

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temperature  $^{13}\text{C}\{^{19}\text{F}\}$  NMR experiments after the initial reaction. Also of interest would be the the reaction of AHF with the methyl and ethyl species in a solvent such as  $\text{CH}_2\text{Cl}_2$  where a stoichiometric amount of AHF can be added.

### 3.10 Summary

Presented in this chapter is evidence for a number of fluoro-complexes of osmium, derived from a variety of synthetic routes. The  $\text{Os}_3(\text{CO})_{12}/\text{XeF}_2$  system highlights the problems associated with elucidating the nature of the resulting complexes, which can be conveniently overcome by recording  $^{19}\text{F}$ ,  $^{13}\text{C}$  and  $^{13}\text{C}\{^{19}\text{F}\}$  NMR spectra. From the  $^{19}\text{F}$  NMR study an extension of the chemical shift regions for fluorine bound to metal centre could be made. The solid product from this reaction " $[\text{Os}(\text{CO})_3\text{F}_2]$ " was shown to exhibit useful properties as a precursor for the formation of other fluoro-complexes. This was illustrated by the reaction of " $[\text{Os}(\text{CO})_3\text{F}_2]$ " with  $\text{PMe}_3$  which resulted in  $\text{OsF}_2(\text{CO})_2(\text{PMe}_3)_2$ . The  $\text{PPh}_3$  analogue of this complex,  $\text{OsF}_2(\text{CO})_3\text{PPh}_3$ , was obtained from the reaction of  $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$  with  $\text{XeF}_2$ .

Other fluorinating agents were also investigated. Anhydrous HF and fluorine gas were shown to be suitable reagents for reactions with low-valent organometallic complexes. The reaction of  $\text{F}_2$  with  $\text{Os}_3(\text{CO})_{12}$  resulted in the formation of the same complexes observed in the  $\text{Os}_3(\text{CO})_{12}/\text{XeF}_2$  system, and it is noteworthy that, although

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$F_2$  is considered as an aggressive fluorinating agent, the reaction occurred smoothly at room temperature, not requiring stringent control of the conditions. For AHF, facile dealkylation of transition-metal methyl complexes generated the appropriate fluoro-species, illustrating the usefulness of this synthetic procedure. It is obvious from these results that metal-fluorine bond formation can conveniently be obtained via a number of synthetic procedures, and that this bond displays a degree of stability. It can be anticipated that numerous fluoro-complexes may be prepared using these reaction methods.

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CHAPTER THREE

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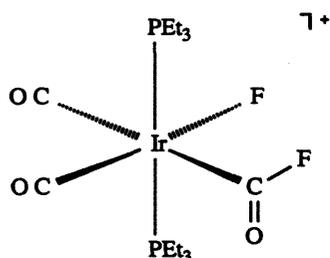
## CHAPTER FOUR

### Reactions Of Five Coordinate Carbonyl Phosphine Complexes With Xenon Difluoride

#### 4.1

##### Introduction

The reaction of  $\text{XeF}_2$  with  $[\text{Ir}(\text{CO})_3(\text{PEt}_3)_2]^+$  has been reported. Oxidative addition to this complex, results in addition to the metal and also across a formal metal-carbon double-bond, producing the fluoroacyl ligand in the room-temperature stable complex,  $[\text{IrF}(\text{CO})_2(\text{COF})(\text{PEt}_3)_2]^+$ .

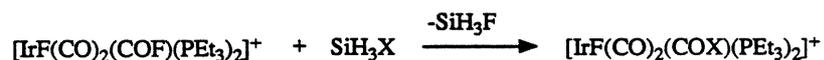


This was the first example of a complex containing a fluoroacyl ligand ( $-\text{COF}$ ) coordinated directly to a metal centre. Characterisation of this species by single crystal X-ray crystallography unambiguously confirmed the octahedral geometry around the iridium, with *trans*-phosphines and the acyl fluoride *cis*- to the iridium-bonded fluorine. The solid state geometry was also shown to be retained in solution by  $^{19}\text{F}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy.

Very recently published work on the analogous chemistry of related five coordinate carbonyl phosphine

iridium complexes has elucidated the controlling factors in the formation of this acyl ligand<sup>2</sup>. For  $[\text{Ir}(\text{CO})_3(\text{PR}_3)_2]^+$ , varying the phosphine ligands revealed a dependency on both electronic and steric affects. The most important factor has proven to be the basicity of the phosphine, i.e. the more basic phosphines increase the electron density on the iridium, stabilising the higher oxidation state and thus enhancing the possibility of oxidative addition. Hence, reactions yielding a fluoroacyl ligand were observed where  $\text{PR}_3 = \text{PEt}_3, \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PEt}_2\text{Ph}$  and  $\text{PEtPh}_2$ , but not where  $\text{PR}_3 = \text{PMePh}_2, \text{PPh}_3$  and  $\text{P}(\text{C}_6\text{H}_{11})_3$ . It was also evident that, for the very bulky phosphines ligands, steric hindrance becomes important. This accounts for the lack of reaction for  $[\text{Ir}(\text{CO})_3(\text{PCy}_3)_2]^+$ , which contains the most basic phosphine of those investigated.

These fluoroacyl complexes display potential as synthetic intermediates. For example, abstraction of the fluoride bound to the carbon by reagents such as  $\text{Me}_3\text{SiX}$  has resulted in the formation of novel acyl complexes e.g<sup>2</sup>.



X= CN, NCS and NCO

Since  $\text{XeF}_2$  readily fluorinates  $\text{Ir}_4(\text{CO})_{12}$ ,  $\text{Os}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$  in a controlled manner, and also affords the novel acyl fluoride complexes outlined above, it was

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considered worthwhile to investigate its reaction with other five coordinate metal complexes, namely  $M(\text{CO})_3(\text{PPh}_3)_2$  ( $M = \text{Ru}$  or  $\text{Os}$ ). Single-crystal X-ray crystallography<sup>3</sup> and IR spectroscopy<sup>4</sup> of these species has revealed their structural similarity to those of the iridium precursors described above.

The previous work on  $[\text{IrF}(\text{CO})_2(\text{COF})(\text{PEt}_3)_2]^+$  highlighted the usefulness of multinuclear NMR spectroscopy in determining reaction products. One of the most noticeable features of the  $^{19}\text{F}$  NMR spectra is the diagnostic chemical shift of the COF ligand. As previously stated, low-valent M-F ( $M =$  transition metal)  $^{19}\text{F}$  chemical shifts are observed at very low frequencies<sup>5</sup>, typically below  $\delta$ -260. For the coordinated COF ligand,  $^{19}\text{F}$  NMR resonances have been observed around  $\delta$ 150. Hence, the  $^{19}\text{F}$  NMR data is particularly useful for distinguishing between these two fluorine environments, and for unambiguously confirming acyl fluoride formation. Low-temperature NMR spectroscopy, as previously demonstrated for  $\text{IrF}(\text{CO})\text{X}(\text{PEt}_3)_2(\text{SF}_3)$  (see Section 1.13), can also provide a valuable tool for investigating thermally unstable or transient species. Hence, the reactions of  $M(\text{CO})_3(\text{PPh}_3)_2$  with  $\text{XeF}_2$  were studied within the NMR probe, the spectra being accumulated at various temperatures in order to identify any intermediates in the reactions.

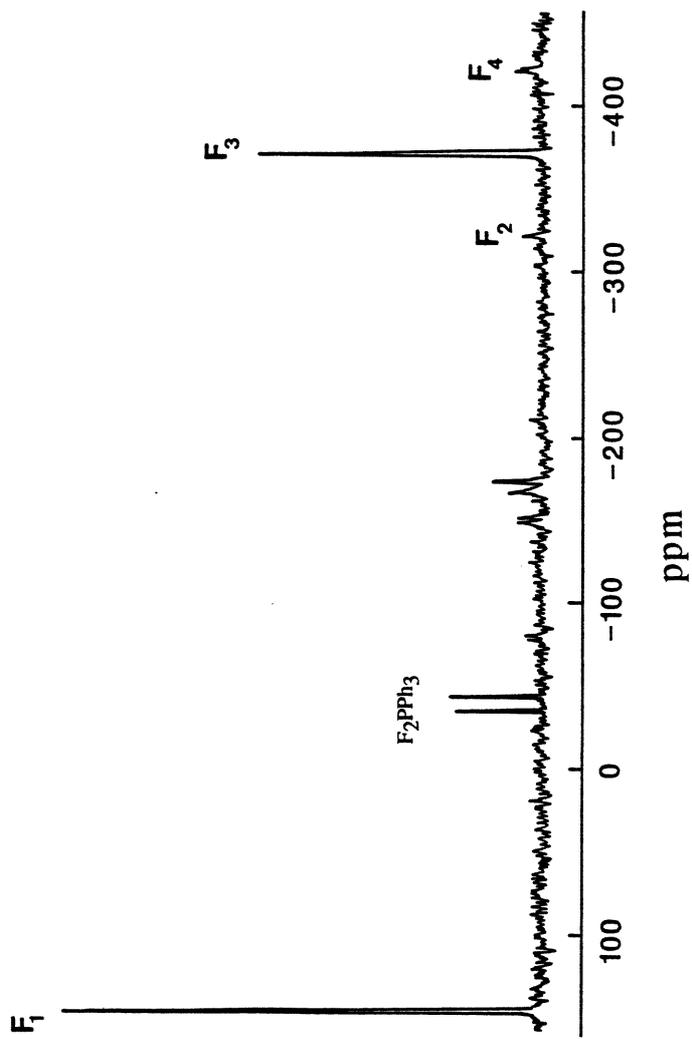
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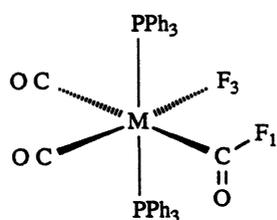
#### 4.2 The Reaction of Os(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> with XeF<sub>2</sub>

The reaction between Os(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> and XeF<sub>2</sub> was followed by <sup>19</sup>F NMR spectroscopy. At 220K, four fluorine resonances were observed at δ146, -321, -370 and -421, F<sub>1</sub>, F<sub>2</sub>, F<sub>3</sub> and F<sub>4</sub> respectively. As previously discussed, the high-frequency resonance, F<sub>1</sub>, is diagnostic of a COF ligand. Consequently the <sup>19</sup>F NMR data indicated the formation of a new fluoro-acyl complex at this temperature.

On warming, the F<sub>1</sub> and F<sub>3</sub> resonances broadened, becoming indistinguishable from the baseline of the spectrum at room temperature. These resonances sharpened upon recooling, implying that they are undergoing a reversible fluxional process. The resonances F<sub>1</sub> and F<sub>3</sub> dominated the <sup>19</sup>F NMR spectrum at this stage of the reaction (Fig.4.1), (F<sub>2</sub> and F<sub>4</sub> represent only minor components at this point which will be discussed later). F<sub>2</sub>, F<sub>3</sub> and F<sub>4</sub> all occur in the region of the spectrum associated with fluorine bound directly to a low-valent metal centre<sup>5</sup>. However, the independent changes in the intensity of these resonances with temperature indicates the formation of three separate complexes in the reaction. Those resonances associated with F<sub>1</sub> and F<sub>3</sub> were observed to be in a ratio of 1:1 and their mutual dependency on the temperature allowed their assignment to the same complex (1a).

Fig 4.1  $^{19}\text{F}$  NMR Spectrum of  $\text{Os}(\text{CO})_3(\text{PPh}_3)_2 + \text{XeF}_2$  after Warming to 240K then Recooling to 200K





1a) M=Os, 1b) M=Ru

A high resolution, low-temperature  $^{19}\text{F}$  NMR spectrum revealed the expected triplet coupling of  $\text{F}_3$  to the mutually *trans*- phosphine ligands ( $^2\text{J}(\text{F}_3\text{P})=30\text{Hz}$ ). The longer-range  $^3\text{J}(\text{F}_3\text{F}_1)$  doublet coupling was not observed on either  $\text{F}_1$  or  $\text{F}_3$ , even approaching the low-temperature limit of the solvent. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum which, at 240K revealed a doublet resonance at 60.1, ( $^2\text{J}(\text{F}_3\text{P})=30\text{Hz}$ ) corresponding to the coupling between the equivalent phosphines and  $\text{F}_3$ , confirmed the structural assignment of (1a) i.e. the formation of a single Os-F bond. Coupling between the phosphine ligands and  $\text{F}_1$  was not observed, although by analogy with  $[\text{IrF}(\text{CO})_2(\text{COF})(\text{PEt}_3)_2]^+$  the magnitude of this coupling is only likely to be of the order of a few Hertz<sup>2</sup>.

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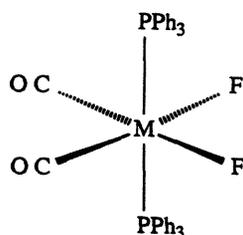
The complex has been assigned with fluoride trans- to carbonyl, rather than to the fluoro-acyl group, on the basis of the position of F<sub>3</sub> in the <sup>19</sup>F NMR spectrum, which is characteristic of such a fluoride environment in neutral complexes (see Section 3.3). As observed from the <sup>19</sup>F and <sup>31</sup>P spectra, which both show broadening of the respective resonances at higher temperatures, (1a) is undergoing some fluxional process which is at coalescence at room temperature. However, a differentiation between an intra- or inter-molecular process is not possible from the evidence available, the fast exchange limit being unobtainable due to further reaction of this species at higher temperatures, as discussed later.

Removal of the solvent at this stage of the reaction yields a yellow solid. The IR spectrum of this material revealed terminal VCO bands at 2053 and 1972 cm<sup>-1</sup>, which is consistent with (1a) (for Os(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> only one IR band is observed<sup>4</sup> (VCO= 1900cm<sup>-1</sup>). The increase in the formal oxidation state of osmium (Os(0) to Os(II)) is evident by the shift of the VCO bands to higher frequency<sup>6</sup>. Also apparent from the IR spectrum is the expected VCO for Os-COF, observed at 1651cm<sup>-1</sup>, which is within the region characteristic of ketonic carbonyls consistent with the formation of an acyl ligand<sup>7</sup>. It is noteworthy that for the iridium system, discussed above, the PPh<sub>3</sub> derivative does not produce the desired acyl-fluoride complex. This is ascribed to the basicity of the phosphine ligand. However

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for  $M(\text{CO})_3(\text{PPh}_3)$  facile reaction does occur implying that the phosphine ligands are not the only governing factors for the reaction but, that the metal centre also plays a significant role.

Complex (1a) appears to be fairly stable in solution at room temperature, resonances for this species still being evident in the  $^{19}\text{F}$  spectra after two days. However, a new  $^{19}\text{F}$  NMR resonance at  $\delta$ -305 eventually appeared in the spectrum slowly growing in intensity over this period. In an attempt to increase the rate of this subsequent reaction, (1a) was refluxed for 6hrs in  $\text{CD}_2\text{Cl}_2$ . The resonance at  $\delta$ -305 was the major signal in the  $^{19}\text{F}$  NMR spectra of the resulting solution, recorded both at 220K and room temperature. The resonance resolved as a triplet, displaying mutual coupling to a triplet resonance at  $\delta$ 1.4 ( $^2J(\text{PF})=29\text{Hz}$ ) in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. This allowed the characterisation of species (2a), *cis*- $\text{Os}(\text{CO})_2\text{F}_2(\text{PPh}_3)_2$ . Assignment of the *cis*- geometry is based on similar arguments to those discussed for  $\text{Os}(\text{CO})_2\text{F}_2(\text{PMe}_3)_2$  (Chapter 3), the fluoride resonance being in the region characteristic of F *trans*- to CO. The formation of this complex from the acyl fluoride undoubtedly results from CO elimination, but the mechanism for the reaction is, as yet, unclear.



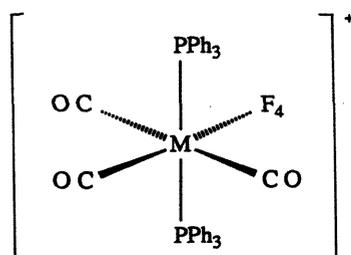
2a) M=Os, 2b) M=Ru

Following the characterisation of the fluoroacyl complex (1a), and the final product (2a), it was of interest to reinvestigate the initial low-temperature reaction in which the two as yet unassigned resonances, F<sub>2</sub> and F<sub>4</sub>, were observed. The absence of these signals in the higher temperature spectra implies that they may have resulted from intermediates in the formation of (1a), hence their assignment may possibly suggest a mechanism for the overall reaction.

In the initial low-temperature spectra, F<sub>2</sub> and F<sub>4</sub> were in relatively greater intensity in the <sup>19</sup>F NMR spectrum recorded at 215K, compared with the spectra recorded at higher temperatures (Fig.4.2). This implies the preferential formation of these species at lower temperature, prior to their further reaction producing (1a). The <sup>19</sup>F NMR resonances F<sub>2</sub> and F<sub>4</sub> were observed as a doublet of triplets and a triplet respectively. Proton decoupling the <sup>19</sup>F NMR

spectrum resulted in a change in  $F_2$  only, which resolved to a triplet. The triplet splittings on both resonances are undoubtedly due to coupling to *trans*-phosphine ligands, subsequently confirmed by a low temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. The  $^{31}\text{P}\{^1\text{H}\}$  resonances for the complexes containing  $F_2$  and  $F_4$  were observed at 60.4 and -10.2 respectively, both signals exhibiting doublet splitting. This means that the initial species are mono-fluorinated complexes.

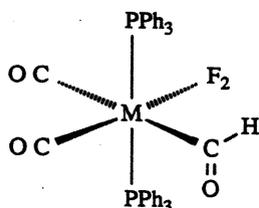
From this evidence,  $F_4$  was attributed to the cationic complex (3a).



3a) M=Os, 3b) M=Ru

The  $^{19}\text{F}$  chemical shift observed for this species (6-421) correlates strongly with that obtained for the analogous  $[\text{Os}(\text{CO})_5\text{F}]^+$  complex at 6-433 (Chapter 3). Both of these resonances are strongly shielded relative to the expected chemical shift region for F *trans*- to CO found in neutral complexes (see NMR discussion, Section 3.3).

A low-temperature  $^1\text{H}$  NMR spectrum of the solution at this stage revealed that  $\text{F}_2$  is coupled to a doublet resonance at  $\delta 10.1$  in the  $^1\text{H}$  NMR spectrum ( $^2\text{J}(\text{HF})=46.4\text{Hz}$ ), confirming that this complex is mono-fluorinated. The triplet splitting of the resonance by the phosphine ligands was not observed. This region of the  $^1\text{H}$  NMR spectrum is characteristic of a formyl ligand ( $-\text{COH}$ ) coordinated to a transition metal<sup>8</sup>, thus the NMR data for this complex may be assigned to complex (4a).



4a)  $\text{M}=\text{Os}$ , 4b)  $\text{M}=\text{Ru}$

The formation of this species in the initial reaction is difficult to rationalise, in particular the source of the hydrogen. Since reactions were carried out in the deuterated solvent,  $\text{CD}_2\text{Cl}_2$ , reaction with the solvent could not give rise to (4a). Various other sources of hydrogen were considered. The  $^1\text{H}$  NMR spectrum of the solvent showed no signs of impurities. Another possibility was that HF had been produced as the decomposition product of a transient fluoride species, and this is the source of the hydrogen.

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Previous work has shown that AHF reacts with  $M(\text{CO})_3(\text{PPh}_3)_2$  resulting in the formation of  $[\text{MH}(\text{CO})_3(\text{PPh}_3)_2]^+$  ( $M=\text{Ru}$  and  $\text{Os}$ ) via protonation of the metal centre<sup>9</sup>. The ruthenium hydride complex could be fluorinated with  $\text{XeF}_2$ , in a molar ratio of 1:1, but, no evidence of the formyl complex was observed at low temperature (240K), in this reaction, as a result of hydride migration to the carbonyl ligand. Instead, (3b) was observed by  $^{19}\text{F}$  NMR spectroscopy to be the major species formed. It is worth noting that the formation of the fluoroacyl ligand bound to a metal-hydride complex was not observed. This suggests that the terminal fluorides in (3a) and (3b) play an important role in the reactivity of the carbonyl ligands.

The source of the hydrogen in (4a) and (4b) would appear, therefore, to be derived from the phenyl groups of the  $\text{PPh}_3$ . This is supported by the observation of weak peaks assignable to fluorinated aromatic molecules in the low-temperature  $^{19}\text{F}$  NMR spectra. The mechanism for this is unclear, but it does appear (see below) that this is merely a side reaction and not important in the overall reaction scheme.

By comparison with the analogous ruthenium system, discussed later, the intensity of the  $^{19}\text{F}$  NMR resonance assigned to (4b) appears to be unaffected by an increase in the temperature, whilst that due to the cationic species is obviously influenced at the temperature where acyl fluoride formation occurs. The implication from this NMR data is that

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the reaction of  $\text{XeF}_2$  with  $\text{M}(\text{CO})_3(\text{PPh}_3)_2$  results in the stepwise formation of (3), and then (1). The formyl species appears to occur from a side reaction, and is unimportant in the formation of (1), as depicted in Scheme 1 and 2.

The formation of a cationic intermediate prior to acyl fluoride formation has also been postulated as the mechanism of the reaction between  $[\text{Ir}(\text{CO})_3(\text{PR}_3)_2]^+$  and  $\text{XeF}_2^{2+}$ .

Two possible processes were envisaged for this mechanism:-

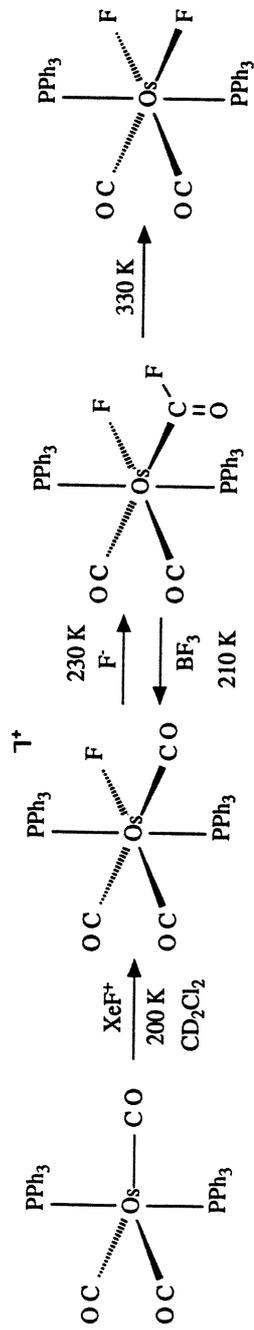
- 1) Prior loss of one of the ligands from the metal coordination sphere.
- 2) Initial addition of a formally positive fragment to the substrate, followed by ligand substitution to incorporate the negative fragment.

The first of these mechanisms was discounted as no ligands were lost in the formation of the acyl fluoride complexes. However, it was also apparent that the alternative mechanism was not completely correct as substitution had not occurred. Hence, the mechanism was considered to involve 2 steps.

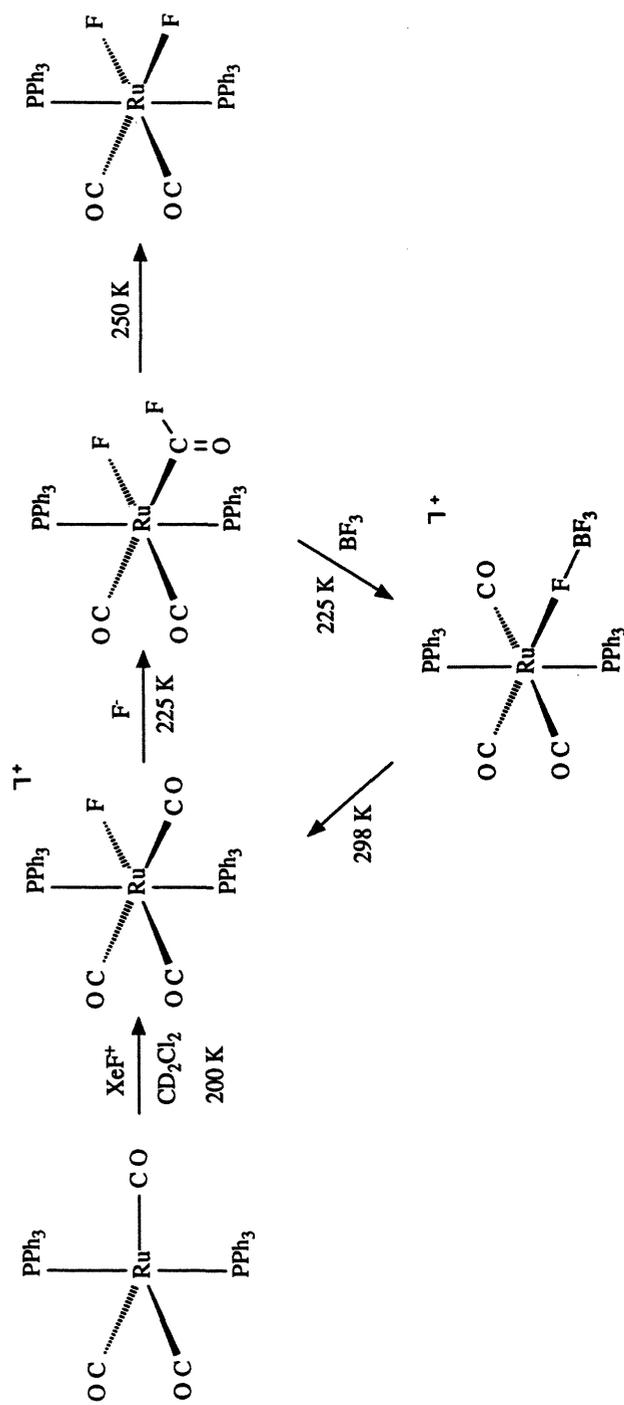
- 1)  $[\text{Ir}(\text{CO})_3(\text{PEt}_3)_2]^+ + \text{XeF}^+ \longrightarrow [\text{IrF}(\text{CO})_3(\text{PEt}_3)_2]^{2+}$
- 2)  $[\text{IrF}(\text{CO})_3(\text{PEt}_3)_2]^+ + \text{F}^- \longrightarrow [\text{IrF}(\text{CO})_2(\text{COF})(\text{PEt}_3)_2]^+$

The initial stage was substantiated by the formation of  $[\text{IrF}(\text{CO})_3(\text{PPh}_3)_2]^{2+}$  from the reaction of  $\text{XeF}_2$  and  $\text{BF}_3$  (i.e.  $\text{XeF}^+\text{BF}_4^-$ ) with  $[\text{Ir}(\text{CO})_3(\text{PPh}_3)_2]^+$  and the feasibility of the

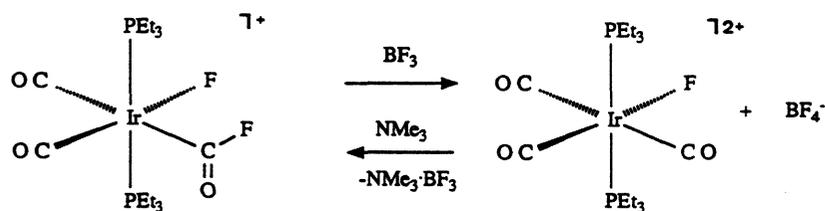
**Scheme 1**



**Scheme 2**



second step was demonstrated by the following reaction.



From the evidence available, it is not possible to differentiate for this second stage whether either direct F- attack at a coordinated CO, or migration of the metal bound fluoride to CO (resulting in a unsaturated intermediate) followed by F- coordination to the iridium centre, is occurring.

Prior to this investigation and those involving  $[\text{Ir}(\text{CO})_3\text{L}_2]^{+1,2}$ , there was only one example of a complex containing a halogen-acyl ligand. Noack<sup>10</sup> noted that the oxidative addition of halogens to the iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , resulted in the initial formation of the halo-acyl ligands ( $-\text{COX}$ ,  $\text{X}=\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ). These reactions ultimately yielded the previously characterised dihalo-tetracarbonyls,  $\text{Fe}(\text{CO})_4\text{X}_2$ , however, with the aid of low-temperature IR spectroscopy, two intermediates were observed during this reaction. At  $-80^\circ\text{C}$   $\text{Fe}(\text{CO})_5$  reacts with  $\text{Br}_2$ , in a solvent mixture of  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ , resulting in the formation of  $[\text{Fe}(\text{CO})_5\text{Br}]\text{Br}$  and

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FeBr(COBr)(CO)<sub>4</sub>. These complexes were characterised from the independent change of their νCO IR bands, at various temperatures.

Warming of the reaction mixture revealed that the acyl complex was stable at -30°C whereas the cationic species was absent at this temperature. Above -30°C, however, CO elimination occurred, and the only νCO bands observed were those attributable to *cis*-Fe(CO)<sub>4</sub>Br<sub>2</sub>. Similar reactions were reported for Cl<sub>2</sub> and I<sub>2</sub>, however for iodine the intermediates displayed a far greater degree of instability.

From the IR data, two possible mechanisms for the reactions were considered. The results suggest either Br<sup>-</sup> attack on a carbonyl group, or a migration of the metal bound Br to the carbonyl followed by Br<sup>-</sup> attack at the resulting vacant coordination site on the metal centre. However, as with the reaction between XeF<sub>2</sub> and [Ir(CO)<sub>3</sub>L<sub>2</sub>]<sup>+</sup>, the inability to isolate the various steps of the reaction precluded definitive assignment to either mechanism.

From the NMR data presented in this thesis it is apparent that the various stages of the reaction between M(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>, (M=Ru and Os), and XeF<sub>2</sub> are being observed at different temperatures. However, since it is not possible to distinguish between the two mechanisms discussed above, it was of interest to perform the reaction of (1a) with BF<sub>3</sub>. The acyl complex (1a) possesses two fluoride ligands, therefore, the preferential, or selective removal of either of these ligands by the fluoride abstractor BF<sub>3</sub><sup>11</sup> should aid

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in the interpretation of the mechanism. This reaction was conveniently accomplished using a glass NMR tube connected to a Youngs tap, which meant that the initial reaction producing (1a) and the subsequent addition of  $\text{BF}_3$  could be performed in two stages and monitored by NMR spectroscopy. On warming the frozen solution of (1a) and  $\text{BF}_3$ , reaction occurred below 215K, resulting in the formation of  $\text{BF}_4^-$  and (3a). Hence, fluoride abstraction by  $\text{BF}_3$  appears to preferentially occur at the acyl fluoride. This is analogous to the reaction of  $[\text{IrF}(\text{CO})_2(\text{COF})(\text{PEt}_3)_2]^+$  with  $\text{BF}_3$ , which produced the novel di-cation,  $[\text{IrF}(\text{CO})_3(\text{PEt}_3)_2]^{2+}$ .

Although these reactions are regarded as occurring at the acyl fluoride, the alternative mechanism of abstraction of the terminal fluoride ligand, followed by the migration of the fluoride bound to carbon, cannot be ruled out from the available evidence. However, the Os-F bond in (3a) was observed, by  $^{19}\text{F}$  NMR spectroscopy, to be unreactive towards residual  $\text{BF}_3$  at this temperature (215K) and upon subsequent warming to room temperature. This implication that the terminal fluoride ligands are inert towards this Lewis acid substantiates removal of  $\text{F}^-$  from the COF ligand. Hence, the reaction with  $\text{BF}_3$  supports the proposed mechanism, in which (1a) results from fluorination (nucleophilic attack by  $\text{F}^-$ ) at a coordinated carbonyl in (3a). The alternative mechanism of ligand migration can also be discounted from the observation of the thermal stability of (3a) (formed in the  $\text{BF}_3$  reaction) even at room temperature, which implies that

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(3a) is stereochemically rigid on the NMR timescale. It is also reasonable to suggest that nucleophilic attack is the mechanism involved in the reaction of  $\text{Fe}(\text{CO})_5$  with  $\text{Br}_2$  and  $[\text{Ir}(\text{CO})_3\text{L}_2]^+$  with  $\text{XeF}_2$  where, previously, a differentiation between nucleophilic attack or ligand migration was not possible.

The susceptibility of a carbonyl to nucleophilic attack can be discussed by considering the molecular orbitals of carbon monoxide<sup>12</sup>. The coordination of CO to a transition metal involves the removal of electron density from the HOMO ( $5\sigma^*$ ), and the addition of electron density to its LUMO ( $2\pi^*$ ), which may enhance its reactivity depending on the metal centre. A metal in a formally high oxidation state and/or with strong  $\pi$ -acid coligands acts strongly as a  $\sigma$ -acceptor, but a weak  $\pi$ -donor (*c.f.*  $\text{Ir}(\text{CO})_3\text{F}_3$  see Section 2.6). Thus, the carbonyl ligands in these complexes are more susceptible to nucleophilic attack than those on a metal in a low oxidation state possessing strongly electron-donating ligands i.e. the most electrophilic carbonyl ligands are found in cationic, high oxidation state metal complexes, as observed for the reactions of the cationic intermediates  $[\text{MF}(\text{CO})_3(\text{PPh}_3)_2]^+$  ( $\text{M}=\text{Ru}, \text{Os}$ ) and  $[\text{IrF}(\text{CO})_3(\text{PR}_3)_2]^{2+}$  with  $\text{F}^-$ .

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#### 4.3 The Reaction Between Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> and XeF<sub>2</sub>

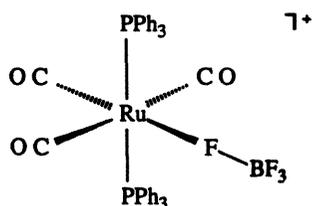
The reaction of Ru(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> with XeF<sub>2</sub> was studied in an identical manner. <sup>19</sup>F and <sup>31</sup>P NMR spectroscopy revealed directly analogous chemistry to the osmium system with the formation of the ruthenium derivatives (1b), (2b), (3b) and (4b). The overall reaction is depicted in Scheme 2. The only difference between the two systems was the temperature of the specific stages. At 220K (3b) and (4b) were observed by <sup>19</sup>F NMR spectroscopy, but, at this point the acyl-fluoride complex (1b) was absent. On warming to 230K then 235K, where formation of the acyl-fluoride complex (1b) occurred the intensity of the resonance due to the cation (3b) was significantly affected (see Fig 4.2). This observation is consistent with the mechanism discussed above. After warming the reaction mixture to 250K and then cooling to 200K, the complex (1b) was observed to be the major species in solution. Above 260K this complex decomposed to the *cis*-difluoride (2b), which exhibits triplet resonances in both <sup>19</sup>F and <sup>31</sup>P NMR spectra at  $\delta$ -378 and  $\delta$ -22.2 respectively (<sup>2</sup>J(PF)=19Hz).

The reaction between the ruthenium fluoroacyl complex (1b) and BF<sub>3</sub> resulted in the formation of the mono-fluoride cation (3b) and BF<sub>4</sub><sup>-</sup> at room temperature. For this system, however, low temperature (215K) <sup>19</sup>F and <sup>31</sup>P NMR spectra

Fig 4.2 Variable Temperature  $^{19}\text{F}$  ( $^1\text{H}$ ) NMR Spectra of the Products from the Reaction Between  $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$  and  $\text{XeF}_2$  (on warming from 200K) ( $\text{F}_1$  not shown)



revealed the formation of a thermally unstable  $\text{BF}_3$  adduct, shown below. The Ru-F resonance for this species is observed as a quartet of triplets at  $\delta$ -302.4. The triplet splitting is due to the coupling to *trans*-phosphines ( $^2J(\text{PF})=10$ ). The  $^{31}\text{P}$  NMR spectrum displays a doublet resonance at  $\delta$ 21.2. The quartet coupling of the Ru-F resonance is related to the  $^{19}\text{F}$  doublet resonance due to coordinated  $\text{BF}_3$  ( $^2J(\text{FF})=88$ ).



Similar observations have been reported for complexes containing  $\text{BF}_4^-$  as a counterion. For species of the type  $[\text{CpM}(\text{CO})_2\text{L}]\text{BF}_4$  ( $\text{M}=\text{Mo}$ ,  $\text{W}$ , and  $\text{L}=\text{CO}$ ,  $\text{PPh}_3$  and  $\text{P}(\text{OPh})_3$ ) the coordinated and terminal fluorine atoms of the  $\text{BF}_4^-$  ligand can be distinguished by their low temperature  $^{19}\text{F}$  NMR signals<sup>13</sup>. As for  $[\text{RuF}(\text{CO})_3(\text{PPh}_3)_2.\text{BF}_3]^+$  the  $^{19}\text{F}$  M-F NMR resonances are observed as quartets below  $\delta$ -300, whereas those due to  $\text{BF}_3$  occur as doublet resonances at  $\sim$ 6155.

Obviously, this low temperature species results from an initial fluoride abstraction of the fluorine bound to the carbonyl in (1b), followed by the interaction of excess  $\text{BF}_3$  with the mono-fluorinated cation. NMR data for all of the described fluoro-complexes are presented in Table 4.1.

**Table 4.1**

NMR Data for Complexes 1 to 4 at 25°C

Complex	$\delta^{31}\text{P}$	$\delta^{19}\text{F}$	Assignment	$^2\text{J}(\text{PF})/\text{Hz}$	Temperature/K
1a)	0.1 (d)	-370 (t) 146 (s)	F <sub>3</sub> F <sub>1</sub>	30	220
1b)	19.6 (d)	-380 (t) 156 (s)	F <sub>3</sub> F <sub>1</sub>	18	220
2a)	1.4 (t)	-305 (t)	-	29	298
2b)	22.2 (t)	-318 (t)	-	19	298
3a) <sup>a</sup>	0.4 (d)	-321 (dt)	F <sub>2</sub>	46 <sup>b</sup> ,25	220
3b) <sup>a</sup>	24.7 (d)	-316 (dt)	F <sub>2</sub>	54 <sup>b</sup> ,16	220
4a)	-10.2 (d)	-421 (t)	F <sub>4</sub>	29	220
4b)	-	-436 (t)	F <sub>4</sub>	19	220

a, <sup>1</sup>H NMR resonance also observed at  $\delta$ 10.7 for 1a) and  $\delta$ 10.1 for 1b)  
b, <sup>2</sup>J(FH)

#### 1.4 Discussion of the Crystal Structure

##### of RuF<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>

Crystals of *cis*- RuF<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> were obtained from a CD<sub>2</sub>Cl<sub>2</sub> solution, by slow vapour diffusion with diethyl ether. A single-crystal X-ray structure determination revealed the solid-state geometry to be as predicted from the NMR analysis. The molecule was effectively octahedral with mutually *cis*- fluoride ligands and mutually *trans*-phosphines. A full set of bond lengths and angles are listed in the Appendix. Although the Ru-C and Ru-P bond lengths slightly shorter than other d<sup>8</sup> Ru(II) carbonyl phosphine complexes they are comparable with these species (see Table 4.2).

**Table 4.2**Selective Bond Length data for d<sup>6</sup> Ruthenium  
Carbonyl Phosphine Complexes

Complex	Ru-P/Å	Ru-C/Å	C-O/Å	Ref
<i>cis</i> -RuF <sub>2</sub> (CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	2.407(1)	1.832(7)	1.149(8)	-
<i>cis</i> -RuI <sub>2</sub> (CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	2.445(1) 2.453(1)	1.881(7) 1.890(7)	1.131(9) 1.096(9)	14
<i>cis</i> -RuCl <sub>2</sub> (CO) <sub>2</sub> (P(Bzl) <sub>3</sub> ) <sub>2</sub>	2.410(2)	1.869(7) 1.858(7)	1.131(9) 1.129(10)	15
<i>cis</i> -RuCl <sub>2</sub> (CO)(CSe)(PPh <sub>3</sub> ) <sub>2</sub>	2.425(7) 2.430(7)	1.854(34)	1.196(40)	16
RuCl <sub>2</sub> (CO)(C <sub>2</sub> H <sub>4</sub> )(PMe <sub>2</sub> Ph) <sub>2</sub>	2.414(1)	1.831(10)	1.136(10)	17

The most interesting features of this structure are the terminal fluoride ligands. Few structures have been reported for low-valent organometallic fluoro-complexes, however the Ru-F bond lengths of 2.008(4) are consistent with the ones previously reported (see Table 2.2). This structural determination is also important in confirming the geometry of the complex. Previously, the differentiation between *cis*- and *trans*- isomers of RuF<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was based on the <sup>19</sup>F NMR chemical shift for this complex, which occurred within a region which had been shown to be characteristic of F *trans*-CO. Although this observation is based on the extensive NMR investigations of fluoro-complexes described in this thesis

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and related recent studies (see 1.12 and 1.13), this represents only the second structural determination of such a carbonyl phosphine complex of a late transition metal for which the  $^{19}\text{F}$  NMR spectrum has been reported. The X-Ray structural and  $^{19}\text{F}$  NMR analysis of both  $[\text{IrF}(\text{COF})(\text{CO})_2(\text{PR}_3)_2]^+$  and  $\text{RuF}_2(\text{CO})_2(\text{PPh}_3)_2$  support the interpretation of the  $^{19}\text{F}$  NMR chemical shift ranges, substantiating many of the structural assignments proposed in this thesis.

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### CHAPTER FOUR

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## CHAPTER FIVE

### Experimental Section

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### EXPERIMENTAL

All preparative manipulations were carried out either on a metal vacuum line (Fig.5.1.) with facilities to connect glass or FEP reaction vessels, via Teflon couplings, (Fig.5.2), or a glass line using standard Schlenk techniques. Preparations requiring AHF were performed using plastic reaction vessels. Care must be exercised when handling this corrosive material.

#### 5.1 Metal Vacuum Line

This consisted of stainless steel or Monel Autoclave Engineers valves (AE-30 series) [Autoclave Engineers Inc., Erie, Pennsylvania, U.S.A.] connected via Autoclave Engineer connectors. Argon arc welded 'U' traps were incorporated to permit separation and condensation of gases in the metal manifold. Inlets for argon [BOC Special Gases] and fluorine [Air Products] (from a 1dm<sup>3</sup> nickel can) were positioned as shown in Fig.5.1. Rough pump outlets were connected to a soda-lime chemical scrubber unit of volume 1dm<sup>3</sup> which neutralised fluorine gas and HF, thereby protecting the rotary pump [Model PSR/2, NGN Ltd., Accrington, Lancashire] which provided a vacuum of 10<sup>-2</sup>mmHg. High vacuum was achieved via outlets to a mercury diffusion pump (the more efficient oil diffusion pumps were avoided because of the reactive nature of fluorine or volatile fluorides to hydrocarbons) coupled to a NGN rotary pump. The pumping system, which provided a vacuum in the region of 10<sup>-5</sup> mmHg,

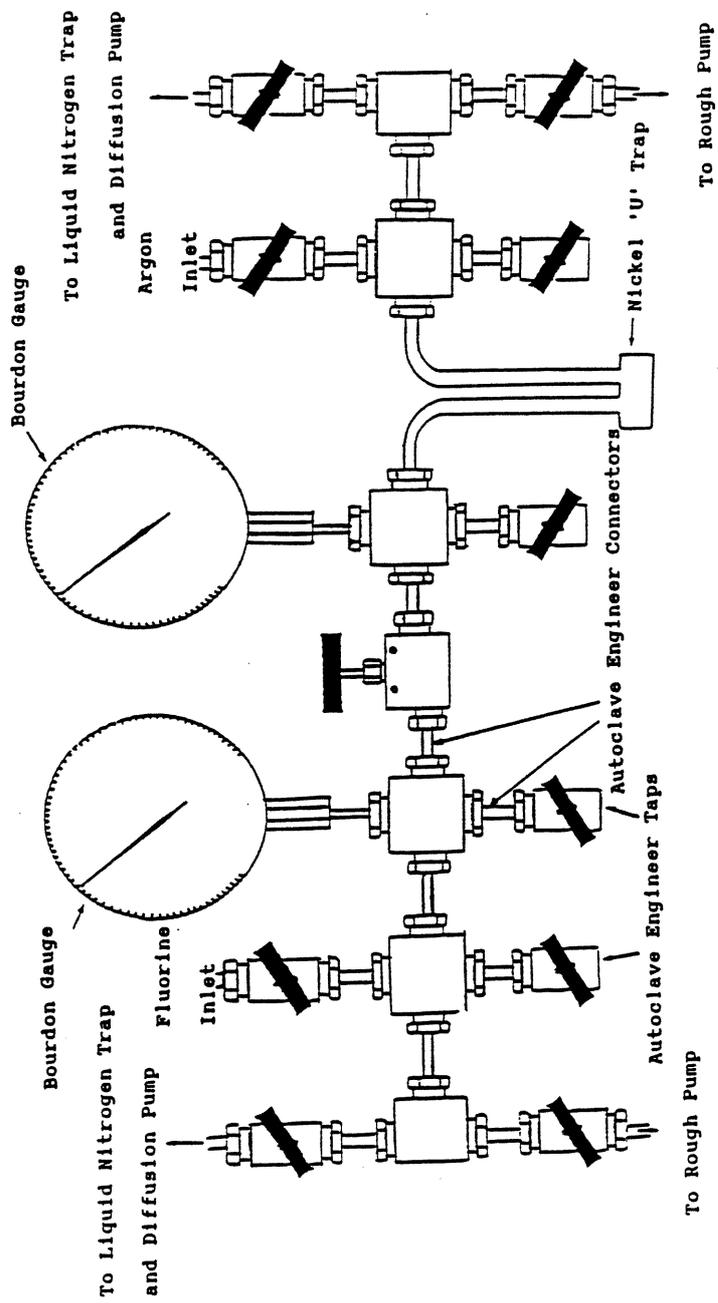


Fig 5.1 Metal Vacuum Line

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was protected by a glass trap immersed in liquid nitrogen. Pressures of 0-1500 mmHg were measured by Bourdon tube gauges [Type IF/66Z, Budenberg Gauge Co., Broadheath, Greater Manchester.] and high vacuum was measured by a Penning gauge situated between the manifold outlet and the liquid nitrogen trap.

## 5.2 Dry Box

Involatile materials were manipulated in a auto-recirculating positive pressure dry box [Vacuum Atmosphere Co., VAC NE 42-2 Dri Lab.], which provided a nitrogen atmosphere with a water and oxygen content of less than 5ppm. The quality of the atmosphere was maintained via circulation through columns of manganese oxide and molecular sieves which removed oxygen and water respectively. The dry box was equipped with a Sartorius balance [Model 1601 MP8]. Static charge build-up was found to affect weighings and therefore, a Zerostat 3 anti-static gun was deployed prior to weighing. Depending on the sensitivity of the various complexes synthesised in this investigation, reaction vessels and connectors were pre-seasoned. This was conveniently achieved by introducing 500mmHg pressure of fluorine gas into the evacuated system. The system was then evacuated to high vacuum ( $10^{-5}$ mmHg), having initially neutralised the  $F_2$  gas through a soda lime trap.

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### 5.3 Reaction Vessels

Various glass and FEP reactors were used during the experimental work. Glass reaction vessels were made to suit the specific reactions, and were fitted with Young's greaseless taps. For the reactions carried out in FEP, in general a straightened 4 mm O.D. x 250mm FEP tube [Production Techniques Ltd., Fleet, Hampshire, UK] was first prepared by sealing at one end by heat moulding into a 5 mm O.D. NMR tube. These were then connected to Chemcon coarse control needle valves [Type STD/VC-4, Production Techniques] by a PTFE 'O' compression union (see Fig.5.2). Reactions were carried out in these FEP tubes, but, before the introduction of the reagents, the system was evacuated to approximately  $10^{-4}$ mmHg to ensure that a vacuum tight system had been obtained. Volatile reagents were transferred into these tubes under static vacuum, whereas non-volatile products were loaded into the evacuated FEP tubes in the dry box and then placed back on to the vacuum line where solvents could be introduced (see Fig.5.2). After reaction, the solvent was either removed to permit the analysis of the resulting solid, or the tubes were sealed under vacuum at the top by heating with a small ring oven under vacuum, whilst keeping the frozen solution at  $-196^{\circ}\text{C}$ . The resulting sealed FEP tubes (Fig.5.3) could then be examined by NMR spectroscopy. All reactions performed with AHF require the use of plastic vessels and couplings, and CARE must be exercised when handling this corrosive material. For larger-

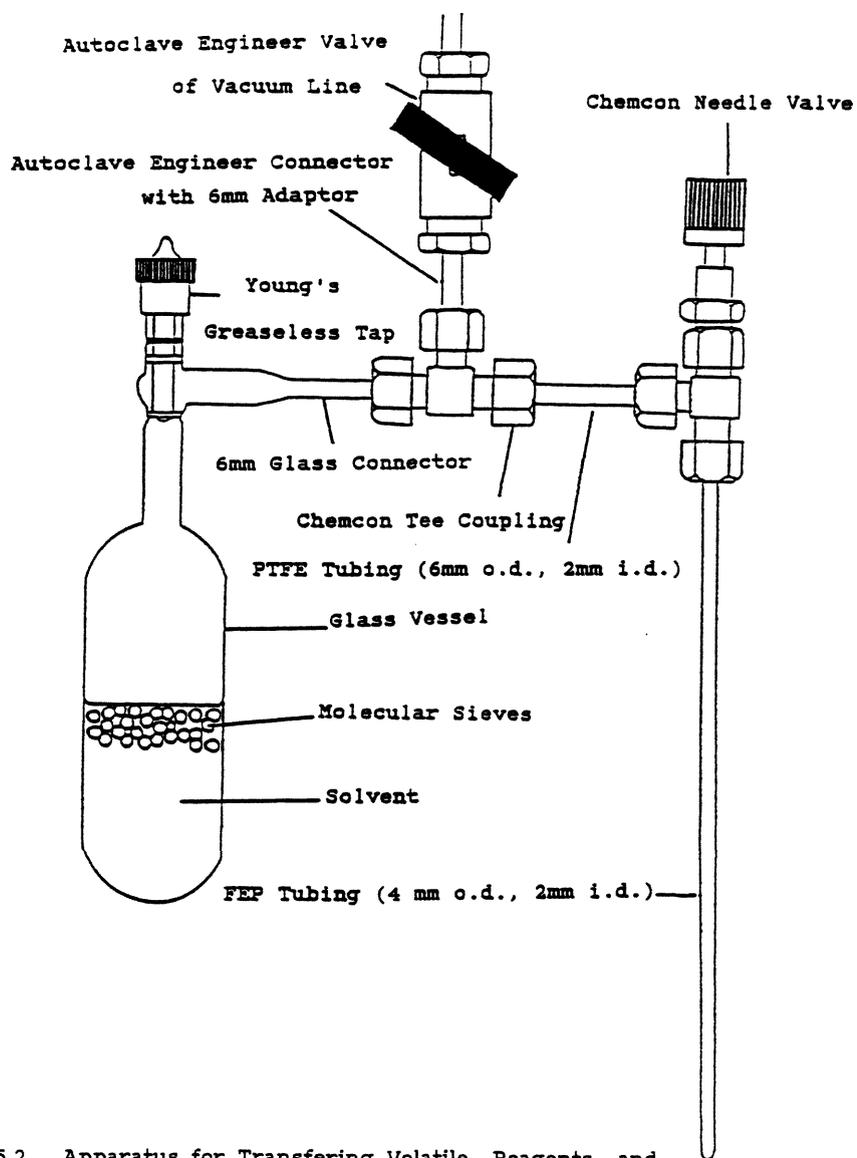


Fig 5.2 Apparatus for Transferring Volatile Reagents and Solvents

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scale reactions 6mm O.D. FEP tubes were prepared and connected to the vacuum line in a similar manner to that described above; or  $\frac{1}{2}$ " O.D. x 150mm FEP tubes (wall thickness 0.062") and Teflon coarse control needle valves  $\frac{1}{2}$ " O.D. (IND/VC.8F. Production Techniques Ltd.) were utilised.

#### 5.4 NMR Spectroscopy

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectroscopies were carried out on a Bruker AM300 spectrometer at 300, 75 and 282 121 MHz respectively and  $^{13}\text{C}$  and  $^{19}\text{F}$  on a Varian VXR600s at the University of Edinburgh SERC Ultra-High NMR service at, 150 and 564 MHz respectively. Spectra were recorded on samples in 4mm O.D. FEP NMR tubes held coaxially in 5mm precision glass NMR tubes containing a small quantity of  $d_6$ -acetone as lock substance.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to external TMS,  $^{19}\text{F}$  NMR spectra to external  $\text{CFCl}_3$  and  $^{31}\text{P}$  to 85%  $\text{H}_3\text{PO}_4$ , using the low-field positive convention.

#### 5.5 Infra-Red Spectroscopy

IR spectra were recorded either as dry powders or Nujol mulls compressed between KBr discs on a Digilab FTS40 FTIR spectrometer using an internal detector. For air-sensitive materials sample preparation was performed in the dry box. Gas-phase spectra were recorded in a copper cell of path length 10cm fitted with AgCl windows. A seal was achieved between the windows and the cell of the body by means of two sets of PTFE gaskets.

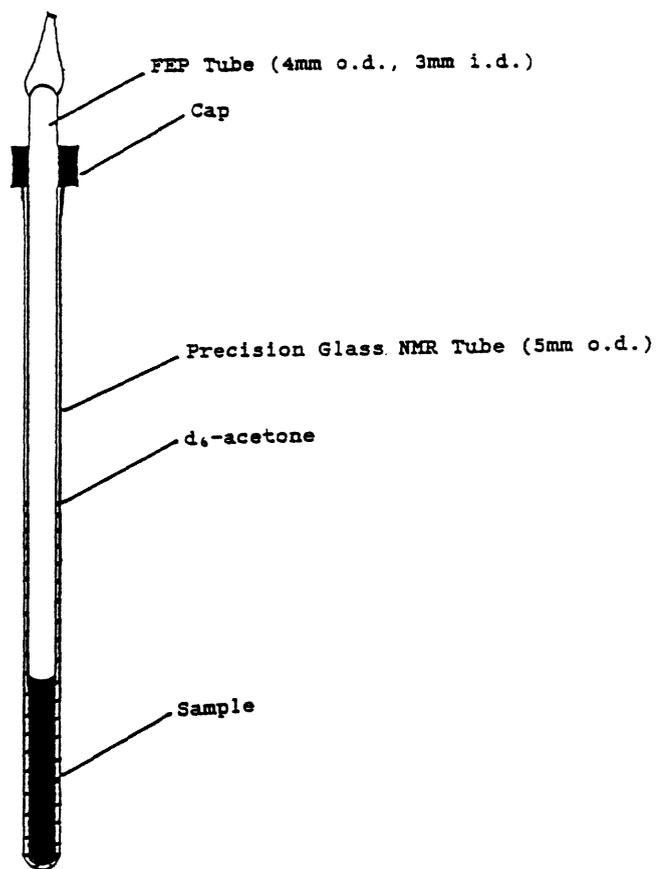


Fig 5.3 4mm FEP NMR Tube

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## 5.6 EXAFS

EXAFS data were collected at the Daresbury Synchrotron Radiation Source operating at 2 GeV (ca.  $3.2 \times 10^{-10}$  J) with an average current of 190 mA in transmission mode on station 7.1. An order-sorting Si(111) monochromator was used, offset to 50% of the rocking curve for harmonic rejection. Several data sets were collected in  $k$  space ( $k$  = photoelectron wave vector/ $\text{\AA}^{-1}$ ), and using EX<sup>1</sup> averaged to improve the signal-to-noise ratio. The pre-edge background was removed by fitting the spectrum to a polynomial and subtracting this from the whole spectrum. The atomic contribution to the oscillatory part of the absorption spectrum was approximated using polynomials, and the optimum function judged by minimizing the intensity of chemically insignificant shells at low  $r$  ( $r$  = radial distance from primary absorbing atom) in the Fourier transform. The data was multiplied by  $k^3$  to compensate for decreased intensity at higher  $k$ . Analysis was performed using EXCURV90<sup>2</sup>, utilising curved-wave theory with phase shifts and back-scattering factors calculated using the normal *ab initio* methods.

### Preparation of EXAFS Samples

The sample cells for these experiments were modified 4mm O.D. FEP NMR tubes, hence allowing the combination of both NMR and solution EXAFS on the same sample. The FEP NMR tubes were prepared as described above. However before the reagents were loaded, part of the FEP tube was flattened

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between two metal plates in a vice. The reactions were then performed as previously described and the FEP tubes sealed at the top by heating with a small ring oven under vacuum, whilst keeping the frozen solution at  $-196^{\circ}\text{C}$ . For  $\text{Ir}(\text{CO})_3\text{F}_3$  the 1:6 ratio of 0.05g of  $\text{Ir}_4(\text{CO})_{12}$  ( $4.52 \times 10^{-5}$  moles) and 0.046g of  $\text{XeF}_2$  ( $2.7 \times 10^{-4}$  moles) provided a suitable sample for an EXAFS experiment. For  $\text{OsF}_6$  molar and 0.1 molar dilutions were obtained by distilling a known volume of  $\text{OsF}_6$  into the appropriate volume of ANF solution.

#### 5.7 Crystal Structure Determination of $\text{RuF}_2(\text{CO})_2(\text{PPh}_3)_2$

Crystals suitable for a single crystal X-ray crystallographic study were obtained by slow vapour diffusion of diethyl ether into a  $\text{CD}_2\text{Cl}_2$  solution of  $\text{RuF}_2(\text{CO})_2(\text{PPh}_3)_2$ . A crystal of dimensions 0.53 x 0.48 x 0.20 mm was isolated in a nitrogen filled glove bag and loaded into a thin walled glass capillary. Unit cell parameters were determined by least squares refinement of setting angles from 31 centred reflections with  $15 < 2\theta < 25^{\circ}$ . Intensities of 3423 reflections in the range  $4 \leq 2\theta \leq 54^{\circ}$  and  $0 \leq h \leq 21$ ,  $0 \leq k \leq 13$ ,  $-25 \leq l \leq 25$  were measured on a Siemens P4 Diffractometer using a  $\theta/2\theta$  scan technique and graphite monochromated  $\text{Mo-K}\alpha$ . No crystal decay was detected from periodically measured check reflections. The data were corrected for Lorentz and polarisation effects. The reflections merged to a unique data set of 2503 reflections

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( $R_{int}=1.8\%$ ) with 2070 having  $I \geq 2\sigma(I)$  regarded as observed. An absorption correction based on was applied to the data set, maximum and minimum transmission factors were 0.931 and 0.781 respectively. Crystal data for  $\text{RuF}_2(\text{CO})_2(\text{PPh}_3)_2 \cdot \text{CH}_2\text{Cl}_2$ ,  $M_r=889.49$ , monoclinic,  $C2/c$ ,  $a=17.081(4)$ ,  $b=10.724(2)$ ,  $c=19.974(3)$  Å,  $\alpha=90^\circ$   $\beta=102.91(10)$  and  $\gamma=90^\circ$ ,  $V=3566$  Å<sup>3</sup>,  $Z=4$ ,  $D=1.656$  gcm<sup>-3</sup>, wavelength of (Mo-K $\alpha$ )=0.71073 Å,  $\mu=48.55$  cm<sup>-1</sup>,  $F(000)=1632$ ,  $T=293\text{K}$ . Structure solution by Patterson methods and least squares refinement were carried out using the SHELXL-PC program package<sup>3</sup>. The hydrogen atoms of the phenyl groups were included in calculated positions (C-H=0.95Å). All non-hydrogen atoms were refined with anisotropic displacement parameters. Final  $R=0.052$ ,  $R_w=0.055$ ,  $w=[\sigma^2(F)+0.0006 F^2]^{-1}$ , for the 183 parameters refined, with largest shift  $/\sigma=0.186$ . Maximum and minimum peak heights in the difference Fourier map were 0.69 and  $-0.65\text{e}\text{\AA}^{-3}$ .

### 5.8 Solvents

The solvents used for these investigations were mainly CD<sub>3</sub>CN (Aldrich 99.5%D 23,686-1), CD<sub>2</sub>Cl<sub>2</sub> (Aldrich 99.6+ atom %D 17,786-5) and AHF (ICI). The deuterated solvents were stored in glass ampoules (connected to a Youngs tap) over molecular sieves and degassed prior to use. The AHF was doubly vacuumed distilled before being transferred to a prefluorinated Kel-F container and stored over BiF<sub>5</sub>.

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## 5.9 Source of Chemicals

Dodecacarbonyl triruthenium,  $\text{Ru}_3(\text{CO})_{12}$ .

Aldrich Chemical Company Ltd.; used as supplied.

Dodecacarbonyl triosmium,  $\text{Os}_3(\text{CO})_{12}$ .

Aldrich Chemical Company Ltd.; used as supplied.

Dodecacarbonyl tetrairidium,  $\text{Ir}_4(\text{CO})_{12}$ .

Aldrich Chemical Company Ltd.; used as supplied.

Dodecacarbonyl triiron,  $\text{Fe}_3(\text{CO})_{12}$ .

Aldrich Chemical Company Ltd.; used as supplied.

Dodecacarbonyl tetrarhodium,  $\text{Rh}_4(\text{CO})_{12}$ .

Aldrich Chemical Company Ltd.; used as supplied.

Octacarbonyl dicobalt,  $\text{Co}_2(\text{CO})_8$ .

Aldrich Chemical Company Ltd.; used as supplied.

Trimethylphosphine,  $\text{PMe}_3$ .

Aldrich Chemical Company Ltd.; stored in a glass ampoule connected to a Youngs greaseless tap to allow easy manipulation on a vacuum line. The reagent was degassed prior to use.

Triphenylphosphine,  $\text{PPh}_3$ .

Aldrich Chemical Company Ltd.; used as supplied.

Disodium hexachloroosmate,  $\text{Na}_2\text{OsCl}_6$ .

Johnson Matthey; used as supplied.

DBU 1,8-Diazabicyclo[5,4,0]undec-7-ene.

Aldrich Chemical Company Ltd.; used as supplied.

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Ruthenium trichloride hydrate,  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ .

Aldrich Chemical Company Ltd.; used as supplied.

Osmium hexafluoride,  $\text{OsF}_6$ .

Kindly supplied by Mr C.D.Puxley; prepared by the thermal reaction of the hydrogenated metal with  $\text{F}_2$  gas in a static system according to the method described by Kaiser et al.<sup>4</sup>.

Decacarbonyl dirhenium,  $\text{Re}_2(\text{CO})_{10}$ .

Aldrich Chemical Company Ltd.; used as supplied.

$^{13}\text{C}$ O 99% labelled carbon monoxide.

MSD Isotopes (Cambrian Gases).

Phosphorus pentafluoride,  $\text{PF}_5$ .

Fluorochem Ltd.; used as supplied.

Arsenic pentafluoride,  $\text{AsF}_5$ .

Fluorochem Ltd.; used as supplied.

Boron trifluoride,  $\text{BF}_3$ .

Aldrich Chemical Company Ltd.; used as supplied.

Dimethyl osmiumtetracarbonyl,  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$ .

Prepared according to the literature method, by the reaction of sodium metal with  $\text{Os}_3(\text{CO})_{12}$  in  $\text{NH}_3$ , followed by the addition of  $\text{CH}_3\text{I}$ <sup>5</sup>.

Tricarbonyl bis(triphenylphosphine)ruthenium,  
 $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ .

Prepared according to the literature method, by the reaction of  $\text{RuCl}_3$  hydrate,  $\text{PPh}_3$ , methanal and KOH in hot 2-methoxyethanol<sup>6</sup>.

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Tricarbonyl bis(triphenylphosphine)osmium,  $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ .

Prepared according to the literature method, from the reaction of  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_2$  with DBU under 80psi of  $\text{CO}$ <sup>7</sup>.

Carbonylchlorohydrido tris(triphenylphosphine)osmium,  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ .

Prepared according to the literature method by the reaction of  $\text{Na}_2\text{OsCl}_6$  hydrate,  $\text{PPh}_3$  and methanal in boiling 2-methoxyethanol<sup>6</sup>.

Nonacarbonyl tris(triphenylphosphine) triosmium,  $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$ .

Prepared according to the literature method, from the thermal reaction of  $\text{Os}_3(\text{CO})_{12}$  and  $\text{PPh}_3$  in xylene. The lower substituted derivatives were separated chromatographically<sup>8</sup>.

Octacarbonyl bis(triphenylphosphine)dirhenium,  $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ .

Prepared according to the literature method, from the thermal reaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{PPh}_3$  in xylene<sup>9</sup>.

Bromo-tetracarbonyl (triphenylphosphine)rhenium,  $\text{ReBr}(\text{CO})_4(\text{PPh}_3)_2$ .

Prepared according to the literature method<sup>10</sup>.

Tetracarbonylmethyl (triphenylphosphine)rhenium,  $\text{Re}(\text{CO})_4(\text{CH}_3)(\text{PPh}_3)$ .

Prepared according to the literature method<sup>11</sup>.

All materials were checked by IR or NMR for authenticity and purity

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Preparation of xenon difluoride XeF<sub>2</sub>.

This was prepared as described by Holloway<sup>12</sup>. Approximately 500mmHg of xenon gas was mixed with 550mmHg of F<sub>2</sub> (i.e. 10% excess of fluorine) into a pre-seasoned one litre glass bulb. The reaction was then propagated by means of an ultra-violet light source. (Formation of XeF<sub>2</sub> is easily identified by the production of white crystals). After about 48hr the excess of fluorine and unreacted xenon were removed at -196°C and -78°C respectively. The product was further purified by sublimation under dynamic vacuum into a glass trap at -78°C and then stored in the dry box at room temperature. The purity was checked by recording NMR and IR spectra.

5.10 <sup>13</sup>CO enrichment of Ru<sub>3</sub>(CO)<sub>12</sub>, Os<sub>3</sub>(CO)<sub>12</sub> and Ir<sub>4</sub>(CO)<sub>12</sub>.

<sup>13</sup>CO enrichment of these carbonyl complexes was afforded by stirring degassed toluene solutions/suspensions of the carbonyl in a sealed glass reactor vessel under approximately 1 atmosphere of 99.5% <sup>13</sup>CO for about one week at 60°C (similar to the method described by Gleeson et al.)<sup>13</sup>.

5.11

Reaction of Ir<sub>4</sub>(CO)<sub>12</sub>, Ru<sub>3</sub>(CO)<sub>12</sub> and Os<sub>3</sub>(CO)<sub>12</sub> with AHF.

0.05 to 0.1g of the appropriate carbonyl complex was loaded into, either a 4mm O.D. or 6mm O.D. FEP tube (connected to a Chemcon tap). The system was then connected

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to the metal vacuum line and evacuated to an approximate pressure of  $10^{-4}$  torr. AHF was distilled into the reaction vessel at  $-196^{\circ}\text{C}$ , from a Kel-F container. The system was then sealed using the Chemcon tap and allowed to warm to room temperature. Generally, the system was left overnight to afford complete dissolution. However, agitation significantly aided this process.

For osmium and ruthenium carbonyls the reactions with AHF were also undertaken on a larger scale (0.4g) using a  $\frac{1}{2}$ " O.D. FEP tube connected to the metal line in a similar way to that described above. Dissolution (~4hr) of these larger samples was conveniently achieved using a mechanical shaker off the line.

#### 5.12

The Reaction of AHF with  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Co}_2(\text{CO})_8$ ,  $\text{Rh}_4(\text{CO})_{12}$ .

These reactions were undertaken in an identical manner to that described above. However, due to the evolution of volatiles, constant venting was necessary. The complete reaction times for these materials varied. For iron and cobalt carbonyls conversion to  $\text{FeF}_2$  and  $\text{CoF}_2$ , respectively, was complete within a couple of days, as evidenced by the colour changes and X-ray powder diffraction.  $\text{Rh}_4(\text{CO})_{12}$  was only observed to decompose with HF resulting in the formation of a metallic mirror.

### 5.13

#### The Reaction of $\text{Ir}_4(\text{CO})_{12}$ with $\text{XeF}_2$ .

Various ratios of  $\text{Ir}_4(\text{CO})_{12}$  :  $\text{XeF}_2$  were investigated. Typically, the NMR samples were prepared with 0.05g of  $\text{Ir}_4(\text{CO})_{12}$  and the appropriate amount of  $\text{XeF}_2$ . For the 1:6 ratio 0.05g of  $\text{Ir}_4(\text{CO})_{12}$  ( $4.52 \times 10^{-5}$  moles) and 0.046g of  $\text{XeF}_2$  ( $2.7 \times 10^{-4}$  moles) are loaded via a dry box into a 4mm O.D. FEP tube pre-seasoned with  $\text{F}_2$  gas. The FEP tube was re-connected to the metal vacuum line (c.f. Fig 5.2). Before the reactor was evacuated the connectors were seasoned with  $\text{F}_2$  gas. The reactor was evacuated to an approximate pressure of  $10^{-4}$  torr, whilst being held at  $-78^\circ\text{C}$  (to prevent the volatile  $\text{XeF}_2$  from being removed). The AHF solvent was distilled into the reaction vessel under static vacuum at  $-196^\circ\text{C}$ . The reaction mixture was allowed to warm slowly to room temperature. Reaction occurred at approximately  $-50^\circ\text{C}$  with the vigorous evolution of xenon gas, necessitating continual temperature quenching and venting of the system. After the vigorous reaction had ceased (5 minutes) the resulting yellow solution was left at room temperature overnight.

For scaled-up preparations (0.075 to 0.15g) of  $\text{Ir}_4(\text{CO})_{12}$ , reactions were performed in an identical manner as described above except that a 6mm O.D. FEP tube was used for the reaction vessel. The isolation of  $\text{Ir}(\text{CO})_3\text{F}_3$  is conveniently achieved by removing the solvent AHF under vacuum through the soda lime trap. The resulting yellow

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solid was then held under dynamic vacuum until an approximate pressure reading of  $0.3 \times 10^{-4}$  mmHg was obtained.

#### 5.14

The Reaction of  $\text{Ir}(\text{CO})_3\text{F}_3$  with  $\text{PMe}_3$ .

Due to the sensitivity of  $\text{Ir}(\text{CO})_3\text{F}_3$ , this material was prepared *in situ* as described above. After complete reaction, the AHF solvent was removed as described above.

The yellow  $\text{Ir}(\text{CO})_3\text{F}_3$  was isolated from the line so that the ampoules of  $\text{CD}_2\text{Cl}_2$  and  $\text{PMe}_3$  could be attached. Before the addition of these chemicals to the  $\text{Ir}(\text{CO})_3\text{F}_3$ , the ampoules were degassed and the connecting tubing seasoned with  $\text{F}_2$  gas. After re-evacuation of the whole system,  $\text{CD}_2\text{Cl}_2$  was distilled on to the  $\text{Ir}(\text{CO})_3\text{F}_3$ , followed by  $\text{PMe}_3$ . The system was allowed to warm slowly to room temperature with occasional cooling and venting of the volatiles. The  $\text{PMe}_3$  was added in excess such that, after the evolution of CO had ceased, further addition of  $\text{PMe}_3$  resulted in no further reaction. The resulting yellow solution was studied by NMR spectroscopy either in the presence of an excess of  $\text{PMe}_3$ , or the volatiles were removed and the resulting solid redissolved in  $\text{CD}_2\text{Cl}_2$ .

#### 5.15

Reaction of  $\text{Os}_3(\text{CO})_{12}$  with  $\text{XeF}_2$  in AHF.

Reactions were carried out in a similar way to those described above for  $\text{Ir}_4(\text{CO})_{12}$ . Ratios of  $\text{Os}_3(\text{CO})_{12}:\text{XeF}_2$  were

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investigated between 2:1 to 1:5 generally using 0.05 to 0.100g of  $\text{Os}_3(\text{CO})_{12}$ . However, for this reaction a scaled-up preparation was also performed utilizing a threaded  $\frac{1}{2}$ " O.D. FEP tube connected to the appropriate Chemcon tap. These samples were also left overnight to ensure complete reaction. Where appropriate, the samples were either sealed for NMR analysis, or the AHF solvent was removed under vacuum through the soda lime trap. The resulting yellow solid was held under dynamic vacuum until an approximate pressure reading of  $0.3 \times 10^{-4}$  mmHg was obtained (~2hr) yielding a white solid.

#### 5.16

##### The Reaction of $\text{Os}_3(\text{CO})_{12}$ with $\text{F}_2$ in AHF.

These reactions were carried out in  $\frac{1}{2}$ " O.D. threaded FEP tubes. The  $\text{Os}_3(\text{CO})_{12}$  was initially reacted with AHF as described above. The reaction vessel was re-connected to the metal vacuum line and stoichiometric amounts of  $\text{F}_2$  gas were added to the frozen solution ( $-196^\circ\text{C}$ ). The system was then allowed to warm slowly to room temperature and then agitated overnight on a mechanical shaker. The AHF was removed as described above, or aliquots of the solution were decanted into pre-prepared 4mm O.D. FEP tubes, for NMR analysis.

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5.17

Reaction of "[Os(CO)<sub>3</sub>F<sub>2</sub>]<sub>4</sub>" with PMe<sub>3</sub>.

"[Os(CO)<sub>3</sub>F<sub>2</sub>]<sub>4</sub>" was prepared by the XeF<sub>2</sub> method described above. The resulting white solid was isolated from the line so that the ampoules of CD<sub>2</sub>Cl<sub>2</sub> and PMe<sub>3</sub> could be attached. Before the addition of these chemicals the ampoules were degassed. The CD<sub>2</sub>Cl<sub>2</sub> was distilled on to the [Os(CO)<sub>3</sub>F<sub>2</sub>]<sub>4</sub>, followed by PMe<sub>3</sub>. The system was allowed to warm slowly to room temperature with occasional cooling and venting of the volatiles. The PMe<sub>3</sub> was added in excess such that, after the evolution of CO had ceased, further addition of PMe<sub>3</sub> resulted in no further reaction. The resulting clear solution contained a small amount of precipitate which was removed by filtration through dried celite under an argon atmosphere.

5.18

The Reaction of Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> with AHF.

The Os(CO)<sub>4</sub>(CH<sub>3</sub>)<sub>2</sub> was sublimed into a pre-prepared 4mm O.D. FEP tube (~40mg) under static vacuum. AHF was condensed onto this white crystalline osmium complex at -196°C. On gradual warming to room temperature, vigorous evolution of methane gas occurred, therefore requiring cooling and venting of the reaction mixture. The resulting clear solution was either left at room temperature or kept below -20°C. See text 3.9 for further discussion.

### 5.19

The Reaction of  $\text{Re}(\text{CO})_4(\text{CH}_3)(\text{PPh}_3)$  with AHF.

This reaction was performed in a similar manner to that described for  $\text{Os}(\text{CO})_4(\text{CH}_3)_2$  except that the  $\text{Re}(\text{CO})_4(\text{CH}_3)(\text{PPh}_3)$  was loaded as a solid and the reaction was carried out using  $\text{CD}_2\text{Cl}_2$  as a solvent. Aliquots of AHF were introduced into the reaction vessel until further addition resulted in no further evolution of methane gas, resulting in a yellow solution. The solvent and excess of AHF were removed and the solid redissolved in  $\text{CD}_2\text{Cl}_2$  for analysis by NMR spectroscopy.

### 5.20

The Reaction of  $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$  with  $\text{XeF}_2$ .

0.05g of  $\text{Os}_3(\text{CO})_9(\text{PPh}_3)_3$  and 0.016g of  $\text{XeF}_2$  (1:3 mole ratio) were loaded into a 4mm O.D FEP tube (connected to a Chemcon tap). Care was taken to keep the two solids separated. The system was then connected to the metal vacuum line and evacuated to an approximate pressure of  $10^{-4}$  torr.  $\text{CD}_2\text{Cl}_2$  was distilled into the reaction vessel at  $-196^\circ\text{C}$ , from a glass ampoule. The system was allowed to warm slowly to room temperature as described in the text. The NMR tube was sealed as previously described and the red brown solution analysed by NMR spectroscopy.

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## 5.21

The Reactions of  $M(\text{CO})_3(\text{PPh}_3)_2$   $M = \text{Ru}$  or  $\text{Os}$ , with  $\text{XeF}_2$ .

These reactions were performed within the NMR instrument according to the manner described in Chapter Four. Typically,  $M(\text{CO})_3(\text{PPh}_3)_2$ , (0.05g) was allowed to react with a 10% excess of  $\text{XeF}_2$  (0.013g,  $7.8 \times 10^{-5}$  moles for  $M = \text{Ru}$  and 0.012g,  $6.9 \times 10^{-5}$  moles for  $\text{Os}$ ). The solids were either loaded in the dry box or in a bucket filled with argon. The solvent  $\text{CD}_2\text{Cl}_2$  was vacuum distilled on to the frozen solids ( $-196^\circ\text{C}$ ) on the vacuum line. At this stage, the frozen sample was sealed as previously described so that the reactions could be monitored by NMR spectroscopy. For these reaction there was no requirement to season the apparatus with  $\text{F}_2$  gas.

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CHAPTER FIVE

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APPENDIX

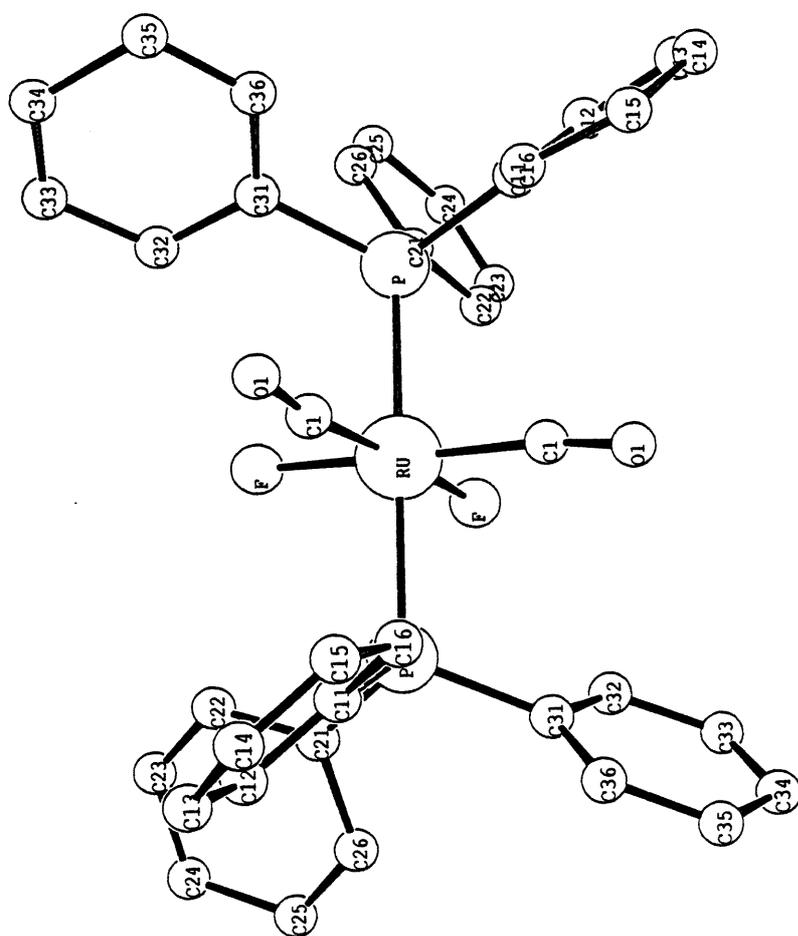


Table 1. Fractional atomic co-ordinates and thermal parameters  
for RuF<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> CH<sub>2</sub>Cl<sub>2</sub>

Atom	x	y	z	Ueq	
Ueq = 1/3 trace of the orthogonalised U					
Ru	0.00000(0)	0.27475(6)	0.25000(0)	0.0453(2)	
P	0.10222(8)	0.27813(15)	0.35472(7)	0.0481(5)	
F	-0.05013(20)	0.4142(3)	0.29291(19)	0.0721(14)	
O(1)	-0.08092(29)	0.0814(6)	0.31786(29)	0.0917(22)	
C(1)	-0.0506(3)	0.1558(7)	0.2908(3)	0.0607(22)	
C(11)	0.17654(19)	0.1565(3)	0.35869(21)	0.0526(20)	
C(12)	0.25834(19)	0.1832(3)	0.36987(21)	0.0716(25)	
C(13)	0.31329(19)	0.0875(3)	0.36853(21)	0.088(3)	
C(14)	0.28637(19)	-0.0349(3)	0.35603(21)	0.085(3)	
C(15)	0.20454(19)	-0.0616(3)	0.34483(21)	0.085(3)	
C(16)	0.14965(19)	0.0341(3)	0.34618(21)	0.0726(25)	
C(21)	0.16061(20)	0.4177(3)	0.37409(20)	0.0539(20)	
C(22)	0.18524(20)	0.4796(3)	0.32088(20)	0.0754(26)	
C(23)	0.23688(20)	0.5817(3)	0.33538(20)	0.084(3)	
C(24)	0.26381(20)	0.6219(3)	0.40303(20)	0.083(3)	
C(25)	0.23919(20)	0.5600(3)	0.45621(20)	0.0778(28)	
C(26)	0.18757(20)	0.4579(3)	0.44174(20)	0.0626(22)	
C(31)	0.06118(22)	0.2533(4)	0.42914(19)	0.0548(20)	
C(32)	-0.00102(22)	0.3316(4)	0.43789(19)	0.0722(24)	
C(33)	-0.03671(22)	0.3142(4)	0.49356(19)	0.097(4)	
C(34)	-0.01021(22)	0.2185(4)	0.54048(19)	0.106(4)	
C(35)	0.05201(22)	0.1403(4)	0.53174(19)	0.101(4)	
C(36)	0.08770(22)	0.1577(4)	0.47607(19)	0.0729(26)	
C(2)	0.50000(0)	0.1668(14)	0.25000(0)	0.213(15)	
Cl	0.4323(3)	0.2659(3)	0.27890(20)	0.1784(21)	
H(12)	0.27668(19)	0.2666(3)	0.37838(21)	0.0800(0)	*
H(13)	0.36901(19)	0.1056(3)	0.37614(21)	0.0800(0)	*
H(14)	0.32378(19)	-0.1002(3)	0.35511(21)	0.0800(0)	*
H(15)	0.18618(19)	-0.1450(3)	0.33632(21)	0.0800(0)	*
H(16)	0.09387(19)	0.0159(3)	0.33856(21)	0.0800(0)	*
H(22)	0.16689(20)	0.4522(3)	0.27483(20)	0.0800(0)	*
H(23)	0.25365(20)	0.6238(3)	0.29917(20)	0.0800(0)	*
H(24)	0.29899(20)	0.6914(3)	0.41288(20)	0.0800(0)	*
H(25)	0.25752(20)	0.5874(3)	0.50228(20)	0.0800(0)	*
H(26)	0.17077(20)	0.4158(3)	0.47795(20)	0.0800(0)	*
H(32)	-0.01908(22)	0.3967(4)	0.40592(19)	0.0800(0)	*
H(33)	-0.07906(22)	0.3674(4)	0.49948(19)	0.0800(0)	*
H(34)	-0.03449(22)	0.2067(4)	0.57840(19)	0.0800(0)	*
H(35)	0.07007(22)	0.0752(4)	0.56371(19)	0.0800(0)	*
H(36)	0.13004(22)	0.1044(4)	0.47013(19)	0.0800(0)	*

\* Isotropic thermal parameter

Table 2. Bond Lengths (Å) for RuF<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> CH<sub>2</sub>Cl<sub>2</sub>

C(11)-P	1.809(3)	C(2)-Cl	1.760(10)
C(21)-P	1.792(3)	P-Ru	2.407(1)
C(31)-P	1.799(4)	F-Ru	2.008(4)
C(1)-O(1)	1.149(8)	C(1)-Ru	1.832(7)

Table 3. Bond Angles (°) for RuF<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> CH<sub>2</sub>Cl<sub>2</sub>

C(21)-P-C(11)	104.0(2)	F-Ru-P	85.0(1)
C(31)-P-C(11)	104.9(2)	C(1)-Ru-P	86.9(2)
C(31)-P-C(21)	104.2(2)	C(1)-Ru-F	92.3(2)
C(12)-C(11)-P	121.8(1)	C(11)-P-Ru	113.1(1)
C(16)-C(11)-P	118.1(1)	C(21)-P-Ru	117.4(1)
C(22)-C(21)-P	118.7(1)	C(31)-P-Ru	112.0(1)
C(26)-C(21)-P	121.0(1)	F-Ru-F	83.7(2)
C(32)-C(31)-P	117.6(1)	O(1)-C(1)-Ru	178.3(5)
C(36)-C(31)-P	122.4(1)	C(1)-Ru-C(1)	91.7(4)
Cl-C(2)-Cl	105.7(8)		

Table 4. Anisotropic thermal parameters (x10<sup>4</sup>)  
RuF<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> CH<sub>2</sub>Cl<sub>2</sub>

Atom	U11	U22	U33	U23	U13	U12
Ru	312(3)	624(4)	388(3)	0(0)	3(2)	0(0)
P	354(7)	646(8)	403(8)	-2(7)	-1(6)	30(7)
Cl	2173(40)	1759(31)	1365(29)	60(23)	281(30)	483(30)
F	655(20)	860(25)	569(21)	-92(19)	-35(19)	257(20)
O(1)	726(30)	1196(42)	798(37)	193(32)	101(29)	-295(33)
C(1)	430(30)	910(46)	437(33)	-35(34)	3(29)	-51(33)
C(2)	1614(154)	736(88)	4463(385)	0(0)	1596(218)	0(0)
C(11)	388(27)	701(38)	433(32)	-78(28)	-24(25)	85(28)
C(12)	507(34)	885(44)	716(44)	-2(37)	54(34)	107(34)
C(13)	500(36)	1182(63)	986(62)	168(53)	212(40)	234(43)
C(14)	698(42)	1146(62)	709(49)	122(45)	140(39)	414(47)
C(15)	911(50)	788(47)	764(52)	-37(39)	-16(45)	262(43)
C(16)	535(33)	753(42)	765(49)	7(37)	-117(35)	168(34)
C(21)	382(26)	660(34)	531(36)	12(29)	9(27)	53(27)
C(22)	519(33)	1085(54)	598(41)	27(40)	-4(34)	-250(38)
C(23)	685(40)	1010(53)	753(52)	172(43)	4(39)	-262(43)
C(24)	605(38)	723(43)	1008(61)	40(42)	-146(42)	-155(35)
C(25)	775(44)	664(41)	772(51)	-123(37)	-87(41)	-26(36)
C(26)	616(34)	664(37)	547(37)	-15(30)	22(32)	-8(31)
C(31)	431(28)	676(41)	502(31)	-37(27)	30(26)	-74(26)
C(32)	529(34)	1093(50)	519(36)	-5(38)	67(31)	156(38)
C(33)	603(41)	1631(81)	700(47)	-129(55)	225(39)	21(50)
C(34)	813(53)	1691(88)	705(50)	22(62)	245(46)	-391(61)
C(35)	1349(78)	1044(62)	652(49)	181(45)	226(57)	-158(59)
C(36)	805(44)	758(43)	619(41)	107(36)	146(38)	-41(39)

The anisotropic displacement parameter has the form:  
exp[-2π<sup>2</sup>(U11h<sup>2</sup>a<sup>2</sup>+ ... +2U12hka\*b\*)]

Table 5. Non-bonded Contacts (Å)  $\text{RuF}_2(\text{CO})_2(\text{PPh}_3)_2 \text{CH}_2\text{Cl}_2$

O(1)...Ru	2.980				
C(11)...Ru	3.534				
C(21)...Ru	3.603				
C(31)...Ru	3.504				
F...P	2.998				
C(1)...P	2.946				
C(12)...P	2.807				
C(16)...P	2.756				
H(12)...P	2.914				
H(16)...P	2.830				
C(22)...P	2.750				
C(26)...P	2.780				
H(22)...P	2.835				
H(26)...P	2.884				
C(32)...P	2.740				
C(36)...P	2.806				
H(32)...P	2.811				
H(36)...P	2.919				
F...P	3.232	2,	0.0000,	0.0000,	0.0000
C(1)...P	3.131	2,	0.0000,	0.0000,	0.0000
C(1)...F	2.771				
C(32)...F	2.965				
H(32)...F	2.208				
F...F	2.680	2,	0.0000,	0.0000,	0.0000
C(22)...F	2.939	2,	0.0000,	0.0000,	0.0000
H(22)...F	2.184	2,	0.0000,	0.0000,	0.0000
C(1)...C(1)	2.630	2,	0.0000,	0.0000,	0.0000
C(13)...C(11)	2.416				
C(14)...C(11)	2.790				
C(15)...C(11)	2.416				
H(12)...C(11)	2.043				
H(16)...C(11)	2.043				
C(21)...C(11)	2.837				
C(31)...C(11)	2.860				
C(36)...C(11)	3.064				
H(36)...C(11)	2.586				
C(14)...C(12)	2.416				
C(15)...C(12)	2.790				
C(16)...C(12)	2.416				
H(13)...C(12)	2.043				
C(21)...C(12)	3.030				
C(15)...C(13)	2.416				
C(16)...C(13)	2.790				
H(12)...C(13)	2.043				
H(14)...C(13)	2.043				
C(16)...C(14)	2.416				
H(13)...C(14)	2.043				
H(15)...C(14)	2.044				
H(14)...C(15)	2.043				
H(16)...C(15)	2.043				
H(15)...C(16)	2.043				
H(36)...C(16)	2.680				
C(21)...H(12)	2.547				
Cl...H(13)	2.972				
Cl...H(15)	2.868	2,	0.5000,	0.5000,	0.0000
C(23)...C(21)	2.416				
C(24)...C(21)	2.790				
C(25)...C(21)	2.416				

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H(22)...C(21)	2.043				
H(26)...C(21)	2.043				
C(31)...C(21)	2.834				
C(24)...C(22)	2.416				
C(25)...C(22)	2.790				
C(26)...C(22)	2.417				
H(23)...C(22)	2.043				
C(25)...C(23)	2.416				
C(26)...C(23)	2.790				
H(22)...C(23)	2.043				
H(24)...C(23)	2.043				
C(26)...C(24)	2.416				
H(23)...C(24)	2.043				
H(25)...C(24)	2.043				
H(24)...C(25)	2.043				
H(26)...C(25)	2.043				
H(25)...C(26)	2.043				
C(31)...C(26)	3.049				
C(31)...H(26)	2.583				
C(33)...C(31)	2.416				
C(34)...C(31)	2.790				
C(35)...C(31)	2.416				
H(32)...C(31)	2.043				
H(36)...C(31)	2.043				
C(34)...C(32)	2.416				
C(35)...C(32)	2.790				
C(36)...C(32)	2.416				
H(33)...C(32)	2.042				
C(35)...C(33)	2.416				
C(36)...C(33)	2.790				
H(32)...C(33)	2.043				
H(34)...C(33)	2.043				
C(36)...C(34)	2.416				
H(33)...C(34)	2.043				
H(35)...C(34)	2.043				
H(34)...C(35)	2.043				
H(36)...C(35)	2.043				
H(35)...C(36)	2.043				
C1...H(34)	3.005	-1,	0.5000,	0.5000,	1.0000
C1...C1	2.805	2,	1.0000,	0.0000,	0.0000
C(2)...C1	1.760	2,	1.0000,	0.0000,	0.0000