SYNTHESIS AND REACTIONS OF LOW-VALENT OSMIUM
AND RUTHENIUM FLUORIDE COMPLEXES

Thesis submitted for the degree of
Doctor of Philosophy
at the University of Leicester

by

Karl Stuart Coleman BSc (Leicester)
Department of Chemistry
Faculty of Science
University of Leicester

August 1996
To My Parents
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 1993 and August 1996. The work has not been submitted, and is not presently being submitted, for any other degree at this or any other university.

Signed: [Signature] Date: 27th September 1996

Department of Chemistry
University of Leicester
University Road
Leicester
U.K.
LE1 7RH
Low-Valent fluoride Complexes of Osmium and Ruthenium

Karl Stuart Coleman

Abstract

A range of low-valent osmium and ruthenium fluoride complexes of the type \([OC-6-13][MF_2(CO)_2(L)_2]\), \(L = \) tertiary phosphine, arsine or nitrogen donor hgan&, have been prepared and fully characterized by a combination of mass spectrometry, infrared spectroscopy, \(^{19}\)F, and \(^{31}\)P(H) (where appropriate) NMR spectroscopies. The compounds \([OC-6-13][RuF_2(CO)_2(PPh_3)_2]\), \([OC-6-13][OsF_2(CO)_2(PPh_3)_2]\) and \([OC-6-13][OsF_2(CO)_2(PCy_3)_2]\) have been further characterized by single crystal X-ray diffraction, the last two representing the first crystallographic analyses of osmium(II) fluoride complexes.

The photolysis and thermolysis of \([RuF_2(CO)_2(PMe_3)_2]\) have been shown to give several novel complexes including \([RuF_2(CO)(PMe_3)_2]\) which is a rare example of fluoride ligand \(trans\) to tertiary phosphine. Reactions of some of the prepared complexes with a variety of reagents have given rise to a number of low-valent cationic fluoride complexes as well as novel alkyl and carboxylato species.

Fluorination of the ruthenium carbonyl \([Ru_2(CO)_3]\) with elemental fluorine has given rise to a plethora of products which have been characterized by \(^{19}\)F NMR spectroscopy.

Hydride complexes of the type \([MH_2(CO)_2(PPh_3)_2]\) and \([MH_2(CO)(PPh_3)_2]\) have been allowed to react with anhydrous hydrofluoric acid and have been shown to give the complexes \([MF_2(CO)_2(PPh_3)_2]\) and \([M_2(F)(CO)_2(PPh_3)_2]^+\) respectively, where \(M = \) osmium or ruthenium.

X-ray crystal structure determinations for the complexes \([OC-6-13][Os(CH_3)(CO)(PPh_3)]\), \([OC-6-13][Os(CH_3)(CO)(PCy_3)]\), \([OC-6-13][Ru(O)(CF_3)(CO)(PCy_3)]\) and \([Ru(\eta^2-CO_2-OO')(CO)(PMe_3)_2]\) are described.
### Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statement</td>
<td>i</td>
</tr>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Contents</td>
<td>iii</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>vii</td>
</tr>
<tr>
<td>Abbreviations</td>
<td>viii</td>
</tr>
</tbody>
</table>

### Chapter One

*Introduction to the Low-Valent Fluoride Complexes of the Platinum Group Metals*

1.1 General Introduction | 1
1.2 The nature of the Metal-Fluorine Bond in Low-Valent Platinum Group Metal Fluoride complexes | 5
1.3 Reactions and Properties of Low-Valent Platinum Group Metal Fluoride Complexes | 14
   1.3.1 Reaction at Metal-Bound Fluorine | 15
   1.3.2 Reaction at Co-ordinated Ligand | 23
   1.3.3 Reaction at the Metal Centre | 27
1.4 Summary | 35
References | 36

### Chapter Two

*Synthesis and Characterization of Low-Valent Osmium and Ruthenium Fluoride Complexes*

2.1 General Introduction | 41
2.2 Introduction to Fluoro complexes of Osmium and Ruthenium | 42
2.3 Synthesis and Characterization of Low-Valent Osmium and Ruthenium Fluoride Complexes. | 44
2.4 Characterization | 47
2.4.1 $^{19}$F and $^{31}$P($^1$H) NMR Spectroscopy 47
2.4.2 Infrared Spectroscopy and Mass Spectrometry 54
2.4.3 X-Ray Crystal Structure Analysis of [OC-6-13] $^{[\text{OsF}_2(\text{CO})_2(\text{PPh}_3)_2]}$ [OC-6-13]$^{[\text{OsF}_2(\text{CO})_2(\text{PCy}_3)_2]}$ and [OC-6-13]$^{[\text{RuF}_2(\text{CO})_2(\text{PEtPh}_2)_2]}$ 56
2.4.4 EXAFS Analysis of [OC-6-13]$^{[\text{OsF}_2(\text{CO})_2(\text{PMc}_3)_2]}$ 64
2.5 Reaction of [(MF$_2$(CO)$_2$)$_2$] with multidentate donor ligands, M = Ru and Os 66
2.6 Summary 69
References 70

Chapter Three
Reactions of the Low-Valent Osmium and Ruthenium Fluoride Complexes [OC-6-13][MF$_2$(CO)$_2$(PR)$_3$]

3.1 Introduction 73
3.2 Reactions of [OC-6-13][MF$_2$(CO)$_2$(PR)$_3$] 73 with the Lewis acid Boron Trifluoride
3.3 Displacement of Weakly Co-ordinated BF$_4^-$ in the Complexes [OC-6-13][MF(BFB)$_3$(CO)$_2$(PR)$_3$] with Tertiary Phosphines and Carbon Monoxide 78
3.4 Reaction of the Complexes [OC-6-13][MF(BFB)$_3$(CO)$_2$(PR)$_3$] 85 with Olefins
3.5 Metal Fluoride Complex Impurities in the Reaction of [OC-6-13][MF(BFB)$_3$(CO)$_2$(PR)$_3$] with Donor Ligands 85
3.6 Photolysis and Thermolysis of [OC-6-13][MF$_2$(CO)$_2$(PR)$_3$] 89
3.7 Reaction of [OC-6-13][MF$_2$(CO)$_2$(PR)$_3$] 102 with MeLi and MeMgBr where R = Ph or Cy, M = Os or Ru
3.8 Reaction of [RuF$_2$(CO)$_2$(PR)$_3$] 108 with Trimethylsilyl Reagents
3.9 Summary 112
References 113
### Chapter Four

**Fluorination of Ruthenium Carbonyl** \([\text{Ru}_3(\text{CO})_{12}]\) **with** \(\text{XeF}_2\) **and** Elemental Fluorine

4.1 Introduction to Platinum Group Metal Carbonyl Fluoride Complexes  
4.2 Reaction between \([\text{Ru}_3(\text{CO})_{12}]\) and \(\text{F}_2\) in AHF  
References

### Chapter Five

**Reaction of Low-Valent Osmium and Ruthenium Hydride Complexes with Anhydrous HF**

5.1 Introduction  
5.2 Reaction of Osmium and Ruthenium Hydrides with AHF  
5.2.1 Reaction of the Hydrides \([\text{OC}-\text{d}-\text{f} 3][\text{MH}_2(\text{CO})_2(\text{PPh}_3)_2]\),  
\(\text{M} = \text{Os and Ru}, \text{with AHF}\)  
5.2.2 Reaction of the Hydrides \([\text{OC}-\text{d}-\text{f} 3][\text{MH}_2(\text{CO})(\text{PPh}_3)_3]\),  
\(\text{M} = \text{Os and Ru}, \text{with AHF}\)  
References

### Chapter Six

**Experimental**

6.1 Analytical Techniques  
6.2 Metal Vacuum Line  
6.3 Glass Vacuum Line (Schlenk Line)  
6.4 Inert Atmosphere Dry-Box  
6.5 Reactions on the Metal Vacuum Line  
6.6 Solvents  
6.7 Chemical Reagents
6.8 Preparation of Osmium and Ruthenium Carbonyl Fluoride Tetramers, \([\text{MFCO}_3]_4\)

6.9 Preparation of \([\text{MFCO}_3]_2(L)_2\), where M = Os, Ru

6.10 Reaction of \([\text{MFCO}_3]_4\) with dppe

6.11 Preparation of \([\text{OC-6-13}]\text{MF}(\text{FBF}_3)(\text{CO}_3)(\text{PPh}_3)\_2\)

where M = Os, Ru

6.12 Preparation of \([\text{OC-6-13}]\text{MFCO}_3(PR_3)_2[\text{BF}_4]\),

where M = Os, Ru and PR_3 = PPh_3, PMe_3

6.13 Preparation of \([\text{OC-6-13}]\text{MFCO}_3(PR_3)_2[\text{BF}_4]\)

where M = Os, Ru and PR_3 = PPh_3, PMe_3

6.14 Reaction of Metal Hydrides with AHF

6.15 Preparation of \([\text{OC-6-13}]\text{MMe}_2(\text{CO}_3)(PR_3)_2\),

where M = Os, Ru, PR_3 = PPh_3, PCy_3

6.16 Reaction of \([\text{OC-6-13}]\text{MFCO}_3(PR_3)_2\]

with MeLi in a 1 : 1 ratio

6.17 Preparation of \([\text{OC-6-13}]\text{MOCO}_3(\text{CF}_3)(\text{CO}_3)(\text{PCy}_3)_2\)

6.18 Photolysis of \([\text{OC-6-13}]\text{MFCO}_3(PR_3)_2\),

M = Os, Ru and PR_3 = PMe_3, PPh_3

6.19 Thermolysis of \([\text{OC-6-13}]\text{MFCO}_3(PR_3)_2\),

M = Os, Ru and PR_3 = PMe_3, PPh_3

6.20 Reaction of \([\text{OC-6-33}]\text{RuCl}_2(\text{CO}_3)(\text{PPh}_3)_2\] with silver tetrafluoroborate, followed by N' Bu_4 F

6.21 Preparation of \([\text{OC-6-33}]\text{OsCl}_2(\text{CO}_3)(\text{PEt}_3)_2\]

6.22 Reaction of \([\text{OC-6-13}]\text{MFCO}_3(PR_3)_2\]

with BF_3.OEt_2, where PR_3 = PPh_3 and PMe_3

References

Appendix

Details of X-Ray Crystal Data Collection, Solution and Refinement
Acknowledgements

I would firstly like to thank my supervisors and friends Prof. John H. Holloway and Dr. Eric G. Hope for their support and guidance throughout my enjoyable time in the Fluorine Research Group at Leicester.

I would also like to acknowledge Dr’s John Fawcett, Gerry Griffith and Graham Eaton for their help in solving crystal structures, recording NMR and mass spectra respectively.

Finally my appreciation goes to members of the fluorine group both past and present for making my time at Leicester a pleasant one. In particular I would like to thank Dr’s Pravat Bhattacharyya, Alan Brisdon (for help with EXAFS), Martin Crossman (polymer analysis) and Graham Saunders for their forever willingness to pass on their chemical and practical experience. I would also like to thank Deborah Jones for taking time to proof read this manuscript and other members of the inorganic staff in particular Dr Dai Davies for useful discussions.

For financial support I am grateful to the E.P.S.R.C. (formally S.E.R.C.).
Abbreviations

AHF : anhydrous hydrofluoric acid
bipy : 2,2'-bipyridine
Cp* : pentamethylcyclopentadienyl (η⁵-C₅Me₅)
Cy : cyclohexyl
δ : NMR chemical shift
d : doublet
DBU : 1,8-diazabicyclo[5.4.0]undec-7-ene
dppe : 1,2-bis(diphenylphosphino)ethane
Et : ethyl
EPR : electron paramagnetic resonance
EXAFS : Extended X-ray Absorption Fine Structure
FEP : tetrafluoroethene / perfluoropropene copolymer
HSAB : hard and soft acids and bases
HOMO : highest occupied molecular orbital
Hz : Hertz
I. D. : internal diameter
IR : infrared
Kel-F : poly(chlorotrifluoroethlyene)
L : unidentate ligand
LUMO : lowest unoccupied molecular orbital
Me : methyl
NMR : nuclear magnetic resonance
O. D. outside diameter
pdma : o-phenylenebis(dimethylarsine)
Ph : phenyl
phen : 1,10-phenanthroline
ppm : parts per million
py : pyridine
q : quartet
t : triplet
t-Bu : tertiary butyl
thf : tetrahydrofuran
υ : stretching frequency
CHAPTER ONE

Introduction to Low-Valent Fluoride Complexes of the
Platinum Group Metals
1.1 General Introduction

The ability of the fluoride ligand to stabilise high oxidation states of the transition-metals is well established. The chemistry of low-valent transition-metal fluoride complexes is, in contrast, relatively unexplored. There are many examples in the literature where low-valent transition-metal compounds of the heavier halogens (chlorine, bromine and iodine) have been investigated, whilst the corresponding fluoride complexes are unknown. For example, kinetic and equilibrium measurements have been reported for the displacement of the heavier halides from the substrates [Pt(L)X] (L = diethylenetriamine, 2,6 bis(methylsulphonylmethyl)pyridine, bis(2-pyridylmethyl) sulphide or 2,2':6':2"-terpyridine, X = Cl, Br, or I) by the nucleophiles Cl, Br and I but not by F.[7]

The combination of a soft acid such as a low-valent transition-metal centre and a fluoride ion, which is a hard base, offers potentially interesting chemistry. Late transition-metal alkoxide complexes, which offer a similar soft/hard combination, are receiving increasing attention due to their reactivity and potential relevance to catalysis. The diverse reactions of late-transition-metal hydroxide, alkoxide and amide complexes include simple insertions of carbon monoxide and alkenes, β-hydride eliminations, oxidative additions and reductive coupling reactions, which take place by mechanisms similar to those previously established for metal alkyl and hydride derivatives. Moreover, complexes so formed by virtue of the lone electron pairs on the attached σ ligands, can undergo facile acid/base reactions and reversible σ ligand metatheses which generally require higher activation energies in comparable metal alkyl and hydride derivatives. This ability to heterolyse gives these compounds another mode of activity not normally open to the alkyls and hydrides, and it is this heterolysis which is believed to be responsible for their catalytic activity. Such compounds are known to catalyse the Wacker olefin oxidation process, carbonylation reactions, hydrogenation of carbon monoxide, ketones and aldehydes, and hydration and alcoholysis of olefins.

The lack of study of low-valent transition-metal fluoride complexes is surprising since the steric and electronic properties of chloro, bromo and iodo organotransition-metal compounds are often used in homogeneous catalyst design. A good example where the ligands surrounding the metal centre have been varied to
design a homogeneous catalyst is the Vaska's system [MX(CO)(phosphine)$_2$], M = Rh or Ir, X = F, Cl, Br or I.$^7-9$ The rhodium analogues have been extensively studied as catalysts for the hydroformylation of formaldehyde to glycol aldehyde (HC(O)CH$_2$OH).$^9$ The hydrogenation product methanol is also formed. The ratio of hydroformylation to hydrogenation was found to be dependent on the nature of the halide (X) and the phosphine ligand. When the phosphine is PPh$_3$ the yield of glycol aldehyde decreases in the order Cl > Br > I > F, whereas the by-product from the competing hydrogenation of formaldehyde follows the opposite order F > I > Br > Cl. Variation of the phosphine results in a decrease in the yield of glycol aldehyde in the order P(p-tolyl)$_3$ > P(m-tolyl)$_3$ > P(p-FC$_6$H$_4$)$_3$ > PEtPh$_3$ > PCy$_3$ > PEt$_2$Ph > P(OC$_6$H$_5$)$_3$ > P(C$_6$F$_5$)$_3$ > AsPh$_3$ for X = Cl.$^7$ The iridium analogues have been reported to catalyse the reaction of silanes HSiR$_3$, (R = Ph, Et and OEt) with alcohols R'OH, (R' = Et and Me) to give dihydrogen and siloxides (OR'SiR$_3$).$^8$ In the particular example of the reaction of HSiEt$_3$ with MeOH, the activity of the catalysts when X was varied could only be estimated qualitatively, with X = Cl, Br and I showing comparable rates and X = F being moderately more reactive.$^8$

Several factors have contributed to the lack of study of low-valent transition-metal fluorides. The principal one appears to be the labelling of a low-valent metal centre and fluoride ion as unstable on the basis of hard / soft acid / base rules. The Pearson system predicts that, in solution, soft acids form more stable complexes with soft bases.$^3$ Therefore, important organotransition-metal systems containing low-valent metal centres with loosely held electron density, which are considered to be soft acids, are not thought to interact favourably with the fluoride ion which is considered to be a hard base due to its high electronegativity, small size and low polarisability. Other factors that have also contributed to this lack of study are not based on chemical predictions but are due to experimental limitations. The difficulty in handling elemental fluorine and anhydrous hydrogen fluoride (AHF) has proved a major deterrent to extending the reactions that exist for the heavier halogens and hydrogen halides, to the fluoride derivatives. For instance, the reaction of [Os$_3$(CO)$_6$(NMe)$_3$] with the heavier hydrogen halides was studied, but the corresponding reaction with AHF was not investigated.$^{10}$ Initially, oxidation of [Ru$_3$(CO)$_{12}$] with the halogens chlorine, bromine and iodine was reported but the
corresponding reaction with fluorine gas was not investigated. This was subsequently investigated seven years later by Holloway. This reaction will be discussed in more detail in Chapter 4.

As a consequence of these difficulties, there have been few reports of transition-metal fluoride complexes. Only one hundred and thirty five complexes of low-valent platinum group metal fluorides are reported in the literature, with many of these reports relying solely on elemental analysis and infrared spectroscopy for characterization. Some of these compounds have been highlighted in a recent review. Much of the earlier work on low-valent fluorides included in this review is in error and many of the complexes poorly characterized. The review fails to distinguish between complexes which have been incorrectly formulated, such as the rhenium carbonyl fluoride complexes proposed by O'Donnell later proven to be incorrect by Holloway, and those which are unambiguously characterized. The area of low-valent metal fluoride complexes has also been extensively discussed in several Ph.D. theses.

The methods which have been used successfully to incorporate fluorine into low-valent transition-metal compounds include:

1) Oxidative fluorination of low-valent transition-metal compounds using non-metal fluorides such as (a) XeF₂, (b) EF₄, (c) NSF₃ or d) binary metal fluorides.

a) [Os₃(CO)₁₂] + 3 XeF₂ → [OsF₃(CO)] + [OsF(CO)₅][HF₂] + [Os₂F₃(CO)₈][HF₂] + [OsF₄(CO)₇] + Xe

b) Trans-[IrCl(CO)(PEt₃)₂] + EF₄ → [IrF₃(CO)(PEt₃)₂] + ClCl₂ + OC

E = S, Se
c) \[ \text{Trans-[IrCl(CO)(PPh_3)_2]} + \text{NSF}_3 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{OC} \quad \quad \text{PPPh}_3 \quad \text{NSF}_2 \quad \text{Cl} \quad \text{F} \quad \text{PPPh}_3 \]

d) \[ \text{[Re}_2\text{(CO)}_{10}] + 2\text{ReF}_6 \xrightarrow{\text{HF}} 2\text{[Re(CO)}_2}\text{F. ReF}_3 \]

II) High-pressure and high-temperature carbonylations of binary transition-metal fluorides; for example, the high-pressure carbonylation of ruthenium pentafluoride affords the tetrameric ruthenium fluoride \([\text{RuF}_2\text{(CO)}_2]_4\). \[^{[23]}\]

III) Halide metathesis reactions involving the replacement of chloride, bromide, iodide or weakly co-ordinating anions with fluoride. The principal problem associated with halide/fluoride exchange is the solubility of the source of \(\text{F}^-\). Silver fluoride is a readily available source of \(\text{F}^-\) but is particularly insoluble in non-polar solvents. This can be overcome by generating AgF \textit{in situ} by the reaction of Ag\(_2\text{CO}_3\) with NH\(_4\)F in methanol. This proved successful in the preparation of Vaska’s fluorides \([\text{MF(CO)}(\text{PPh}_3)_2]_4\), \(\text{M} = \text{Rh or Ir}\), from the chloride analogues. \[^{[24]}\]

Other examples include use of an excess of caesium fluoride which reacts with the five co-ordinate ruthenium complex \([\text{RuHCl(CO)}(\text{P'}\text{Bu}_2\text{Me})_2]\), resulting in chloride/fluoride exchange, to give the five co-ordinate ruthenium fluoride \([\text{RuHF(CO)}(\text{P'}\text{Bu}_2\text{Me})_2]\). \[^{[25]}\]

The origin of the fluoride ion in these metathetical reactions can often be important as the corresponding reaction using AgF or NaF fails to produce the ruthenium fluoride complex in any significant amount. \[^{[25]}\]

This illustrates the importance of the counterion and lattice energies in metathesis reactions.

IV) Fluoride abstraction from a polyfluoro anion, such as BF\(_4^-\), by a metal complex. \[^{[26]}\]

The reaction of \textit{trans-[RuCl}_2\text{(dppe)}_2\] with AgBF\(_4\) under a CO atmosphere results in the formation of \textit{trans-[Ru(CO)}_2\text{(dppe)}_2][\text{BF}_4]\), the desired product, and the formation of \textit{trans-[RuF(CO)}(\text{dppe})_2][\text{BF}_4]\), via the abstraction of fluoride from the BF\(_4^-\) counterion. \[^{[26]}\]
V) Activation of carbon-fluorine bonds by metal complexes. Carbon-fluorine bond activation is an area of research that has attracted much attention over recent years and has been the subject of a recent review.\[27\] The first mild, high-yield oxidative addition of a C-F bond to a transition-metal centre was reported in 1987 by Richmond and co-workers.\[28\] This was achieved by treating the Schiff base ligand \(\text{C}_6\text{F}_5\text{C} = \text{N}-\text{C}_6\text{H}_4\text{NH}_2\) (1) with \([\text{W}(\text{CO})_3(\text{PrCN})_3]\) in THF at room temperature, which afforded the air-stable seven-coordinate tungsten(II) fluoride complex \([\text{WF}(\text{C}_6\text{F}_5\text{C} = \text{N}-\text{C}_6\text{H}_4\text{NH}_2)(\text{CO})_3]\) (2) (Figure 1.0).\[28\]

![Figure 1.0](image)

Although the number of fluoride derivatives in the literature is increasing, many of the compounds have only a single literature citation, focusing mainly on preparation and identification. There are very few reports describing the chemical reactivity of these compounds. However, the final part of this introduction discusses the nature of the metal-fluorine bond and attempts to group together and summarise the reported reactions of low-valent platinum group metal fluoride complexes.

1.2 The nature of the Metal-Fluorine Bond in Low-Valent Platinum Group Metal Fluoride complexes

This section describes the nature of the M-F bond compared with the M-X bond, where X = Cl, Br or I. The stretching frequency of a reporter ligand such as CO has traditionally been used to evaluate the relative X ligand donor strength, where X = halide or alkoxide. The greater ligand donor strength results in a decrease in CO
stretching frequency, due to increased back-bonding between the metal and the CO ligand which reduces the bond order of the carbonyl ligand. In Vaska's compounds \([MX(CO)(PPh_3)_2]\) the CO stretching frequency decreases in the order \(X = I > Br > Cl > F\) which is opposite to that expected in terms of variation of electronegativity.\(^{[24]}\)

This can be readily explained in terms of \(\pi\)-donor ability of the halide which is expected to follow the order \(F > Cl > Br > I\). The \(\nu(\text{NO})\) frequencies of the complexes \([\text{RuCl}_2X(\text{bipy})(\text{NO})]\), where \(X = F\) or \(Cl\), with \(X\) trans to NO show a similar trend with \(X = F\) having the lower \(\nu(\text{NO})\) frequency\(^{[29]}\) (\(X = F, \nu(\text{NO}) = 1880, 1868 \text{ cm}^{-1}\); c.f. \(X = Cl\), \(\nu(\text{NO}) = 1891, 1878 \text{ cm}^{-1}\)). The crystallographic data for the two complexes confirms that the \(\pi\)-donor ability of the halides is important. The Ru-F bond length was found to be 1.942(5) Å which is shorter than that of other M-F separations of d\(^6\) transition metal fluoride complexes which have been structurally characterized (c.f. \([\text{ReF}(\text{CO})_3(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)\]), Re-F = 2.039(4) Å\(^{[31]}\) [Cp^*\text{IrF}(\text{Ph})(\text{PMes}_2)], Ir-F = 2.069(4) Å\(^{[22]}\) [\text{IrF}(\text{CO})(\text{CO})_2(\text{PET}_{3})][\text{BF}_4],\) Ir-F = 1.998(3) Å\(^{[33]}\) [\text{IrF}(\text{Cl})(\text{NSF}_2)(\text{CO})(\text{PPh}_3)_2],\) Ir-F = 2.089(4) Å\(^{[22]}\) and \([\text{RuF}_2(\text{CO})_3(\text{PPh}_3)_2],\) Ru-F = 2.011(4) Å\(^{[22]}\)). The Ru-NO bond length of 1.706(7) Å is considerably shorter than that in the chloride complex fac(\(\text{Cl}\))-\([\text{RuCl}_3(\text{bipy})(\text{NO})]\) (Ru-NO = 1.754(3) Å\(^{[36]}\)). The shortening of the Ru-F and Ru-NO bond lengths in the fluoride complex along with the lengthening of the N-O separation (N-O = 1.140(9) Å for the fluoride complex and 1.131(5) Å for the chloride complex), is a result of a greater degree of back-bonding from the metal to NO in the fluoride complex.

However, interpretation of data obtained from other techniques, such as NMR spectroscopy, is not quite as straightforward. \(^{31}\)P NMR spectroscopic studies on trans-[\text{IrX}(\text{CO})(\text{PPh}_3)_2] showed only minor variations in chemical shift, \(\delta\), as \(X\) was varied. Although a trend was observed, \(X = F(\delta -24.4) < Cl(\delta -22.5) < I(\delta -19.5)\), interpretation is difficult since the differences are small and the chemical shift is sensitive to a number of factors such as local diamagnetic and paramagnetic shielding, shielding due to remote currents and other sources such as hydrogen-bonding, concentration, temperature and solvent.\(^{[30]}\) In the rhodium trans-[\text{RhX}(\text{CO})(\text{PPh}_3)_2] series there is no apparent trend in the \(^{31}\)P chemical shift. This is probably a consequence of the differing conditions under which the spectra were recorded, i.e. different solvents and temperature, both of which have an effect on the chemical
However, the magnitude of the $^1J$(RhP) coupling constant was found to follow the order $X = \text{F}(-135.5 \text{ Hz}) > \text{Cl}(-126.9 \text{ Hz}) > \text{Br}(-125.0 \text{ Hz}) > \text{I}(-123.5 \text{ Hz})$, where the magnitude of the coupling constant increases with the electronegativity of $X$. This trend only appears to apply to the halogens in $[\text{RhX(CO)(PPh}_3)_2]$, as the carboxylate group $X = \text{CF}_3\text{C(O)O}^-$ which is more electronegative than $\text{CH}_3\text{C(O)O}^-$ gives rise to a smaller $^1J$(RhP) coupling constant than its non-fluorine containing counterpart. Similarly, no relationship between $^1J$(RhP) and the electronegativity of the halogens was found in the three co-ordinate complexes $[\text{RhX(PCy}_3)_2]$, $X = \text{F, Cl, Br or I}$. This indicates that little, if any, useful information can be obtained on the nature of the halide from this coupling constant. The $^{103}\text{Rh}$ chemical shifts for $[\text{RhX(CO)(PPh}_3)_2]$ follow the normal halogen dependence, the shielding of the metal centre increasing in the order $\text{F(ô 5711)} < \text{Cl(ô 5488)} < \text{Br(ô 5436)} < \text{I(ô 5324)}$. Chemical shifts in NMR spectroscopy are related to the shielding constant $\sigma$. This is dependent on four components; local diamagnetic shift ($\sigma_d$), local paramagnetic shielding ($\sigma_p$), shielding due to remote currents and other sources of shielding such as hydrogen bonding, with the first two terms dominating. Diamagnetic and paramagnetic shielding give rise to nuclear shielding and deshielding respectively. The shielding constant $\sigma$ may be written as a sum of diamagnetic and paramagnetic contributions, ($\sigma = \sigma_d + \sigma_p$), with $\sigma_d$ positive and $\sigma_p$ negative. The paramagnetic term is used to describe the contributions from the field induced non-spherical circulation of the electron density and not to denote the presence of unpaired electrons. The paramagnetic term is insignificant in proton NMR spectroscopy, but becomes important in metal NMR, hence the larger chemical shift range. The paramagnetic contribution to shielding ($\sigma_p$) depends on the distance of the metal $d$ electrons from the nucleus ($r$) and the average excitation energy of states with the appropriate symmetry ($\Delta E$) (Equation 1.0).

\[
\sigma_p = -\frac{2}{3} \left( \frac{e \hbar}{mc} \right) \left( \frac{1}{r^3} \right) \frac{1}{\Delta E}
\]
From the UV electronic absorption spectra, the halide complexes \([\text{RhX(CO)(PPh}_3]_2\) were found to have values of \(\lambda_{\text{max}}\) in the order \(X = \text{F}(358 \text{ nm}) < \text{Cl}(367 \text{ nm}) < \text{Br}(369 \text{ nm}) < \text{I}(372 \text{ nm})\).\(^{[46]}\) The corresponding iridium complexes follow the same order.\(^{[46]}\) This is attributed to the relative positioning of the \(a_1(d_{^g})\) and \(b_{1e}\) molecular orbital energy levels. Strong acceptor ligands such as \(\Gamma\) greatly stabilise the \(b_{1e}\) level, whereas strong \(\sigma\)-donor ligands destabilise the \(d_{^2}^e\) level. As \(\Gamma\) is both a strong \(\pi\)-acceptor and a good \(\sigma\)-donor it should have the least energetic \(d_{^2}^g \rightarrow b_{1e}\) transition, as \(E = 1/\lambda\), which is found. As \(\text{F}\) is a good \(\pi\)-donor but a poor \(\sigma\)-donor it has the most energetic \(d_{^2}^e \rightarrow b_{1e}\) transition (Figure 1.1).\(^{[46]}\)

**Figure 1.1 Molecular Orbital Energy Level Correlation Diagram for C\(_{3v}\) Complexes\(^{[46]}\)**

Based on this argument where \(\Delta E\) is large, when \(X = \text{F}\), \(\sigma_p\) should be small and hence the fluoride complex should contain the most shielded rhodium centre, as \(\sigma_p\) is a deshielding term. However, it has been noted\(^{[56]}\) that the trend observed for \(\delta\) \((^{103}\text{Rh})\) is opposite to that expected based on the \(1/\Delta E\) term, as the fluoride was found to have the most deshielded metal centre even after temperature effects are taken into consideration. This can vary the chemical shift by as much as 0.6 ppm / °C.\(^{[43]}\) The variation in \(\delta\) \((^{103}\text{Rh})\) was found, however, to be consistent with increasing \(d\) electron
distance from the metal centre and increasing M-X bond covalency on going down the halide group from fluorine to iodine (the nephelauxetic effect). Therefore the $<1/r^3>$ term is largest when $X = F$ and hence $\sigma_p$ will be larger, so that the fluoride complex should contain the most deshielded rhodium centre which is in accord with that found experimentally. It is not possible to gauge the relative importance of the individual terms $1/\Delta E$ and $<1/r^3>$, but if the $\delta^{(10)}$Rh is dominated by $\sigma_p$ effects, then one could assume that in this particular system the $<1/r^3>$ term dominates over the $\pi$-effects of the halide (which have until so far explained the infrared and electrochemical spectra). This accounts for the failure of NMR spectroscopy to concur with the established effects identified from other techniques.

Electrochemical experiments on the complexes trans-[MX(CO)(PPh$_3$)$_2$], $M = Rh$ or Ir, $X = F, Cl, Br$ or $I$, have shown that the half-wave potentials for the complexes follow the order $X = F [-2.34 V (Rh), -2.55 V (Ir)] < Cl [-2.05 V (Rh), -2.22 V (Ir)] < Br [-2.00 V (Rh), -2.07 V (Ir)] < I [-1.89 V (Rh), -1.96 V (Ir)].$ These values suggest that it is harder to reduce the fluoride complexes than those of the heavier halides. This is attributed to the greater overall electron donor property ($\sigma + \pi$) of fluoride compared to that of the heavier halides, demonstrating that the fluoride complexes contain the most electron-rich metal centres. The spectral data gathered for trans-[MX(CO)(PPh$_3$)$_2$], $M = Rh$ or Ir, suggests that the most electron-rich metal centre follows the order $X = F > Cl > Br > I$. These observations are opposite to expectations based on electronegativity arguments, suggesting metal-halide $\pi$-bonding dominates in the electronic structure of the rhodium(I) and iridium(I) compounds with the fluoride ligand being the best $\pi$-donor and poorest $\pi$-acceptor.

More recently, the ($\sigma + \pi$) donor strength of a range of anionic ligands ($X$) in the five co-ordinate trans-[RuHX(CO)(P$^3$Bu$_2$Me)$_2$] complexes (Figure 1.2) $X = I, Br, Cl, F, OEt, OCPb$_3$, OSiMe$_3$, OH, OB(mesityl)$_2$, OCH$_2$CF$_3$, NHPh, OPh, SPb and CpPh, have been calculated based on their CO stretching frequency. Theoretical calculations have also been employed to explain the observed trends. The CO stretching frequency (which acts as an indicator of back-bonding and thus of donor power of $X$) established the following ranking of total ($\sigma + \pi$) ligand donor strength, OEt > OCPb$_3$ > OSiMe$_3$ > $F = OCH$_2$CF$_3$ > OH = OB(mesityl)$_2$ > NHPh = OPh > SPb.
> Cl > C₂Ph = Br > I. Thus, X = OEt leads to a lower CO stretching frequency in [RuHX(CO)(P'Bu₂Me)₂] and X = I has the highest CO stretching frequency due to poor back-bonding. The trend in this series which is most relevant here is that of the halides. The CO stretching frequency decreases along the series I(1908 cm⁻¹) > Br(1906 cm⁻¹) > Cl(1904 cm⁻¹) > F(1892 cm⁻¹). Hence, the donor strength increases along the series F > Cl > Br > I which is analogous to that observed in the complexes [MX(CO)(PPh)₂], M = Rh, Ir. Alkoxides, which are significantly better π-donors than the halides, lower ν(CO) the most, which is good evidence for the π-effect being important in these complexes.

Figure 1.2

The five co-ordinate species react readily with pyridine to give the six co-ordinate complexes [RuHX(CO)(P'Bu₂Me)₂(py)]. The ν(CO) values exhibit the same trend with variation in X as those of the five co-ordinate species, all being shifted to lower frequencies. It was believed that ν(CO) would reflect only the σ-donor strength of X, as there can be no conventional (two centre) Ru-X π-bonding in the pyridine adducts since the Ru(d) / X(pre) have two-orbital / four electron interactions and, therefore, have a net destabilising effect. However, it was shown by qualitative molecular orbital analysis that the π*-orbital of CO is of the correct symmetry to interact with the out-of-phase combination of the filled / filled dπ / X lone pair couple and thereby relieves the four electron destabilisation. This leaves some degree of X→Ru π interaction and so explains the similar trend.

It was also suggested in this study that ¹⁹F NMR chemical shifts could be related to the extent of F→Ru π-donation. Co-ordination of the predominantly σ-donor ligand pyridine to the five co-ordinate complex [RuHF(CO)(P'Bu₂Me)₂] resulted in a low frequency shift from that of the starting material (δ -311) to δ -491, whereas co-ordination of CO (a π-acceptor ligand) gave a shift to higher frequency,
The co-ordination of the σ-donor ligand pyridine is believed to increase the electron density at the metal centre reducing the electrophilicity of the ruthenium and thus F→Ru π-donation, whereas co-ordination of CO creates additional synergic (push-pull) interactions wherein fluorine lone pairs, filled \( dt \)-orbitals and empty CO \( \pi^* \)-orbitals interact to enhance fluoride π-donation. On this basis it was believed that a lower-frequency chemical shift could be regarded as an indication of small F→Ru π-donation and a higher frequency shift as increased F→Ru π-donation.

Figure 1.3 Molecular Orbital Energy Level Diagram for Carbon Monoxide with \( s \) and \( p \) Mixing

\[
\begin{align*}
6\sigma & \quad \downarrow \\
2p & \quad LUMO \\
5\sigma & \quad HOMO \\
4\sigma & \quad 1\pi \\
3\sigma & \quad 2s \\
2\sigma & \quad 1s \\
& \quad \text{Carbon} \quad \text{Oxygen}
\end{align*}
\]
Extended Hückel Theory (EHT) and core- \textit{ab initio} calculations have been used to predict the structures of the five co-ordinate complexes. In all cases, the square pyramid is preferred with the phosphine ligands mutually \textit{trans}, the hydride ligand in the apical position and the X group \textit{trans} to CO. This permits synergic interactions between the $\pi$-donating X group and the $\pi^*$-orbital of CO. The CO stretching frequency was also calculated theoretically and the trend observed was identical to that observed experimentally. The CO stretching frequency has been observed to depend on the nature of the metal centre. Electrostatic interactions are said to raise the CO vibration frequency above that of free CO \cite{Cu} due to loss of electron density from the weakly antibonding HOMO (5$\sigma$) of CO (Figure 1.3). In a study by Caulton et al.\cite{Cu} the $\pi$-donation of F and Cl were said to be similar in the complexes [RuHX(CO)(P'Bu$_2$Me)$_2$], X = halide, with the differences in CO stretching frequency believed to be due to the ionicity of the two bonds, Ru-F being more ionic than Ru-Cl. If this were the case, the increased electrostatic interaction between the metal and the CO in the case of the fluoride should lead to a higher CO stretch than in the chloride case and not lower as experimentally observed.

It was concluded, therefore, that it must be the changes in the lower-bonding C/O $\sigma$-orbitals in addition to that in the weakly bonding 5$\sigma$ that contribute to the overall trend down the halide group. This conflicts with the currently accepted idea that 5$\sigma$ is CO-antibonding, and is thought to be a consequence of the low lying $d$ orbital energies, as calculated by the authors.\cite{Cu} It was put forward that moving down a group in the periodic table has little effect on the $\pi$-system since the increase in the Ru-X bond length results in a decreased overlap of orbitals therefore diminishing the donating power of the higher energy orbital. However, moving across the periodic table from the halogens (Group 17) to the nitrogen group (Group 15), increases the $\pi$-donating strength of the X lone pair(s), hence the lower CO stretching frequencies observed for the alkoxides compared to the halides. The increase in ionicity of the Ru-X bonds when going up the group of halides is said to dominate over the $\pi$-effect for [RuHX(CO)(P'Bu$_2$Me)$_2$] compounds and lowers the CO stretching frequency, contradicting Caulton’s earlier statements which suggest that $\pi$-effects are important.\cite{Cu} Although Caulton et al. came to a conclusion concerning the CO stretching frequency in the compounds [RuHX(CO)(P'Bu$_2$Me)$_2$], it is very difficult to
see how such a conclusion was obtained. The theoretical calculations employed were at a basic level [Hartree-Fock and level two Molecular Perturbation theory (MP2)] dealing with only the valence electrons for the theoretical complexes [RuHX(CO)(PH₃)₂]. This, along with the fact that the models used were unable to predict the correct stretching frequency for free CO [1901 cm⁻¹ (MP2) and 2265 cm⁻¹ (Hartree-Fock) compared with 2143 cm⁻¹ experimentally] and that the calculated CO stretching frequencies of the complexes differed only by 3 cm⁻¹ suggests that little weight should be placed on these calculations. The important thing obtained from this study is that the CO stretching frequency for [RuHX(CO)(P'Bu₂Me)₂] follows the trend X = F < Cl < Br < I which is analogous to the trend observed in the Vaska's halides [MX(CO)(PPh₃)₂], where M = Rh or Ir.

In the cationic platinum fluoride complexes [PtF(PR₃)₃][BF₄], PR₃ = PEt₃ and PPh₃, Dixon et al.⁴⁷ have suggested that the ¹J(PtF) coupling constant may be used as an indication of the strength of the Pt-F bond; whereby the lower the value, the weaker the Pt-F bond. This is supposedly supported by the facile hydrolysis of [PtF(PPh₃)₃][BF₄] which has the lower ¹J(PtF) value, (66 Hz cf. 250 Hz for [PtF(PEt₃)₃][BF₄]).⁴⁷ However, caution must be used when assigning bond strengths based on coupling constants as ¹J(PtF) interactions are only an indication of the s character in the Pt-F bond. No π-donation from the fluoride to the metal is taken into account, which has been shown here to be important in the electronic structure of low-valent metal fluoride complexes. This reaction has been studied in more detail by Peck²⁰ who compared the EXAFS data for [PtF(PPh₃)₃][SbF₆] and [PtF(PEt₃)₃][BF₄] in order to ascertain whether the Pt-F bond lengths are sufficient to explain the difference in ¹J(PtF). The Pt-F bond length in both complexes were found to be the same within the limits of the technique (± 0.02 Å), however, the reactivity of the [PtF(PPh₃)₃]⁺ complex was found to be affected considerably by the counterion chosen.²⁰

Based on a study of both the fluoride and the chloride complexes [PtXL₃]⁺, X = halide and L = PPh₃ or PEt₃, Dixon et al.⁴⁷ have suggested that the trans influence of fluoride is slightly greater than that of chloride, based on absolute values of ¹J(PtP) for the phosphine ligands trans to X, with the lower value indicating a larger trans influence. This is opposite to the generally accepted order of trans influence i.e. Cl >
F. However, in the \([\text{PtX}(\text{Ph}_{3})_3][\text{BF}_4]\) complex, the trans influence of fluoride is less than that of chloride as the magnitude of \(1J(\text{PtP})\) is greater. This has been attributed to the weak Pt-F bond in this particular complex. The validity of this study is doubtful as the differences between magnitude of the \(1J(\text{PtP})\) coupling constants is only 19 Hz. In addition, the spectra were recorded in different solvents. In particular, the fluoride complexes were recorded in acetone as opposed to dichloromethane for the chlorides. Since acetone is never totally anhydrous, this may result in the fluoride ligand being hydrogen bonded to the water present which, in turn, have an effect on the coupling constant.\(^{47}\)

In summary, it is very difficult to ascertain the exact nature of the M-F bond and make comparisons with other M-X bonds where X = Cl, Br or I. The main reason being that the probe used to study the nature of the M-X bond is considerably affected by a variety of factors. However, it is possible to generalise that the \(\pi\)-donating properties of the halides where \(F > Cl > Br > I\) play a part in the metal-halide bond, the significance of this effect depending on the system being studied. NMR spectroscopy, in particular \(\text{^19F\ NMR}\) chemical shifts, may prove useful in the future (as more are reported) as indicators of the extent of F\(\rightarrow\)M \(\pi\)-donation. Nevertheless, the method will be only qualitative, with low frequency chemical shifts denoting little or no F\(\rightarrow\)M \(\pi\)-donation. Similarly, systematic crystallographic studies may provide a useful insight into the nature of the M-F bond as the number of structural studies on metal fluoride complexes increases. In this thesis, the synthesis of a number of low-valent osmium(II) and ruthenium(II) fluoride complexes are described together with their \(\text{^19F\ NMR}\) data. Some of the complexes have been characterized crystallographically in an attempt to understand the nature of the M-F bond.

1.3 Reactions and Properties of Low-Valent Platinum Group Metal Fluoride Complexes

Of the one hundred and thirty five low-valent platinum group metal fluoride complexes reported, the reactivity of only fifteen has been discussed. The reactions can be summarised under three headings:-

a) Reaction at metal-bound fluorine.

b) Reaction at co-ordinated ligands.
c) Reaction at the metal centre, i.e. substitution and oxidative addition.
Each of these will be discussed in turn.

1.3.1 Reaction at Metal-Bound Fluorine

The earliest report of reaction at a transition-metal fluoride bond was in 1971. The discovery of the simple molecular fluoride complexes trans-[MF(CO)(PPh3)2], where M = Rh or Ir, prepared from the reaction of the chloride with silver carbonate in methanol followed by addition of ammonium fluoride, led to the first investigation into the nature of the metal-fluorine bond. Solution conductivity measurements indicated that the d5 square planar fluoride complexes trans-[MF(CO)(PPh3)2] are weak electrolytes in methanol [Λm = 22 Ω⁻¹ (Ir), 35 Ω⁻¹ (Rh), for a 1 : 1 electrolyte the value ca. 100 Ω⁻¹ is expected]. This suggests a solvolytic equilibrium (Figure 1.4). On the basis of this equilibrium the lability of the fluoride ligand was exploited by simple anion metathesis in methanol solvent to yield a range of new d5 square planar derivatives trans-[MY(CO)(PPh3)2], where Y = Cl, Br, I, CN, NCS, NCO, N2, OH, OPh, O2CH, O2CMe, ONO2 and ONClO3. The dissociation of the fluoride complexes in methanol, resulting in the formation of the aforementioned complexes, is thought to be due to the considerable affinity of the fluoride ligand for methanol (or water) as a consequence of strong hydrogen bonding to the hydroxyl group. It is also possible for the bromo, iodo, azido and thiocyanato complexes to be obtained from the chloro analogue trans-[MCl(CO)(PPh3)2] via simple substitution. However, the majority of the compounds listed are not accessible by the latter route.

Figure 1.4

\[
\text{Ph}_2\text{P} \begin{array}{c} \text{MeOH} \\ \text{OC} \end{array} \text{M} \begin{array}{c} \text{F} \\ \text{PPh}_3 \end{array} \rightleftharpoons \left[ \text{Ph}_2\text{P} \begin{array}{c} \text{MeOH} \\ \text{OC} \end{array} \text{M} \begin{array}{c} \text{MeOH} \\ \text{PPh}_3 \end{array} \right]^{-[F]} \\
\text{M} = \text{Rh and Ir}
\]
Reaction of \([\text{RhF}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2]\), prepared by the addition of \(\text{PPh}_3\) to the tetrameric fluoride \([\text{RhF}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)]_4\), with \(\text{Me}_3\text{SiOTf}\), resulted in the abstraction of the fluoride bound to rhodium to give the triflate complex \([\text{Rh}(\text{OTf})(\text{C}_2\text{F}_4)(\text{PPh}_3)_2]\), where the OTf group is oxygen bound to the central rhodium atom and formation of fluorotrimethylsilane.\(^{46}\) No mention was made as to whether the triflate complex can be prepared from the chloride analogue \([\text{RhCl}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2]\) by addition of silver triflate or \(\text{Me}_3\text{SiOTf}\) but, given that the abstraction of the chloride by \(\text{AgBF}_4\) is straightforward, chloride abstraction with \(\text{AgOTf}\) and the corresponding co-ordination of the triflate should be facile.

Replacement of the fluoride is also possible in the complexes \([\text{RhF}(\text{PCy}_3)_2]\), \([\text{RhF}(\text{C}_2\text{H}_4)(\text{PCy}_3)_2]\) and \([\text{RhF}(\text{PCy}_3)(\text{L})]\), where \(\text{L} = \text{C}_2\text{H}_4\), \(\text{CO}\) and \(\text{C}_2\text{Ph}_2\), by addition of univalent anions \((Y)\) in a benzene - water biphasic system, to give \([\text{RhY}(\text{PCy}_3)_2]\), \([\text{RhY}(\text{C}_2\text{H}_4)(\text{PCy}_3)_2]\) and \([\text{RhY}(\text{PCy}_3)(\text{L})]\) where \(Y = \text{Cl}, \text{Br}, \text{I}\) and \(\text{N}_3\).\(^{47}\) The water presumably helps labilise the rhodium-fluorine bond as well as to solubilise \(\text{NaY}\).

A number of cationic d\(^8\) platinum fluoride complexes have been reported, \([\text{PtF}(\text{PET}_3)_3][\text{BF}_4]\), \([\text{PtF}(\text{PPh}_3)_3][\text{BF}_4]\), \(\text{trans-}[\text{PtF}(\text{PET}_3)_2(\text{PPh}_3)][\text{ClO}_4]\), \(\text{trans-}[\text{PtF}(\text{PET}_3)_2(\text{OFPPh}_3)][\text{ClO}_4]\) and \([\text{PtF}(\text{PMe}_2\text{Ph})_3][\text{BF}_4]\), formed from the simple metathetical reactions of \(\text{AgF}\) with the chloride complexes.\(^{47}\) Hydrolysis of these platinum compounds are reported to give the hydroxy-bridged species \([\text{Pt}(\text{OH})_2(\text{PR}_3)_4]\)^\(^{45}\), which are known to be formed from the reaction of the chloride complexes with \(\text{AgBF}_4\) in wet acetone.\(^{49}\) The complex \([\text{PtF}(\text{PPh}_3)_3][\text{BF}_4]\) is believed to be the most easily hydrolysed due to the steric effects of the bulky \(\text{PPh}_3\) groups causing a distortion of the co-ordination geometry towards a lengthening of the Pt-F bond or possibly towards a tetrahedral geometry.\(^{47}\) However, as previously mentioned, EXAFS studies by Peck\(^{20}\) have shown that the Pt-F bonds in \([\text{PtF}(\text{PPh}_3)_3]^+\) and \([\text{PtF}(\text{PET}_3)_3]^+\) are similar. In the platinum complexes, the HF\(_2^-\) counterion in \([\text{PtF}(\text{PPh}_3)_3][\text{HF}_2]\) can be readily exchanged with \(\text{BF}_4^-\) or \(\text{BPh}_4^-\) by adding \(\text{LiBF}_4\) or \(\text{NaBPh}_4\) respectively, whereas the addition of \(\text{LiClO}_4\) is believed to result in the loss of phosphine and the formation of the dimer \([\text{Pt}_6(\mu-\text{F})_2(\text{PPh}_3)_4][\text{ClO}_4]\), with characterization relying on elemental analysis and conductivity measurements.\(^{59}\)
The room temperature condensation of the vanadium(V) trimethylsilylamido complex \([\text{Me}_3\text{SiO}]_3\text{V}=\text{NSiMe}_3\) with the platinum fluoride complex \textit{trans}-[\text{Pt(Me)}\text{F(PEt}_3)_2] produces a novel heterobimetallic complex\(^{[51]}\) in which the vanadium and platinum are bridged by a nitrido ligand, along with fluorotrimethylsilane (Figure 1.5). Complexes which contain two or more different metal atoms are interesting because of their potential use as polyfunctional catalysts and precursors for the preparation of bi- and polymetallic heterogeneous catalysts.

Crystallization of the \(\mu_2\)-nitride complex \(\text{trans}-[(\text{Me}_3\text{SiO})_3\text{V}=\text{N-Pt(Me)(PEt}_3)_2]\) (3) affords the \textit{cis} isomer which was characterized by single crystal X-ray diffraction. Slow isomerisation of the \textit{cis} isomer to the thermodynamically favoured \textit{trans} isomer is observed in benzene solution.

**Figure 1.5**

\[
\begin{align*}
\text{Me}_3\text{SiO} & \quad \text{V}=\text{N-SiMe}_3 + \quad \text{PE}_3 & \quad \text{F-SiMe}_3 & \quad \text{Me}_3\text{SiO} & \quad \text{V}=\text{N-Pt-Me} & \quad \text{PE}_3 \\
\text{Me}_3\text{SiO} & \quad \text{V}=\text{N-SiMe}_3 & \quad \text{PE}_3 & \quad \text{F-SiMe}_3 & \quad \text{Me}_3\text{SiO} & \quad \text{V}=\text{N-Pt-Me} & \quad \text{PE}_3 \\
\end{align*}
\]

The \textit{trans} \(\mu_2\)-nitride bimetallic complex is also the major product from the condensation of the trimethylsilylamido compound with the \textit{trans}-[\text{Pt(Me)}\text{Cl(PEt}_3)_2], with the attendant formation of chlorotrimethylsilane\(^{[51]}\). However, this reaction requires a temperature of 80°C compared with room temperature for the reaction with the platinum fluoride complex. This lower temperature of reaction can be attributed to the greater driving force of reaction arising from the formation of the Si-F bond in fluorotrimethylsilane which is considerably stronger than the Si-Cl bond in chlorotrimethylsilane. Similar chemistry is observed for rhodium and iridium.
[MX(CO)(PPh3)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 trans-[(Me2SiO)3V=N-M(CO)(PPh3)].

A recent study on the reactivity of the metal-fluorine bond in an iridium(III) complex has appeared in the literature. This once again centres around the ease with which the metal-fluorine bond dissociates in solution. The aryl iridium(III) fluorides [Cp'lr(aryl)F(PMe3)] have been synthesised from the reaction of the triflate compound [Cp'lr(aryl)(OTf)(PMe3)] with TAS-F, an organic solvent soluble source of F, where Cp' = Cp*; aryl = Ph, p-tolyl, Cp' = (C6Me4Et); aryl = Ph. The complex where Cp' = Cp* and aryl = Ph has been characterized by X-ray crystallography. These complexes were found to differ in reactivity from their related chloride, bromide and iodide analogues. The fluoride ligand was found to be easily displaced by Lewis bases such as phosphines and pyridines. The reaction of the aryl fluoride complex (4) with six equivalents of triethylphosphine in the presence of forty-six equivalents of water leads to a mixture of the fluoride complex (4) [® 'P{'H} NMR (M-ds) 6 = 24.5 (d) V(PF) = 54 Hz, 19F NMR (C6D6) δ = -432.0 (d) J(PF) = 54 Hz] and the aquo species [Cp*Ir(Ph)(OH2)(PMe3)]F (5), [19F NMR (thf-d8) δ = -27.7 (s)]. No 19F NMR signal was observed for F. Allowing the reaction to stand leads to the formation of [Cp*lr(Ph)(PEt3)(PMe3)]F ·xH2O (6), [19F NMR (THF-d8) δ = -22.5 (d) J(PF) = 25 Hz, PEt3, γ = 47.6 (d) J(PP) = 25 Hz, PMe3]. Once again, no 19F NMR signal was observed for the fluoride counterion. Complete conversion was achieved after twenty four hours (Figure 1.6). Similar results were obtained using 4-((dimethylamino)pyridine as the ligand.[22] The same experiment without the addition of water results in no reaction, suggesting that the ease of replacement of the fluoride ligand in the presence of water is due to the dissociation of the iridium-fluoride bond. This dissociation is caused by the high affinity of the fluoride ion for water due to strong hydrogen bonding to the hydroxyl group. The weakly co-ordinated water is then easily replaced by phosphines or pyridines. This is analogous to results obtained by Vaska who observed the dissociation of the Ir-F and Rh-F bonds in methanol.[24]
Figure 1.6

\[
\text{Cp^*(PMe_3)Ir} \quad \xrightarrow{\text{H}_2\text{O}, \text{THF}} \quad \left[ \text{Cp^*(PMe_3)Ir} \quad \xrightarrow{\text{Ph}} \quad \text{F}_\text{OH}_2 \right] \quad \text{F} \cdot \text{H}_2\text{O}
\]

(4)

\[
\text{L} = \text{PEt}_3, \quad \text{N} \quad \text{NMe}_2
\]

(5)

\[
\left[ \text{Cp^*(PMe_3)Ir} \quad \xrightarrow{\text{Ph}} \quad \text{F}_\text{OH}_2 \right] \quad \text{F} \cdot \text{H}_2\text{O}
\]

(6)

The iridium(III) aryl fluorides also undergo rapid halide exchange upon reaction with the organic halides PhCH₂Br, Me₂SiCl, MeCOCl and CH₂Cl₂ (RX) to give RF and [Cp'Ir(aryl)X(PMe₃)], where X = halide. However, the reactions were found to be highly variable and irreproducible.[32] The reactivity of the Ir-F bond in these metathetical reactions can be explained by the greater R-F bond strength compared to that of R-Cl which acts as a driving force for reaction on account of the presumably greater strength of the Ir-Cl bond compared to that of the Ir-F bond.

Interestingly, the cyclopentadienyl iridium aryl fluoride complexes were found to react with the activated alkyne dimethyl acetylenedicarboxylate (DMAD) to give the metallacycle [Cp'Ir(C₆H₅(CO₂Me)C=C(CO₂Me))(PMe₃)] (8). The metallacycle is thought to be formed via the cationic intermediate [Cp'Ir(C₆H₅(CO₂Me)C=C(CO₂Me))(PMe₃)]⁺F (7). This is believed to be formed via initial co-ordination of the alkyne to the metal centre with concomitant dissociation of the fluoride and then attack at the ortho carbon of the aryl ligand. Deprotonation of (7) by F⁻ then occurs to give the final product (8) (Figure 1.7).
A similar reaction was observed for the triflate complex [Cp*Ir(Ph)(OTf)(PMe3)], but addition of base is required to aid the deprotonation step. Base is not required in the fluoride case presumably because fluoride is more basic than triflate. Olefins and unactivated acetylenes undergo no reaction with the iridium(III) aryl fluoride complexes. In contrast, the iridium hydroxy compound [Cp*Ir(Ph)(OH)(PMe3)] reacts readily with ethene and DMAD, with insertion into the metal-oxygen bond to give [Cp*Ir(Ph)(\(\eta^1\)-C2H4OH)(PMe3)] (9) and the enol complex [Cp*Ir(Ph)(\(\eta^1\)-(CO2Me)C=CH(OH))(PMe3)] (10) respectively (Figure 1.8).
One of the most commonly studied reactions of metal fluoride complexes is the abstraction of the fluoride ion from the metal centre. Silyl and trimethylsilyl compounds R₃SiX (R = H or alkyl, X = halide or pseudohalide) are known to attack R'F compounds (R'F = fluoroformate) to give silyl fluoride or trialkysilyl fluoride and R'-X. The corresponding reactions do not work with chloroformate (R'-Cl) in the place of R'F, due to the greater strength of the Si-F bond compared to that of Si-Cl which acts as a driving force for reaction. The use of silyl reagents has been extended to reactions involving metal fluorine bonds. Formal activation of Si-N and Si-H bonds by the iridium aryl fluoride complex [Cp*IrF(Ph)(PMe₃)] has been observed. Reaction of the iridium aryl fluoride [Cp*IrF(Ph)(PMe₃)] with 1-(trimethylsilyl)imidazole is thought to form an intermediate cation [Cp*Ir(Ph)(N₂(C₃H₃-SiMe₃)(PMe₃)]⁺F⁻, (11), from the co-ordination of the imidazole to the metal centre via the nitrogen lone pair with concomitant dissociation of fluoride. The fluoride ion then rapidly desilylates the imidazole to give the imidazolate complex [Cp*Ir(N₂(C₃H₃))(Ph)(PMe₃)], (12), the driving force for the desilylation reaction being formation of the strong Si-F bond in FSiMe₃ (Figure 1.9). A similar reaction with the silane HSiMe₃ was expected to lead to either deprotonation of HSiMe₃ to give [Cp*Ir(p-tolyl)(SiMe₃)(PMe₃)] with the formation of HF, or desilylation to give [Cp*Ir(H)(p-tolyl)(PMe₃)] with the formation of FSiMe₃. However, no such reaction was observed and the complex [Cp*Ir(Me)(SiMe₂F)(PMe₃)] (16) was isolated. It was suggested that formation of (16) occurred by dissociation of the Ir-F bond to give the transient intermediate (13) followed by a σ bond metathesis reaction between the dissociated fluoride species and silane to produce the cationic iridium(III) silyl complex (14). Alkyl migration then
occurs giving (15) followed by attack of F at the silyl group to give the final product \([\text{Cp}^*\text{Ir}(\text{Me})(\text{SiMe}_2\text{F})(\text{PMe}_3)]\) (16) (Figure 1.10).

Figure 1.9

\[
\begin{align*}
\text{Cp}^*(\text{PMe}_3)\text{Ir} & \quad \xrightarrow{\text{Ph}} \quad \text{F} \\
\text{SiMe}_3 & \\
(4) & \\
\end{align*}
\]

(11)

-\text{Me}_3\text{SiF}

\[
\begin{align*}
\text{Cp}^*(\text{PMe}_3)\text{Ir} \quad \xrightarrow{\text{Ph}} \\
\text{SiMe}_3 & \\
(12) & \\
\end{align*}
\]

Figure 1.10

\[
\begin{align*}
\text{Cp}^*(\text{PMe}_3)\text{Ir} & \quad \xrightarrow{\text{p-tolyl}} \quad \xrightarrow{\text{F}} \\
\text{Cp}^*(\text{PMe}_3)\text{Ir} & \quad \xrightarrow{\text{p-tolyl}} \quad \text{F.xH}_2\text{O} \\
\text{Me} & \quad \text{SiMe}_2 & \\
(4) & & (13) & & (14) & & (15) & & (16) & & \text{alkyl migration} & \text{F attack}
\end{align*}
\]

\[\text{Cp}^*(\text{PMe}_3)\text{Ir} \quad \xrightarrow{\text{Me}} \quad \text{F.xH}_2\text{O} \quad \xrightarrow{\text{alkyl migration}} \quad \text{F.xH}_2\text{O} \quad \xrightarrow{\text{F attack}} \quad \text{Cp}^*(\text{PMe}_3)\text{Ir} \quad \xrightarrow{\text{SiMe}_3} \quad \text{F.xH}_2\text{O} \]
It is clear from these reactions of the iridium fluoride complexes, that the dissociation of the Ir-F bond is fundamental to the overall reactivity of the compounds \([\text{Cp}'\text{Ir(aryl)(F)(PMe}_3\text{]}, \text{Cp}' = \text{Cp*}, (\text{CsMe}_4\text{Et})\text{ and aryI} = \text{Ph, p-tolyl, and is responsible for the significant difference from the corresponding chloride complexes, which are inert in all the reactions described}^{[22][24]}\). Although the reactions described were carried out in dry solvents, trace amounts of water could be responsible for the observed ease of dissociation of the Ir-F bond in relatively non-polar solvents. It is this dissociation that has played an important role in the reactions described. The authors were aware of the problem of trace amounts of water and offered this as an explanation for the erratic results obtained in the halide metathesis reactions. The complex \([\text{(CsMe}_4\text{Et})\text{IrF(Ph)(PMe}_3\text{)]}\), which was characterized crystallographically, has a long Ir-F bond length (2.069(4) Å), when compared to other structurally characterized Ir(III) complexes (e.g. \([\text{IrF(COF)(CO)}_2\text{(PEt}_3\text{)]}^+\text{Ir-F} = 1.998(3)\text{ Å})^{[33]}\). This long Ir-F separation may indicate a degree of dissociation as the atomic radii of iridium and fluorine used for covalent bonding are 1.32 Å and 0.66 Å respectively, which would give an ideal Ir-F covalent separation of 1.96 Å.\(^{[159]}\) This may account for the reactivity of the Ir-F bond in the presence of other ligands. The reactivity of the fluoride complexes is, however, very similar to that of the corresponding triflate complexes.\(^{[32][35]}\) This is unsurprising as the triflate complexes have been shown by conductivity measurements to be slightly dissociated in solvents such as thf and benzene, the degree of dissociation increasing at lower concentrations.\(^{[24]}\)

Unlike the iridium(III) aryl complexes, the ruthenium(II) fluoride complex \([\text{RuH(F)(CO)}(\text{P}^2\text{Bu}_3\text{Me}_2)]\) was found to react readily with the primary silane HSiMe\(_3\) with the cleavage of the M-F bond and formation of an Si-F bond to give \([\text{RuH}_2(\text{CO})(\text{P}^2\text{Bu}_3\text{Me}_2)]\) and FSiMe\(_3\).\(^{[156]}\) The heavier halides (Cl and I) showed no reaction with HSiMe\(_3\) due to the weaker Si-Cl and Si-I bonds compared to that of Si-F which acts as the driving force in the fluoride reaction.\(^{[56]}\)

1.3.3 Reaction at Co-ordinated Ligand

Silyl compounds XSIR\(_3\) where R = H or alkyl and X = halide or pseudo-halide, have been found to react with fluoroacetyl complexes \([\text{Ir(COF)}(\text{CO})_2\text{(PR}_3\text{)]}^+\)\(^{[23][37]}\). Although acyl complexes of the transition-metals are known, fluoroacetyl complexes of
the type [Ir(COF)F(CO)2(PR3)2]^+ where PR3 = PEt3, PMe3, PMe2Ph, PEt2Ph and PEtPh2, represent the first examples of halogenacyl complexes to be reported in the literature. The fluoroacyl complexes are readily prepared by the reaction of the five co-ordinate iridium(I) cations [Ir(CO)3(PR3)2]^+ with the oxidative fluorinating agent XeF2. The fluoroacyl complex [Ir(COF)F(CO)2(PEt3)2][BF4] was found to react preferentially with the silyl compounds XSiH3 (X = CN, NCS and NCO) at the fluorine bound to carbon (fluoroacyl group) as opposed to the fluorine bound directly to the metal centre. The reaction of the fluoroacyl complex [Ir(COF)F(CO)2(PEt3)2][BF4] with XSiH3 at -13°C afforded novel iridium acyl complexes, where the fluorine bound to the carbonyl group had been substituted with X, [IrF(COX)(CO)2(PEt3)2][BF4], along with formation of FSiîÎ3. No reaction with the iridium bound fluorine was observed even at higher temperatures. Although the groups CN, NCS and NCO are all capable of linkage isomerism by binding via one or other end of the group, the linkage displayed was the same as that observed for the starting species XSiH3. Therefore no information as to whether these products are kinetically or thermodynamically controlled could be obtained.

The Lewis acid BF3 is also known to abstract fluorine from ligands of some transition-metal complexes and to abstract metal bound halogens. The iridium fluoride complex trans-[IrClF(SF3)(CO)(PEt3)2], which contains metal-bound fluorine as well as a fluorine in a ligand, reacts with BF3(g) to yield the novel complex trans-[IrClF(CO)(PEt3)2(SF3)][BF4]+. This shows that the Lewis acid BF3 preferentially removes a fluorine from a ligand, in this case SF3, as opposed to a metal-bound fluorine. The metal-bound fluorine remains unaffected even in the presence of excess of BF3(g) as evidenced by the low frequency resonance in the 19F NMR spectrum (δ ~ 360.9). This can be rationalised in terms of electrostatics as the iridium complex is now cationic and therefore the metal centre binds strongly to the electronegative fluoride. Similarly the iridium(III) acyfluoride complex [IrF(COF)(CO)2(PEt3)2]^+ (17), reacts cleanly with BF3(g) at -73°C, the Lewis acid abstracting the acyfluoride and forming the dicationic iridium(III) species [IrF(CO)2(PEt3)2][BF4]2 (18), which was characterized by X-ray crystallography and NMR spectroscopy (Figure 1.11). The Ir-F bond remains intact even after further addition of BF3(g) and warming to room temperature. An attempt was made to
synthesize an amide group that was bound to the iridium centre by reaction of a co-
ordinated CO group with the amine NMe₃. The amine was found to react with the
BF₄⁻ counterion to give the adduct BF₃,NMe3 and F⁻ which regenerated the fluoroacyl
complex (Figure 1.11). The exact mechanism for the regeneration of the fluoroacyl
complex is unclear, but there is no evidence for fluorination of the carbonyl group
trans to fluoride. It is possible that the metal bound fluorine migrates from the metal
centre to the carbon of the carbonyl group leaving a vacant co-ordination site which is
then filled by F⁻. Alternatively, the F⁻ could attack the nucleophilic carbon of the
carbonyl group directly. It is also possible that the reaction involves BF₄⁻ and the
dication [IrF(CO)₃(PEt₃)₂]⁺ in which attack at the BF₄⁻ by NMe₃ leads to transfer of
F⁻ to the dication. The corresponding reaction with PMe₃ at -73°C leads to the
formation of the analogous adduct PMe₃·BF₃ with regeneration of the fluoroacyl
complex. However, upon warming to -13°C the unusual dication
[IrF(CO)₃(C(O)PMe₃)(PEt₃)₂]⁺ (19), is formed with the fluorine of the fluoroacyl
group replaced by PMe₃ (Figure 1.12). This unusual complex exhibits a doublet of
triplets in the Ir-F region (δ - 387.8) in the ¹⁹F NMR spectrum due to coupling to Pₐ
and Pₐ with a 2J(PF) and 3J(PF) couplings of 37 and 58 Hz respectively. The ³¹P(¹H)
spectrum shows two doublets at δ 4.2 (2J(PF) = 37 Hz) and δ 38.8 (3J(PF) = 58 Hz)
for the two mutually trans Pₐ,Et₃ groups and PₐMe₃ respectively with the expected
intensity of 2 : 1. Surprisingly, the 3J(PF) coupling is considerably larger than that of
2J(PF) and the 3J(PF) coupling constant in the fluoroacyl complex (ca. 2 Hz). No
comment on this particularly large value can be made as PMe₃ bound to CO is rather
unusual. The resonance at δ 38.8 for PₐMe₃ is considerably shifted from the region
usually associated with PMe₃ bound to iridium(III) (δ -35 to -50)[43] and is in fact
near to the ³¹P chemical shift of Me₂P(O), δ 36.0.[42] No Pₐ-Pₐ coupling was detected,
suggesting that PₐMe₃ is not directly bound to the metal: cis-P-P coupling in
iridium(III) complexes is normally in the range of 10 - 25 Hz.[43] The ¹³C(¹H)
spectrum showed three distinct CO environments (δ 151.3 Cₐ, δ 161.9 Cₐ and δ 207
Cₐ), Pₐ showed a 1J(CP) coupling of 49 Hz to Cₐ and 1J(CP) trans coupling of 27 Hz
to Cₐ. The 1J(CP) coupling is small compared to usual 1J(CP) values but still lies in
the range expected (ca. 100 Hz).[43] The large 3J(CP) coupling is in keeping with the
large value of trans three bond coupling in the fluoroacyl complex \( \text{ca.} \ J_{\text{CF}} = 47 \text{ Hz} \).\(^{[57]}\)

If the two reactions of NMe\(_3\) and PMe\(_3\) with the iridium(III) dication \([\text{IrF(CO)}_3(\text{PEt}_3)_2]^+\) are compared, it can be seen that the former (NMe\(_3\)) attacks the BF\(_4^+\) counterion whereas the latter (PMe\(_3\)) attacks the metal complex. This can be rationalised in terms of the HSAB theory. In equilibrium experiments, BF\(_3\), which is classified as a hard acid, shows a preference for the hard base NMe\(_3\) over the phosphine base.\(^{[60]}\) Therefore, it is not surprising that the hard NMe\(_3\) base attacks the hard, low-polarisable, BF\(_4^+\) counterion while the softer phosphine base attacks the soft polarisable metal centre.

**Figure 1.11**

\[
\begin{array}{c}
\begin{array}{c}
\text{OC} \\
P
\end{array} & \begin{array}{c}
\text{CO} \\
\text{PF}
\end{array} & \begin{array}{c}
\text{F} \\
\text{PB}_{3}\text{O}
\end{array}
\end{array}
\rightarrow \begin{array}{c}
\begin{array}{c}
\text{OC} \\
P
\end{array} & \begin{array}{c}
\text{CO} \\
\text{PF}
\end{array} & \begin{array}{c}
\text{F} \\
\text{PB}_{3}\text{O}
\end{array}
\end{array}
\rightleftharpoons \begin{array}{c}
\begin{array}{c}
\text{OC} \\
P
\end{array} & \begin{array}{c}
\text{CO} \\
\text{PF}
\end{array} & \begin{array}{c}
\text{F} \\
\text{PB}_{3}\text{O}
\end{array}
\end{array}
\right] \rightleftharpoons \begin{array}{c}
\begin{array}{c}
\text{OC} \\
P
\end{array} & \begin{array}{c}
\text{CO} \\
\text{PF}
\end{array} & \begin{array}{c}
\text{F} \\
\text{PB}_{3}\text{O}
\end{array}
\end{array}
\right.
\]

(17) (18)

**Figure 1.12**

\[
\begin{array}{c}
\begin{array}{c}
\text{OC} \\
P
\end{array} & \begin{array}{c}
\text{Li} \\
\text{P}
\end{array} & \begin{array}{c}
\text{C} \\
\text{O}
\end{array} & \begin{array}{c}
\text{P}_{2}\text{Me}_3 \\
\text{PB}_{3}\text{O}
\end{array}
\end{array}
\right] \rightleftharpoons \begin{array}{c}
\begin{array}{c}
\text{OC} \\
P
\end{array} & \begin{array}{c}
\text{Li} \\
\text{P}
\end{array} & \begin{array}{c}
\text{C} \\
\text{O}
\end{array} & \begin{array}{c}
\text{P}_{2}\text{Me}_3 \\
\text{PB}_{3}\text{O}
\end{array}
\end{array}
\right.
\]

(19)
1.3.3 Reaction at the Metal Centre

a) Substitution / Addition Reactions

Other more simple reactions of low-valent platinum group metal fluorides include straightforward ligand replacement. Vaska's fluoride [IrF(CO)(AsPh3)2] has been shown to react with PMe2Ph and PPh3Ph to give the corresponding phosphine derivative [IrF(CO)(phosphine)2]. The iridium fluoride complex [IrF(CO)(PPh3)2] has also been reported to react with olefins and acetylenes to form adducts of the type [IrF(CO)(L)(PPh3)2], where L = C2F4, C2(CN)4, C2(CF3)2, C2(CO2Me)2, CH2=CHCN, MeCH=CHCN and CN=CHCN. The rhodium fluoride complex [RhF(CO)(AsPh3)2] also forms a similar adduct with C2(CN)4. Similar adducts have been observed from the reactions of the chloride analogues. When L = C2F4, the adduct of the fluoride complex is significantly more stable than the chloride analogue which readily loses C2F4 on attempted crystallization. This increase in stability is attributed to the π-bonding effects of the halide ligands (π-donor ability decreases F > Cl > Br > I) and to the close approach of the unsaturated molecule to the iridium centre which arises from the smaller size of the fluorine atom. Similarly, Vaska's fluorides [MF(CO)L2] (M = Rh, L = PPh3 or AsPh3; M = Ir, L = PPh3) form adducts with SO2 to give the fluoride complexes of the type [MF(CO)(SO2)L2] where the coordinated SO2 lies in the apical position of the square pyramid.

In addition to Vaska's rhodium and iridium fluorides other d8 metal fluorides have been reported. However, these are often synthesised using Vaska's fluorides. The dinitrogen iridium Vaska's fluoride analogue [IrF(N2)(PPh3)2] has been prepared by the reaction of the fluoride [IrF(CO)(PPh3)2] with furouyl azide. The dinitrogen compounds of the heavier halides can also be synthesised in this manner under analogous conditions, so in this case no useful information could be obtained regarding the effect of the halogen bound to iridium on the reactivity of the coordinated dinitrogen compounds. The dinitrogen stretching frequencies in the compounds [IrX(N2)(PPh3)2] were found to follow a trend analogous to that of the CO stretching frequency in the carbonyl compounds; F < Cl < Br < I. This can be explained, once again, in terms of the increase in π-acceptor strength of the halide from fluorine to iodine, which moves the electron density away from the metal and...
towards the halogen and reduces back donation to the carbonyl group (dinitrogen) causing an increase in the CO (N₂) stretching frequency.

The reaction of the [IrX(CO)(EPh₃)₂], X = halide, E = P or As, with tridentate ligands has been reported to give different products depending on the halogen. Reaction with bis[3-(dimethylarsino)propyl]phenylphosphine (dap) affords only the five co-ordinate compound [IrF(CO)(dap)]. However, reaction of the analogous heavy halides [IrX(CO)(EPh₃)₂], X = Cl, Br, I, affords a mixture of ionic and covalent products [Ir(CO)(dap)]⁺X⁻ and [IrX(CO)(dap)] respectively. If the tridentate ligand is changed to bis[3-(dimethylarsino)propyl]phenylarsine (tas), only ionic products of the type [Ir(CO)(tas)]⁺X⁻, where X = F, Cl, Br or I, are obtained. No explanation for the anomalous behaviour of the fluoride derivative was offered. Unfortunately, no NMR data for these compounds are reported, the analysis relying almost entirely on conductivity measurements. The lack of spectroscopic data precludes definitive characterization of the compounds.

Reactivity of complexes containing a fluorine bound directly to the metal has been briefly mentioned for the Ti'-tetrafluoroethylene rhodium complex [RhF(C₂F₄)(PPh₃)₂]. The complex was found to be reactive to simple Lewis bases. The addition of one equivalent of CO results in nearly instantaneous substitution of the tetrafluoroethylene ligand to yield the rhodium fluoro Vaska analogue trans-[RhF(CO)(PPh₃)₂].

The rhodium(I) olefin complex [RhF(cyclooctene)₂], has been used as a starting material for the synthesis of novel rhodium(I) fluoride complexes and more generally for rhodium compounds containing a variety of univalent anionic ligands in cases where direct chloride replacement is not possible. The complex is also readily prepared by the metathetical reaction of [RhCl(cyclooctene)₂] with AgF. Reaction with PPh₃ results in the replacement of the weakly bound cyclooctene to give the fluoride analogue of Wilkinson’s catalyst [RhF(PPh₃)₃]. Interestingly this fluoride analogue could not be prepared from the chloride [RhCl(PPh₃)₃] by addition of AgF. Addition of PPh₃ to the rhodium(I) fluoride polymer [RhF(cyclooctene)₉] in the presence of CO results in the formation of trans-[RhF(CO)(PPh₃)₂]. Reaction with the sterically bulky phosphine PCy₃ ligand under argon is believed to form a monomeric three co-ordinate rhodium(I) fluoride complex [RhF(PCy₃)₂] (28) (Figure
1.13), via the intermediate [RhF(C₈H₁₈)(PCy₃)]₂. This three co-ordinate fluoride complex was characterized by ³¹P(¹H) NMR spectroscopy. The ³¹P(¹H) NMR spectrum showed a doublet of doublets at δ = 55.0 with ¹J(RhP) and ²J(PF) coupling constants of 206 Hz and 165 Hz respectively. The large ²J(PF) coupling constant was explained in terms of the molecule being trigonal with the PCy₃ ligands lying somewhere between 90° and 180° from the fluoride ligand, the coupling constant being expected to lie between the value for ²J(PF) cis coupling (20 - 29 Hz) and ²J(PF) trans coupling (139 - 165 Hz).[27] The ¹J(RhP) constant is related to the s-character of the orbital of the metal used in bonding to the phosphorus. The ¹J(RhP) value for this compound is large when compared to typical values for four co-ordinate rhodium(I) trialkyl- or triarylphosphine complexes (100 - 150 Hz). This is in keeping with a three co-ordinate complex which has increased s-character and hence a large coupling constant. Further support for the three co-ordinate structure was obtained as facile addition of ligands (L) was observed producing the rhodium(I) complexes [RhF(L)(PCy₃)]₂, where L = carbonyl, ethylene and diphenylacetylene. The reactivity of the complex [RhF(cyclooctene)]₂ was analogous to that of the chloride and bromide complexes which also form three co-ordinate species [RhX(PCy₃)]₂ X = halide upon addition of PCy₃, and compounds of the type [RhX(PCy₃)₂(L)] upon addition of a second ligand, L = C₂H₄, CO and C₆H₅Ph. However, the fluoride derivatives were found to be significantly more stable than the heavier halide analogues.[27][28]

Figure 1.13

The three co-ordinate fluoride complex [RhF(PCy₃)₂] shows markedly different reactivity to the heavier halide derivatives upon exposure to dinitrogen and dioxygen. The chloro, bromo and iodo complexes [RhX(PCy₃)₂] where X = Cl, Br or
I, add dinitrogen at room temperature under one atmosphere of dinitrogen, the reaction times following the order Cl\(4 - 5\) days) \(>\) Br(3 h) \(>\) I(15 min), whereas the fluoride complex does not react. This difference in rate of addition was explained by the authors to be due to increasing electron density on the rhodium in the order F \(<\) Cl \(<\) Br \(<\) I, this increase in electron density facilitating the nucleophilic attack on the nitrogen.\(^{37}\) This argument seems to be based solely on \(\sigma\)-donor properties of the halides which follows the order F \(>\) Br \(>\) Cl \(>\) F. Surprisingly, the possible influence of the \(\pi\)-donor ability (which follows the order F \(>\) Br \(>\) Cl \(>\) I), which would increase the electron density on the rhodium centre in the fluoride complex, was not taken into account, whereas, spectral data for Vaska’s halides \([\text{MX(CO)\(L\)}_2]X = \text{halide} \text{ L = phosphine}\), are consistent with the fluoride complex being the most electron-rich metal centre. This suggests that metal-halide \(\pi\)-bonding dominates in the electronic structure of the rhodium(I) and iridium(I) compounds, \([\text{MX(CO)\(L\)}_2]\), \(M = \text{Rh or Ir}\) and \(X = \text{F, Cl, Br, or I}\), with fluoride the best \(\pi\)-donor and the weakest \(\pi\)-acceptor.\(^{34}\) Electrochemical studies have also shown the Vaska’s fluoride complexes are the most difficult to reduce, which supports the spectral data.\(^{13}\) This is opposite to that reported for the three co-ordinate rhodium complexes \([\text{RhX(\text{PCy})}_2]\), \(X = \text{halide}\), even though trigonal planar complexes are expected to have an empty \(d\) orbital which may accept electron density from the filled \(p\pi\) orbital of the halogen. This should strengthen the \(M\)-X bond, especially as trigonal geometry is said to lead to relatively weak \(\sigma\)-bonding.\(^{77}\) Similarly, the heavier halides of \([\text{RhX(\text{PCy})}_2]\), \(X = \text{Cl, Br or I}\), were found to bind dioxygen rapidly, while the corresponding fluoride complex reacts differently forming \(\text{Cy}_3\text{P(O)}\). The reactivity of these three co-ordinate complexes cannot therefore be rationalised in terms of electronegativity of the halogen only, as suggested by the authors, other factors such as kinetic and thermodynamic effects need to be considered.

b) Oxidative Addition Reactions

The most extensively studied and readily prepared of all the low-valent organometallic fluorides are the rhodium and iridium Vaska’s derivatives, \([\text{MF(CO)(\text{PPh})}_2]\), \(M = \text{Rh and Ir}\), as already discussed.\(^{12}\) Oxidative addition to sixteen-electron systems such as the co-ordinatively unsaturated square planar
complexes of rhodium(I), iridium(I) and platinum(II) are common, with a variety of d^6 rhodium(III), iridium(III) and platinum(IV) fluorides being prepared.\textsuperscript{113} The preparation of rhodium(III) and iridium(III) fluoride complexes is almost entirely by the oxidative addition of a substrate to Vaska’s type derivatives [MX(CO)(PR\textsubscript{3})\textsubscript{2}], where M = Rh or Ir and X = F, Cl, Br or I. When X = Cl, Br or I the substrate must be a fluorinating agent such as XeF\textsubscript{2}, but when X = F, the substrate could be a variety of relatively small molecules. The reactions described are more common for M = Ir and PR\textsubscript{3} = PPh\textsubscript{3}, where the iridium(III) fluorine bond is believed to be more stable.\textsuperscript{113} Oxidative addition of substituted silanes (HSiR\textsubscript{3}) afford [IrF(H(SiR\textsubscript{3})(CO)(PPh\textsubscript{3})\textsubscript{2}] derivatives, SiR\textsubscript{3} = SiPh\textsubscript{3}, SiMeCl\textsubscript{2}, Si(OEt)\textsubscript{3} and SiF\textsubscript{3}.\textsuperscript{78,79} Methyliodide yields [IrF(I)(Me)(CO)(PPh\textsubscript{3})\textsubscript{2}] \textsuperscript{79} and tetrachloro-o-quinone provides a catecholate complex [IrF(1,2-0\textsubscript{2}C\textsubscript{6}Cl\textsubscript{4})(CO)(PPh\textsubscript{3})\textsubscript{2}]\textsuperscript{77}. The stability of these species has not been discussed. This is surprising since the oxidative addition of silanes to fluoro Vaska’s complexes results in the metal-bound fluorine being cis to either a hydride or the silyl group (SiR\textsubscript{3}), or even both, assuming the phosphine ligands are mutually trans \textit{which} is nearly always the case. One would not expect such a compound to be particularly stable, due to the strength of the H-F bond and the Si-F bond which could act as a driving force for the \textit{cis} elimination of HF or FSiR\textsubscript{3}. Similarly, the halogens (X\textsubscript{2}), where X = Cl, Br or I, oxidatively add to Vaska’s fluoride [RhF(CO)(PPh\textsubscript{3})\textsubscript{2}] to afford the rhodium(III) fluoro halide complexes [RhFX\textsubscript{2}(CO)(PPh\textsubscript{3})\textsubscript{2}].\textsuperscript{80} The iridium analogue has also been shown to oxidatively add I\textsubscript{2} to give [IrF(I)(CO)(PPh\textsubscript{3})\textsubscript{2}].\textsuperscript{80-81} The reaction of SF\textsubscript{5}Cl with [MF(CO)(PPh\textsubscript{3})\textsubscript{2}] has also been reported to give [MCl\textsubscript{2}(F)(CO)(PPh\textsubscript{3})\textsubscript{2}] where M = Rh or Ir.\textsuperscript{113} The \textit{ortho}-metallated arylidiazene iridium(III) fluoride cation [IrF(η\textsuperscript{2}-N=NC\textsubscript{6}H\textsubscript{3}-2-Br)(CO)(PPh\textsubscript{3})\textsubscript{2}]\textsuperscript{+} (ZI) is obtained from the oxidative addition of the substituted aryl diazonium tetrafluoroborate to [IrF(CO)(PPh\textsubscript{3})\textsubscript{2}].\textsuperscript{82} The \textit{ortho}-metallated complex can be readily deprotonated using NEt\textsubscript{3}, NaOH or NaOAc to give the neutral complex [IrF(η\textsuperscript{2}-N=NC\textsubscript{6}H\textsubscript{3}-2-Br)(CO)(PPh\textsubscript{3})\textsubscript{2}] (ZII) (Figure 1.14).\textsuperscript{82}
Although few oxidative addition reactions are described for the fluoride complexes [MF(CO)(PPh₃)₂], M = Rh or Ir, the corresponding reactions with the heavier halides are well known and documented, with there being no significant differences in the reactivity. The stereochemistry of the oxidative addition, whether cis or trans addition, is not certain. In the absence of reliable NMR spectroscopic data, especially ¹⁹F NMR data, no real conclusions can be drawn as to the method of addition. Detailed kinetic studies of the oxidative addition of MeI and O₂ to the iridium Vaska's fluoride and the heavier halides have been reported, as well as enthalpy changes in similar oxidative addition reactions. These studies have shown that there is no set trend in halide dependence as the rate of reaction and changes in enthalpy are associated with the substrate used. The rate of reaction is also thought to be associated with the transition state of the reaction as discussed for the opposing trends for the oxidative addition of methyl iodide vs dioxygen to iridium(I) Vaska's halides [IrX(CO)(PPh₃)₂]. The nucleophilic attack of iridium(I) on the electrophilic carbon of MeI is believed to lead to a five co-ordinate transition state with the MeI bound to the iridium in a σ-bonded fashion. The strong σ bonding of the halides, (X), to the iridium centre (Ir-X), with X = I the best σ-donor, results in poor σ-overlap between the iridium and the methyl group of MeI which destabilises the transition state [Figure 1.15(A)], and therefore decreases the rate of reaction. The rate of oxidative addition of MeI to [IrX(CO)(PPh₃)₂] follows the trend X = F > Cl > Br > I. This is also in keeping with the greater electron density on the metal centre which will
enhance nucleophilic attack. The rate of dioxygen addition follows the opposite order I > Br > Cl > F. The transition state for this reaction is thought to be six co-ordinate [Figure 1.15(B)]. This corresponds to the ease with which the metal centre is oxidised, the most electron rich metal centre (X = F) being the most difficult. The oxidative addition of dioxygen is reversible in all cases.\(^{179}\)

**Figure 1.15 Proposed Transition States for the Oxidative Addition of O\(_2\) and Mel to \([\text{IrF(CO)}(\text{PPh}_3)_2]\).**

(A)\[
\begin{array}{c}
\text{OC} \\
\text{F} \\
\text{PPh}_3 \\
\text{I} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

(B)\[
\begin{array}{c}
\text{OC} \\
\text{F} \\
\text{PPh}_3 \\
\text{O} \\
\text{PPh}_3
\end{array}
\]

c) Reaction at the Metal Centre which is not Oxidation or Straightforward Substitution

The five co-ordinate ruthenium complex \([\text{RuHCl(CO)}(\text{P}^\text{Bu}_2\text{Me}_2)]\) is readily prepared from the reaction of \(\text{RuCl}_3\) with \(\text{P}^\text{Bu}_2\text{Me}\) in refluxing 2-methoxyethanol.\(^{183}\) The chloride can be replaced with fluoride, bromide and iodide by simple halide metathesis using NaI, NaBr and CsF\(^{25}\) to give \([\text{RuHX(CO)}(\text{P}^\text{Bu}_2\text{Me}_2)_2], X = \text{F, Br or I}\). These unsaturated complexes readily form six co-ordinate adducts upon addition of CO or pyridine to give compounds of the type trans-[\(\text{RuHX(CO)}(\text{L}(\text{P}^\text{Bu}_2\text{Me}_2)]\), where \(\text{L} = \text{CO or pyridine.}\(^{25}\) The \(\pi\)-stabilised unsaturated square pyramidal species \([\text{RuHX(CO)}(\text{P}^\text{Bu}_2\text{Me}_2)]\), \(X = \text{halide}\) have been shown to react differently with dihydrogen.\(^{25}\) The reaction of the iodide complex with dihydrogen forms the \(\eta^1-\text{H}_2\) compound \([\text{RuH}(\text{H}_2)(\text{CO})(\text{P}^\text{Bu}_2\text{Me}_2)_2]\) addition of the non co-coordinating base DBU results in dehydrohalogenation and the formation of \([\text{RuH}_2(\text{H}_2)(\text{CO})(\text{P}^\text{Bu}_2\text{Me}_2)_2]\). The corresponding chloride complex failed to react with dihydrogen. However, addition of dihydrogen to the fluoride complex led to the formation of \([\text{RuH}_2(\text{H}_2)(\text{CO})(\text{P}^\text{Bu}_2\text{Me}_2)_2]\) without the need for additional base. This was attributed to the significant driving force for the formation of HF, [H-F bond strength
(573 kJ mol⁻¹) > H-Cl (426 kJ mol⁻¹) > H-I (297 kJ mol⁻¹)]. Filled $d\pi$(Ru) - $p\pi$(X) repulsions were also believed to play an important role in the driving force for elimination, as such repulsions are thought to be greater when X = F.⁵⁶

The reactivity of [RuHX(CO)(P'Bu₂Me)₂] (23), X = F, Cl or I, with alkynes was also studied. Addition of an internal alkyne such as dimethylacetylene, MeCCMe, to the five co-ordinate ruthenium complex leads to no reaction when X = F or Cl but when X = I, syn (cis) addition of Ru-H to the triple bond occurs. Similarly no other X groups (OSiPh₃, OR₆ and OPh) exhibit reactivity with MeCCMe under the same conditions. Since these X groups are stronger π-electron donors than iodide, the difference in reactivity can be explained in electronic terms in as much as the iodide complex contains a more electrophilic centre which facilitates addition of Ru-H to the triple bond (since the alkyne which is electron rich is attracted to the electron deficient metal centre). The halide complexes [RuHX(CO)(P'Bu₂Me)₂], X = Cl or I, react with the terminal alkyne phenylacetylene, with insertion of the alkyne into the Ru-H bond, to give the products [Ru(HC=CHPh)X(CO)(P'Bu₂Me)₂], the reaction being faster for X = I. However, reaction with the fluoride complex results in the formation of three products, as determined by $^{31}$P, $^{19}$F and $^1$H NMR spectroscopies. The first of these [Ru(HC=CHPh)F(CO)(P'Bu₂Me)₂], is similar to the complex formed in the reaction with the five co-ordinate ruthenium iodide and chloride compounds. The second product [Ru(PhC=CH₂)F(CO)(P'Bu₂Me)₂] results from a different regiochemistry of alkyne insertion, which could be attributed to the fluoride complex being less sterically hindered when compared to the complexes of the much larger heavier halides, thus allowing the alkyne to approach in a different manner. The third product, [RuH(C₂Ph)(CO)(P'Bu₂Me)₂] (24), was formed as a result of HF elimination. An explanation for the observed HF elimination is thought to be related to a hydrogen-bonding interaction between the fluoride and the acidic alkyne proton (Figure 1.16).⁵⁶ This same product is also isolated in the reaction [RuHX(CO)(P'Bu₂Me)₂], where X = OSiPh₃ and OCH₂CF₃, with phenylacetylene.⁵⁶
In summary, the reactivity of the five co-ordinate unsaturated compounds [RuHX(CO)(P’Bu2Me)2] is dominated by the Ru-H bond when X = Cl or I and by Ru-X bond cleavage when X = OCH2CF3 or OSiPh3. However, the reactivity of the fluoride, X = F, is unique as it displays reactivity at both the Ru-H bond and the Ru-F bond.\[56]\]

1.4 Summary

In the reactions discussed above it is clear that fluoride, bound directly to a metal centre, has a profound effect on the reactivity of platinum group metal halo complexes with both increases and decreases in reactivity observed. The unusual behaviour of fluoride as a ligand offers potential for some interesting chemistry as organometallic fluorine chemistry progresses. The present study outlined in subsequent chapters describes the synthesis of some novel air-stable fluoride complexes of ruthenium and osmium and discusses their reactivity with a number of reagents.
Chapter One References


CHAPTER TWO

Synthesis and Characterization of Low-Valent Osmium and Ruthenium Fluoride Complexes
2.1 General Introduction

Derivatives of carbonyl halide complexes of osmium and ruthenium have been well studied for the heavier halogens (Cl, Br and I) and their preparations and chemistry has been reviewed. These compounds all contain at least one CO group and one halide ligand (X) and, in addition, at least one ligand (L) which contains one or more Group III - IVA donor atoms. They can be generally formulated as \([\text{MX}_m(\text{CO})_nL_{6-m-n}]\) for neutral compounds, where \(m = 2\) and \(n = 1, 2\) or \(3\), \([\text{MX}_m(\text{CO})_nL_{6-m-n}]^+\) for cationic compounds where \(m = 1\) and \(n = 1, 2, 3\) or \(4\) and \([\text{MX}_m(\text{CO})_nL_{6-m-n}]^-\) for anionic compounds where \(m = 3\) and \(n = 2\), \(M = \text{Os or Ru}\).

The substituted halide complexes \([\text{MX}_2(\text{CO})_2(L)\text{Cl}_2]^-\) (X = Cl, Br or I, L = donor ligand and M = Os or Ru) can be synthesised via a number of routes:

a) Ligand substitution, where the ligand (L) replaces co-ordinated CO in the neutral metal carbonyl halide complex \([\{\text{M(\text{CO})}_3\text{Cl}_2\}]_2\), breaking the bridging M-X-M bond.\(^{[3,4]}\)

b) Direct interaction of L with the neutral polymeric metal carbonyl halide \([\{\text{M(\text{CO})}_3\text{Cl}_2\}]_2\).\(^{[5]}\)

c) Carbonylation of substituted metal halides such as \([\text{MX}_3L_0]\) where \(X = \text{Cl}\) or \(\text{Br}\), or \([\text{MX}_3L_0]\) where \(X = \text{Cl}\).\(^{[6,7]}\)

d) Carbonylation of \([\text{MCl}_3]\), in alcoholic media followed by the addition of the appropriate ligand.\(^{[8]}\) Treatment of the carbonylated \([\text{MCl}_3]\) solution with bromide or iodide salts gives the corresponding bromide or iodide complex. In contrast to \([\text{RuCl}_3]\), which may be readily carbonylated in a variety of alcohol solvents, carbonylation of \([\text{OsCl}_3]\) is slow and generally incomplete owing to its poor solubility, and it is therefore a poor source of \([\text{OsX}_2(\text{CO})_2L_2]\) complexes.

e) Carbonylation of \([\text{OsCl}_3]\)\(^2\), where \(X = \text{Cl}\) or \(\text{Br}\), followed by the addition of the appropriate ligand.\(^{[9]}\) The use of \([\text{OsCl}_3]\)\(^2\) overcomes the solubility problems encountered with \([\text{OsCl}_3]\).

2.2 Introduction to Fluoro complexes of Osmium and Ruthenium

Although there are many examples of ruthenium and osmium substituted carbonyl-chloride, -bromide or -iodide complexes, the number of corresponding fluoride complexes is smaller. Prior to the work described here, there have been only
two examples of substituted low-valent osmium carbonyl fluoride complexes reported in the literature. The aryldiazio compound \([\text{OsF(CO)}_2(\text{N=NPh})(\text{PPh}_3)_2]\), characterized by IR spectroscopy and elemental analysis, was reported in 1975.\(^7\) This complex was believed to be the product from the reaction of the five co-ordinate aryldiazio cation \([\text{Os(CO)}_2(\text{N=NPh})(\text{PPh}_3)_2]^+\) with the fluoride donor \(\text{NEt}_4\text{F} \cdot 2\text{H}_2\text{O}\).\(^8\) The corresponding ruthenium cation, \([\text{Ru(CO)}_2(\text{N=NPh})(\text{PPh}_3)_2]^+\), has been cited in the literature but there has been no mention of its reaction with \(\text{NEt}_4\text{F} \cdot 2\text{H}_2\text{O}\). More recently, well characterized fluoroacyl complexes of osmium and ruthenium were identified from the oxidative addition of \(\text{XeF}_2\) to the neutral compounds \([\text{M(CO)}_3(\text{PPh}_3)_2], \text{M} = \text{Os and Ru}\).\(^9\) The mechanism of the reaction appears to involve the oxidation of the metal centre by \(\text{XeF}_2\) followed by nucleophilic attack by \(\text{F}^-\) at co-ordinated \(\text{CO}\) to give \([\text{MF(COF)(CO)(PPh}_3)_2]\). The ruthenium fluoroacyl complex is unstable at room temperature and eliminates \(\text{CO}\) to give the ruthenium difluoride complex \([\text{OC-d-i\text{5}}][\text{RuF}_2(\text{CO})_2(\text{PPh}_3)_2]\) which has been characterized by single crystal X-ray diffraction. The analogous osmium complex was obtained by heating the fluoroacyl complex.\(^9\)

Although there have been only two reports in the literature concerning low-valent osmium fluoride complexes, more examples of ruthenium complexes have been reported. The cationic ruthenium fluoride complex \(\text{trans-[RuF(CO)(dppe)}_2]^+\) was obtained as a by-product via an unexpected fluoride ion abstraction from the polyfluoro anion \(\text{BF}_4^-\) during the synthesis of the dicarbonyl cation \(\text{trans-[RuCl}_2(\text{dppe)}_2]^+\) from reaction of \(\text{trans-[RuCl}_2(\text{dppe)}_2]\) with \(\text{AgBF}_4\) under a positive pressure of \(\text{CO}\).\(^1\) Two further ruthenium(II) fluoride complexes have been reported that are also formed by fluoride ion abstraction from the anion \(\text{BF}_4^-\). The reaction of \([\text{OC-d-i\text{5}}][\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]\) with \(\text{AgBF}_3\) in \(\text{CH}_2\text{Cl}_2\), which is a non-coordinating solvent, afforded the complex \([\text{OC-d-i\text{5}}][\text{RuF}_2(\text{BF}_3)_2(\text{CO})_2(\text{PPh}_3)_2]\), containing weakly co-ordinating \(\text{BF}_3^-\). Upon reaction with water, fluoride ion abstraction from the weakly co-ordinated \(\text{BF}_3^-\) occurs leading to the formation of the metal-bound fluoride containing aquo and hydroxy species \([\text{OC-d-i\text{5}}][\text{RuF}(\text{CO})_2(\text{OH})_2(\text{PPh}_3)_2][\text{BF}_3] \) and \([\text{OC-d-i\text{5}}][\text{RuF(OH)(CO)}_2(\text{PPh}_3)_2]\) in a 3 : 1 ratio, as confirmed by \(^{19}\)F and \(^{31}\)P NMR spectroscopy.\(^1\)
A π-stabilised unsaturated ruthenium(II) hydrido fluoride complex, trans-
\([\text{RuFH(CO)(P' Bu2Me)2}] (25)\) characterized by \(^1\text{H}, ^{19}\text{F}\) and \(^{31}\text{P}\) NMR spectroscopy,
has been reported from the simple halide metathesis reaction of the corresponding
chloride complex with CsF (Figure 2.1). This is a rare example of a low-valent
hydrido fluoride complex; the only other examples of this class contain rhenium.
This hydrido fluoride complex has been studied in great detail. Reaction with
pyridine (py) or CO give the six co-ordinate adducts \([\text{RuFH(CO)(py)}(\text{P' Bu2Me})2] \)
and \([\text{RuFH(CO)2(P' Bu2Me)2}] \) respectively. The reactivity of the Ru-H bond has also
been exploited to give additional ruthenium(II) fluoride complexes. Reaction with
phenylacetylene at room temperature yields three products. Figure 2.2. The first,
\([\text{Ru(HC=CHPh)F(CO)(P' Bu2Me)2}] (26)\), is a α-vinyl ruthenium fluoride complex
formed from the simple insertion of the carbon-carbon triple bond into the Ru-H
bond.
The complex can also be formed from the metathetical reaction of the
corresponding chloride complex \([\text{Ru(HC=CHPh)Cl(CO)(P' Bu2Me)2}] \) with CsF. The
second product formed, \([\text{Ru(PhC=CH2)F(CO)(P' Bu2Me)2}] (27)\), was presumably due
to a different regiochemistry of Ru-H insertion into the alkyne. The third product
isolated, \([\text{RuH(C=CPh)(CO)(P' Bu2Me)2}] (28)\) contained no metal-bound fluorine and
is probably formed as a result of HF elimination. All of the products were
characterized using \(^1\text{H}, ^{19}\text{F}\) and \(^{31}\text{P}\) NMR spectroscopies. The nitrosyl fluoride
complex \([\text{RuF(Cl)}2(\text{NO})(\text{bipy})], \) where the fluoride ligand is trans to the nitrosyl
group, has also been isolated and characterized by X-ray crystallography. Reaction
of \([\text{Ru(FBF3)2(CO)(Cyttp}]\), formed by the protonation of cis,mer-
[\text{RuH2(CO)(Cyttp})] with HBF\(_4\), with NaF in an acetone/water mixed-solvent system
gives the fluoride complex \([\text{RuF(CO)}(\text{OH2})(\text{Cyttp})]^+ \). Reaction of the aquo complex
with CO or CNBu-t yields the complexes \([\text{RuF(CO)(L)(Cyttp})]^+ \) in which the weakly
bound water has been replaced by L (CO or CNBu-t).

Other low-valent ruthenium fluorides which have been reported are poorly
characterized, which leads to ambiguity in their formulations. Such compounds
include the triply fluoride-bridged cation \([\text{Ru2(μ-F)3(PPhMe2)3]} \)^+, believed to be
formed from the reaction of the cyclooctadiene complex \([\text{RuH(cod)(PPhMe2)3}]^+ \) with
HF. Similarly, a number of cyclopentadienyl ruthenium(II) fluoride complexes have
also been reported but, because of the uncertainty about their nature, will not be discussed here.\textsuperscript{[21,22]}

\textbf{Figure 2.1}

\begin{center}
\includegraphics[width=0.5\textwidth]{figure2.1.png}
\end{center}

\textbf{Figure 2.2}

\begin{center}
\includegraphics[width=0.7\textwidth]{figure2.2.png}
\end{center}

\section*{2.3 Synthesis and Characterization of Low-Valent Osmium and Ruthenium Fluoride Complexes.}

Recently, the first osmium(II) complexes stabilised only by carbonyl and fluoride ligands were reported.\textsuperscript{[23]} The fluorination of [Ossf(CO)$_{12}$] with XeF$_2$ in AHF afforded four carbonyl fluoride complexes, \textit{cis}-[Osf$_2$(CO)$_4$], [Osf(CO)$_3$][HF$_2$], [Osf$_2$F$_4$(CO)$_7$] and [Osf$_2$F$_3$(CO)$_9$][HF$_2$], which were identified by $^{19}$F and $^{13}$C($^{19}$F) NMR spectroscopies. Removal of the AHF solvent was said to result in loss of CO and polymerisation to give the tetrameric carbonyl fluoride complex, \{[Osf$_2$(CO)$_3$]$_4$\}.\textsuperscript{[24]} Similarly, the fluorination of [Ru$_6$(CO)$_{12}$] with XeF$_2$ affords ultimately the ruthenium analogue, \{[RuF$_2$(CO)$_3$]$_4$\}.\textsuperscript{[24]} A reinvestigation of this reaction is discussed in detail in Chapter Four. The tetrameric ruthenium fluoride complex, has also been prepared from the high-pressure, high-temperature carbonylation of ruthenium pentafluoride \{[RuF$_3$]$_4$\} and characterized by single crystal X-ray diffraction.\textsuperscript{[25]}
In the present study, the preparation of the carbonyl fluoride tetramers \([\text{MF}_2\text{(CO)}_3]_4\), \(M = \text{Os and Ru}\), has been modified. Although the use of \(\text{XeF}_2\) in their preparation is convenient for small scale reactions, the large amount of xenon gas produced during reaction which needs constant venting, and the cost of using large amounts of \(\text{XeF}_2\), renders it unsuitable for larger scale preparations. Consequently, fluorine gas was investigated as an oxidative fluorinating agent and was found to give the same tetrameric products. Preparative details are described in Chapter Six.

The preparation of the series of complexes of the type \(\text{mer,trans}-(\text{IrF}_3\text{(CO)}_2)_2\), \(L = \text{tertiary phosphine, amine or arsine}\), by the reaction of \(\text{fac-}(\text{IrF}_3\text{(CO)}_3)\) and the appropriate Lewis base has proven to be a convenient route into substituted low-valent transition-metal fluorides.\(^{26}\) This type of substitution of carbonyls by various \(\pi\)-acceptor ligands such as phosphines and arsines and predominantly \(\sigma\)-donor ligands such as amines is well established in the literature.\(^{27}\) The formation of tetrameric carbonyl fluorides of osmium and ruthenium, and the lability of the carbonyl ligands renders them suitable for this same type of substitution reaction and a number of osmium(II) and ruthenium(II) fluoride complexes have been prepared in this laboratory. A preliminary report of the reaction of the osmium tetramer \([\text{OsF}_2\text{(CO)}_3]_4\) with \(\text{PMe}_3\) outlines the formation of the difluoride complex \([\text{OC-6-i5}]\text{[OsF}_2\text{(CO)}_2\text{(PMe}_3)_2]\).\(^{28}\) This complex, identified by \(^1\text{H}\), \(^{19}\text{F}\) and \(^{31}\text{P}\) NMR spectroscopies, is analogous to the triphenylphosphine complexes \([\text{OC-6-i3}]\text{[MF}_2\text{(CO)}_2\text{(PPh}_3)_2]\), where \([\text{OC-6-i3}]\) denotes the \(\text{cis,cis,trans}\) arrangement of ligands, isolated from the oxidative addition of \(\text{XeF}_2\) to the metal(0) complexes \([\text{M(CO)}_3\text{(PPh}_3)_2]\), where \(M = \text{Os and Ru}\).\(^{109}\) The work outlined in this thesis builds on this and a series of complexes of the type \([\text{OC-6-i3}]\text{[MF}_2\text{(CO)}_2(L)_2]\), where \(L = \text{tertiary phosphine, amine or arsine}\), have been prepared by the reaction of the carbonyl fluorides \([\text{MF}_2\text{(CO)}_3]_4\) with the appropriate Lewis base. This extends the preliminary work of Brewer\(^{28}\) on \([\text{OC-6-i3}]\text{[OsF}_2\text{(CO)}_2\text{(PMe}_3)_2]\) to include a number of different ligands, and the ruthenium fluoride analogues.

The extremely air-sensitive off-white solids \([\text{MF}_2\text{(CO)}_3]_4\) are not soluble in common organic solvents. However, upon addition of a Lewis base in an inert atmosphere rapid reaction occurs at room temperature. Carbon monoxide gas is evolved and the metal complexes dissolve affording a yellow solution. Removal of the
solvent after effervescence is complete yields the air-stable compounds $[OC-6-13][MF_2(CO)_3(L)_2]$, where $L =$ Lewis base, $M =$ Os and Ru (Figure 2.3). The difluoride complexes were characterized by $^{19}F$, $^{31}P$ NMR spectroscopies, IR spectroscopy, mass spectrometry and microanalysis. The ligand arrangement in a number of the compounds was confirmed by X-ray crystallography.

**Figure 2.3**

$$[MF_2(CO)_3]_4 + 8L \rightarrow 4 \begin{array}{c} \text{OC} \text{F} \\ \text{OC} \\ \text{L} \\ \text{L} \end{array} + 4 \text{CO(g)}$$

$M =$ Os and Ru

$L =$ PPh$_3$, PPh$_2$Et, PMe$_3$, PCy$_3$, PPh$_2$(C$_6$F$_5$)$_3$, P(p-tolyl)$_3$, P(p-FC$_6$H$_4$)$_3$,
PE$_3$, PPh$_2$Me, PPhMe$_2$, PPh$_2$Et, py and AsPh$_3$.

There are five possible isomers of $[MX_2(CO)_3L_2]$, where $X =$ halide, $L =$ Lewis base (Figure 2.4). All have been reported for the heavier halides (Cl, Br or I) where $M =$ Ru.$^{[1,29]}$ Where $M =$ Os and $X =$ Cl, Br or I, all except (D) have been reported.$^{[1]}$ In contrast, the reaction of $[MF_2(CO)_3]_4$ with donor ligands leads to only one isomer of $[MF_2(CO)_3L_2]$, structure (A) (Figure 2.4). In the heavier halide complexes (A) and (B) were found to be the most stable isomers and, as a consequence were the isomers formed in the majority of the reactions. The occurrence of (C), (D) and (E) was less common (Figure 2.4). Generally (A) is the thermodynamic product, formed under high temperature conditions, whereas (B) is the kinetic product, found at lower temperatures.$^{[1,2]}$ Slow conversion of (B) to (A) is normally observed.$^{[1,2]}$ For $X =$ F isomer (A) is the most stable both on steric and electronic grounds. The ligands L (generally tertiary phosphines) are trans to one another, and the fluoride ligand, which is the strongest $\pi$-donor of the halides, is aligned with the $\pi$-acid carbonyl. This allows synergic (push-pull) interactions which give rise to the least energetic structure. This alignment of both fluorines and carbonyls is not possible in any other isomer.
2.4 Characterization

2.4.1 $^{19}$F and $^{31}$P($^1$H) NMR Spectroscopy

The $^{31}$P($^1$H) and $^{19}$F NMR spectra of complexes (29-54) each show one resonance respectively with mutual triplet couplings (Figures 2.5 and 2.6). This indicates that a single species exists in solution, containing two equivalent sets of phosphine and fluoride ligands, the coupling of which is characteristic of $\text{cis} \ 3J(\text{PF})$ interactions ($\text{ca.} \ 29 - 37 \text{ Hz for Os and } 20 - 28 \text{ Hz for Ru}$). The chemical shift for the fluoride resonance is in the region characteristic of fluorine trans to a carbonyl ligand, suggesting that the complexes have a $\text{cis,cis,trans}$ arrangement of ligands, which can be abbreviated to [OC-6-13] (Figure 2.7). When $L = \text{PPh}_3$, these data correspond exactly to those reported recently for the octahedral [OC-6-13][MF$_2$(CO)$_2$(PPh$_3$)$_2$], obtained as the final products from the reactions of [M(CO)$_3$(PPh$_3$)$_2$] with XeF$_2$, where M = Os and Ru. The $^{19}$F and $^{31}$P($^1$H) NMR data for complexes (29-54) are presented in Table 2.1.
Figure 2.5 $^{31}$P($^1$H) NMR Spectrum of $[OC-6-13][OsF_2(CO)_2(PPh_3)_2]$

![Figure 2.5](image1)

Figure 2.6 $^{19}$F NMR Spectrum of $[OC-6-13][OsF_2(CO)_2(PPh_3)_2]$

![Figure 2.6](image2)
The $^{19}\text{F}$ chemical shift and $^{2}\text{J}(\text{PF})$ coupling constants in the complexes $\text{mer,trans-}[\text{IrF}_3(\text{CO})(\text{PR}_3)_2]$, were reported to be sensitive to changes in the phosphine ligand. A study of the $^{19}\text{F}$ NMR data in Table 2.1 suggests that this is also true for the osmium(II) and ruthenium(II) complexes $[\text{MF}_2(\text{CO})_2(\text{PR}_3)_2]$ (29 - 54). There is a general shift to low frequency in the $^{19}\text{F}$ NMR resonance as the basicity of the phosphine increases although there are exceptions. Similarly, the magnitude of the $^{2}\text{J}(\text{PF})$ coupling constant increases as the cone angle of PR$_3$ decreases. Analogous trends have been reported in the complexes $\text{trans-}[\text{IrF(COF)}(\text{CO})_2(\text{PR}_3)_2][\text{BF}_4]$ and $\text{mer,trans-}[\text{IrF}_3(\text{CO})(\text{PR}_3)_2]$. This increase in the magnitude of the $^{2}\text{J}(\text{PF})$ coupling constant as cone angle decreases cannot be explained solely in terms of the $s$ character in the phosphorus lone pair and its contribution to the M-P bond, as previously inferred. Other factors such as steric effects may have a significant contribution since phosphines containing small substituents, such as trimethylphosphine, undergo a large C-P-C angle opening (Figure 2.8) upon co-ordination which increases the $s$ character in the C-P bond but reduces the $s$ character in the phosphorus lone pair. Thus, it would be expected that a smaller $^{2}\text{J}(\text{PF})$ value would be obtained as the $s$ character in the metal-phosphorus bond decreases. However, this is not so since, when the cone angle decreases the $^{2}\text{J}(\text{PF})$ coupling constant increases in magnitude. As the coupling constant in this particular system is a $^{2}\text{J}(\text{PF})$ coupling, the influence of the fluoride ligand must also be considered.
Table 2.1 $^{31}$P($^1$H) and $^{19}$F NMR Data for [OC-6-i3][OsF$_2$(CO)$_2$L$_2$]

<table>
<thead>
<tr>
<th>L</th>
<th>cone angle$^{[31,32]}$ /°</th>
<th>$\delta$($^{19}$F)/ppm</th>
<th>$\delta$($^{31}$P)/ppm</th>
<th>$^2$J(P-F)/Hz</th>
<th>$\Delta^{31}$P/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh$_3$ (29)</td>
<td>145</td>
<td>-303.3</td>
<td>1.0</td>
<td>30.0</td>
<td>7.0</td>
</tr>
<tr>
<td>PEt$_2$Ph (30)</td>
<td>140</td>
<td>-310.3</td>
<td>4.4</td>
<td>32.5</td>
<td>16.7</td>
</tr>
<tr>
<td>PM$_3$ (31)</td>
<td>118</td>
<td>-315.2</td>
<td>-14.8</td>
<td>38.0</td>
<td>47.4</td>
</tr>
<tr>
<td>PCY$_3$ (32)</td>
<td>170</td>
<td>-309.6</td>
<td>15.5</td>
<td>28.5</td>
<td>4.2</td>
</tr>
<tr>
<td>PPh$_2$(C$_6$F$_5$) (33)</td>
<td>158</td>
<td>-309.5</td>
<td>2.8</td>
<td>32.5</td>
<td>27.5</td>
</tr>
<tr>
<td>P(p-tolyl)$_3$ (34)</td>
<td>145</td>
<td>-302.7</td>
<td>-3.0</td>
<td>31.5</td>
<td>-0.5</td>
</tr>
<tr>
<td>P(p-FC$_6$H$_4$)$_3$ (35)</td>
<td>145</td>
<td>-308.8</td>
<td>-4.0</td>
<td>31.7</td>
<td>4.8</td>
</tr>
<tr>
<td>PPh$_3$ (42)</td>
<td>145</td>
<td>-324.3</td>
<td>21.6</td>
<td>19.8</td>
<td>27.6</td>
</tr>
<tr>
<td>PEt$_2$Ph (43)</td>
<td>140</td>
<td>-327.1</td>
<td>24.8</td>
<td>22.4</td>
<td>37.1</td>
</tr>
<tr>
<td>PM$_3$ (44)</td>
<td>118</td>
<td>-328.7</td>
<td>3.3</td>
<td>28.0</td>
<td>65.5</td>
</tr>
<tr>
<td>PCY$_3$ (45)</td>
<td>170</td>
<td>-324.3</td>
<td>36.6</td>
<td>19.6</td>
<td>25.3</td>
</tr>
<tr>
<td>PPh$_2$(C$_6$F$_5$) (46)</td>
<td>158</td>
<td>-321.2</td>
<td>21.7</td>
<td>25.4</td>
<td>46.4</td>
</tr>
<tr>
<td>P(p-tolyl)$_3$ (47)</td>
<td>145</td>
<td>-327.5</td>
<td>15.7</td>
<td>21.9</td>
<td>18.2</td>
</tr>
<tr>
<td>P(p-FC$_6$H$_4$)$_3$ (48)</td>
<td>145</td>
<td>-333.1</td>
<td>14.9</td>
<td>22.5</td>
<td>23.7</td>
</tr>
<tr>
<td>PEt$_2$ (49)</td>
<td>132</td>
<td>-330.2</td>
<td>28.8</td>
<td>22.6</td>
<td>48.9</td>
</tr>
<tr>
<td>PMe$_3$Ph (50)</td>
<td>136</td>
<td>-324.5</td>
<td>16.9</td>
<td>25.2</td>
<td>44.6</td>
</tr>
<tr>
<td>PM$_2$Ph (51)</td>
<td>122</td>
<td>-325.1</td>
<td>7.8</td>
<td>25.4</td>
<td>55.4</td>
</tr>
<tr>
<td>PEt$_2$Ph (52)</td>
<td>136</td>
<td>-327.0</td>
<td>24.3</td>
<td>20.7</td>
<td>41.9</td>
</tr>
<tr>
<td>C$_6$H$_5$N (53)</td>
<td>-</td>
<td>-269.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AsPh$_3$ (54)</td>
<td>-</td>
<td>-349.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Recorded in CD$_2$Cl$_2$

$^b$($\delta_{complex} - \delta_{free ligand}$)

Table 2.2 $^{31}$P($^1$H) and $^{19}$F NMR Data for [OC-6-13][RuF$_2$(CO)$_2$L$_2$]

<table>
<thead>
<tr>
<th>L</th>
<th>cone angle$^{[31,32]}$ /°</th>
<th>$\delta$($^{19}$F)/ppm</th>
<th>$\delta$($^{31}$P)/ppm</th>
<th>$^3$J(P-F)/Hz</th>
<th>$\Delta^{31}$P/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh$_3$ (42)</td>
<td>145</td>
<td>-324.3</td>
<td>21.6</td>
<td>19.8</td>
<td>27.6</td>
</tr>
<tr>
<td>PEt$_2$Ph (43)</td>
<td>140</td>
<td>-327.1</td>
<td>24.8</td>
<td>22.4</td>
<td>37.1</td>
</tr>
<tr>
<td>PM$_3$ (44)</td>
<td>118</td>
<td>-328.7</td>
<td>3.3</td>
<td>28.0</td>
<td>65.5</td>
</tr>
<tr>
<td>PCY$_3$ (45)</td>
<td>170</td>
<td>-324.3</td>
<td>36.6</td>
<td>19.6</td>
<td>25.3</td>
</tr>
<tr>
<td>PPh$_2$(C$_6$F$_5$) (46)</td>
<td>158</td>
<td>-321.2</td>
<td>21.7</td>
<td>25.4</td>
<td>46.4</td>
</tr>
<tr>
<td>P(p-tolyl)$_3$ (47)</td>
<td>145</td>
<td>-327.5</td>
<td>15.7</td>
<td>21.9</td>
<td>18.2</td>
</tr>
<tr>
<td>P(p-FC$_6$H$_4$)$_3$ (48)</td>
<td>145</td>
<td>-333.1</td>
<td>14.9</td>
<td>22.5</td>
<td>23.7</td>
</tr>
<tr>
<td>PEt$_2$ (49)</td>
<td>132</td>
<td>-330.2</td>
<td>28.8</td>
<td>22.6</td>
<td>48.9</td>
</tr>
<tr>
<td>PMe$_3$Ph (50)</td>
<td>136</td>
<td>-324.5</td>
<td>16.9</td>
<td>25.2</td>
<td>44.6</td>
</tr>
<tr>
<td>PM$_2$Ph (51)</td>
<td>122</td>
<td>-325.1</td>
<td>7.8</td>
<td>25.4</td>
<td>55.4</td>
</tr>
<tr>
<td>PEt$_2$Ph (52)</td>
<td>136</td>
<td>-327.0</td>
<td>24.3</td>
<td>20.7</td>
<td>41.9</td>
</tr>
<tr>
<td>C$_6$H$_5$N (53)</td>
<td>-</td>
<td>-269.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>AsPh$_3$ (54)</td>
<td>-</td>
<td>-349.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Recorded in d$_2$-acetone

$^a$($\delta_{complex} - \delta_{free ligand}$)
Co-ordination chemical shifts $\Delta^{31}P$ ($\delta_{\text{complex}} - \delta_{\text{free ligand}}$) are determined by the electronegativity of the substituents on the phosphorus and the change in C-P-C angle (Figure 2.8) upon co-ordination of the phosphine ligand. The magnitude of $\Delta^{31}P$ tends to be smaller for large ligands because the C-P-C angles of phosphines with bulky substituents generally open less on co-ordination. It is evident from Table 2.1 and 2.2 that $\Delta^{31}P$ for the fluoride complexes is related to the cone angle of the phosphine ligand, which influences the opening of the C-P-C angle and hence results in an increase in the co-ordination shift. In addition, there is a linear correlation between the $^{31}P$ chemical shift of the free phosphine, $\delta$, and $\Delta^{31}P$ for the fluoride complexes (29-53), (Figure 2.9). A similar correlation has been observed in the ruthenium chloride complexes, [OC-6-75][RuCl$_2$(CO)$_2$(PR$_3$)$_2$], PR$_3$ = PMePh$_2$, PEt$_3$, PEtPh$_2$ and PPh$_3$, and in the iridium fluoride complexes mer,trans-[IrF$_3$(CO)(PR$_3$)$_2$], PR$_3$ = PCy$_3$, PPr$_3$, PPh$_3$(C$_6$F$_5$), P(p-tolyl)$_3$, PPh$_3$, PEtPh$_3$, PMePh$_3$, PEt$_3$, PMe$_2$Ph and PMe$_3$.

Figure 2.8 Schematic Diagram of (I) Cone angle and (II) Angle Between Substituents on Phosphines

![Schematic Diagram](image)

It has been suggested previously that $^{19}F$ NMR chemical shifts can be related to the extent of F$\rightarrow$M $\pi$-donation. A shift to lower frequency is said to indicate little or no F$\rightarrow$M $\pi$-donation, whereas high frequency shifts reflect an increase in F$\rightarrow$M $\pi$ donation. Co-ordination of the predominantly $\sigma$-donor ligand pyridine to the five co-ordinate ruthenium complex [RuHF(CO)(P'Bu$_2$Me)$_2$], in which the fluoride ligand is trans to CO and the phosphines are mutually trans, forming the six co-ordinate complex [Ru HF(CO)(P'Bu$_2$Me)$_2$(Py)], results in a low frequency shift.
Figure 2.9 A Graph Showing the Relationship Between Cone Angle and the Co-ordination Chemical Shift for a) [OsF₂(CO)₂(PR₃)₂] and b) [RuF₂(CO)₂(PR₃)₂]
from $\delta -311$ to $\delta -491$. Co-ordination of the $\pi$-acid CO to the five co-ordinate complex, generating [RuHF(CO)$_2$(P'Bu$_2$Me)$_2$], results in a shift to higher frequency, $\delta -202$. Previous work within this group and the results presented here contradict this view. For cis-[OsF$_2$(CO)$_4$], containing only fluoride and the $\sigma$-donor / $\pi$-acceptor ligand CO, and [OC-6-13][OsF$_2$(CO)$_2$(Py)$_2$], which contains the predominately $\sigma$-donor ligand pyridine, the $^{19}$F chemical shifts are $\delta -342.5$ and $\delta -286.8$ respectively. This is the reverse of that expected if $\delta (^{19}$F) can be directly related to the F $\rightarrow$ M donation as suggested for the di(t-butyl)methylphosphine ruthenium complexes. Typically, a terminal fluoride trans to a carbonyl group would occur between $\delta -270$ and $\delta -350$. The $^{19}$F chemical shift for [RuHF(CO)$_2$(P'Bu$_2$Me)$_2$(py)] ($\delta -491$) is, in fact, more typical for a cationic fluoride complex (cf. [OsF(CO)$_3$]$^+$ $\delta (^{19}$F) -433.0[22] and [MF(CO)$_3$(PPh$_3$)$_2$]$^+$ where $M =$ Os, $\delta (F) -421.0$ and $M =$ Ru, $\delta (F) -$436.0),[24] a bridging fluoride ligand (cf. [Os$_2$F$_4$(CO)$_7$] $\delta (\mu-F) -412.0$ and [Os$_2$F$_3$(CO)$_9$]$^+ \delta (\mu-F) -465.0$[23]), or a fluoride ligand trans to another halide (cf. mer-[IrF$_3$(CO)$_3$] $\delta (F$ trans $F) = -476.0$[23]).

To obtain more information on the character of the M-F bond and how this is related to $\delta (^{31}$P), it is necessary to consider a series of complexes cis,cis,trans-[MX$_2$(CO)$_2$(PPh$_3$)$_2$], M = Os or Ru, where only the anionic ligand X is varied. Such a comparison is difficult for osmium as only the chemical shift for the chloride complex has been reported. However, for the ruthenium complexes, extensive NMR data is available. The $^{31}$P NMR data for the compounds [RuX$_2$(CO)$_2$(PPh$_3$)$_2$] (Table 2.3) show that the $^{31}$P chemical shift decreases in the order $F > SCN > Cl > Br > I$. Chemical shifts in $^{31}$P NMR spectroscopy are related to the total shielding constant $\sigma$, which receives contributions from paramagnetic shielding ($\sigma_p$) and local diamagnetic shielding ($\sigma_d$) terms. The paramagnetic shielding term being dominant. The $\sigma_p$ term depends upon the distance of the metal $d$ electrons from the nucleus ($r$) and the average excitation energy of the states with the appropriate symmetry ($\Delta E$), (see Equation 1.0, Chapter One). In the complexes [RuX$_2$(CO)$_2$(PPh$_3$)$_2$] the phosphorus nuclei are most deshielded for X = F. Therefore, the $\sigma_p$ contribution to $\sigma$ is at a maximum when $X = F$ as $\sigma_p$ is a deshielding term. The variation in $\delta (^{31}$P) is consistent with the increasing $d$ electron distance from the metal centre and increasing
M-X bond covalency, which follows the order F < SCN < Cl < Br < I (the nephelauxetic effect).

Table 2.3 $^{31}$P and Co-ordination Chemical Shifts for the complexes $^{cis, cis, trans-}\{\text{RuX}_2(\text{CO})_2(\text{PPh}_3)_2\}$

<table>
<thead>
<tr>
<th>X</th>
<th>$\delta^{31}\text{P} / \text{ppm}$</th>
<th>$\Delta^{31}\text{P} (\delta_{\text{complex}} - \delta_{\text{ligand}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>21.6*</td>
<td>27.6</td>
</tr>
<tr>
<td>Cl</td>
<td>17.1*</td>
<td>23.1</td>
</tr>
<tr>
<td>Br</td>
<td>13.3*</td>
<td>19.3</td>
</tr>
<tr>
<td>I</td>
<td>7.8*</td>
<td>13.8</td>
</tr>
<tr>
<td>SCN</td>
<td>20.9*</td>
<td>26.9</td>
</tr>
</tbody>
</table>

*From reference [36], relative to H$_3$PO$_4$, recorded in CDCl$_3$.

2.4.2 Infrared Spectroscopy and Mass Spectrometry

Positive ion FAB mass spectra of (29-54) confirm the mononuclear nature of the complexes. Although no parent ion for the complexes was observed, the correct isotope patterns for the fragments $[M - F]^+$ or $[M - F - CO]^+$ were obtained (Chapter Six, Table 6.1). The infrared spectra of complexes (29-54) show two bands of equal intensity in the $\nu$(CO) region, characteristic of mutually cis carbonyl ligands. There is no significant change in $\nu$(CO) as PR$_3$ is varied, since the phosphine ligands are cis to the CO group and, therefore, have little effect on such values (Table 2.4). Upon comparison with the heavier halides [OC-6-33][OsX$_2$(CO)$_2$(PPh$_3$)$_2$] X = Cl, Br or I, there is an increase in $\nu$(CO) in the order F < Cl < Br < I for the asymmetric vibration. The symmetric or in phase vibration, however, remains relatively constant, with the symmetric stretch at higher wave numbers. When X = H, $\nu$(CO) is at its highest (asymmetric stretch) as expected since H can act only as a $\sigma$-donor ligand since there are no $\pi$-orbitals available for synergic interactions with the metal $d$ orbitals and the $\pi^*$-orbital of CO, (the symmetric stretch, however, is the lowest) (see Table 2.5). Unfortunately, there seems to be no clear trend in the ruthenium analogues, although
when $X = F$ $\nu$(CO) attains its lowest value. The compounds $cis,cis,trans$-
$[MX_2(CO)_3(PR_3)_2]$ are electronically saturated eighteen electron metal complexes, and
should therefore be unable to accept $\pi$-donation from the halide.$^{[19]}$

<table>
<thead>
<tr>
<th>$M = Os$</th>
<th>$M = Ru$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(CO) / cm$^{-1}$</td>
<td>$\nu$(CO) / cm$^{-1}$</td>
</tr>
<tr>
<td>$\nu_t$</td>
<td>$\nu_m$</td>
</tr>
<tr>
<td>PPh$_3$ (29)</td>
<td>2017, 1937</td>
</tr>
<tr>
<td>PEt$_3$ (30)</td>
<td>2031, 1950</td>
</tr>
<tr>
<td>PMe$_3$ (31)</td>
<td>2024, 1939</td>
</tr>
<tr>
<td>PCy$_3$ (32)</td>
<td>2005, 1925</td>
</tr>
<tr>
<td>PPh$_2$(C$_6$F$_5$) (33)</td>
<td>2029, 1959</td>
</tr>
<tr>
<td>P(p-tolyl)$_3$ (34)</td>
<td>2021, 1942</td>
</tr>
<tr>
<td>P(p-F-C$_6$H$_4$)$_3$ (35)</td>
<td>2035, 1962</td>
</tr>
<tr>
<td>PEt$_3$ (36)</td>
<td>2034, 1963</td>
</tr>
<tr>
<td>PMe$_2$Ph (37)</td>
<td>2026, 1941</td>
</tr>
<tr>
<td>PMe$_2$Ph (38)</td>
<td>2043, 1945</td>
</tr>
<tr>
<td>PEt$_3$Ph (39)</td>
<td>2023, 1943</td>
</tr>
<tr>
<td>C$_3$H$_7$N (40)</td>
<td>2010, 1940</td>
</tr>
<tr>
<td>AsPh$_3$ (41)</td>
<td>2050, 2007</td>
</tr>
</tbody>
</table>

However, theoretical studies on the eighteen electron halide complexes
$[RuHX(CO)(P'Bu$_2$Me)$_2$L]$, $L = pyridine$ or CO, have shown that the CO $\pi^*$-orbitals
interact to stabilise the Ru-X $\pi^*$-orbitals thus allowing some degree of net Ru-X $\pi$-
bonding.$^{[19]}$ It is evident from Table 2.5 that the fluoride complexes contain the lowest
$\nu$(CO), contrary to expectations based on simple electronegativity arguments. The
lowering of $\nu$(CO) is due to the $\pi$-donor effect of the fluoride which increases back-
bonding from the metal to the $\pi^*$-orbital of the CO ligand, decreasing the C=O bond.
order and hence lowering the CO stretching frequency. This suggests that the metal-halide \( \pi \)-bonding dominates the electronic structure of the osmium(II) and ruthenium(II) compounds, with fluoride being the best \( \pi \)-donor and poorest \( \pi \)-acceptor of the halides as suggested by Fenske and Hall.\(^{198}\) Similar ‘reversed’ effects of halides on the stretching frequencies of nitrosyl and carbonyl ligands have been observed in Vaska’s halides trans-[MX(CO)(PPh\(_3\))\(_2\)] where M = Ir and Rh.\(^{141}\) [Re(η\(^5\)-C\(_2\)H\(_2\))(X)(NO)(PR\(_3\))],\(^{145}\) [Re(Cl\(_2\))F(NO)(bipy)],\(^{148}\) [RuH(X)(CO)(PMe\(_2\)Me)_2],\(^{133}\) and [RuH(X)(CO)(py)(PMe\(_2\)Me)_2]\(^{113}\) (py = pyridine and X = halide).

Table 2.5 CO Stretching Frequencies for the Complexes cis,cis,trans-

\[\text{[MX_2(CO)_2(PPh_3)_2]}\]

<table>
<thead>
<tr>
<th>X</th>
<th>M = Os</th>
<th>M = Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\nu_s)</td>
<td>(\nu_as)</td>
</tr>
<tr>
<td>H</td>
<td>2020</td>
<td>1990(^a)</td>
</tr>
<tr>
<td>F</td>
<td>2017</td>
<td>1937(^b)</td>
</tr>
<tr>
<td>Cl</td>
<td>2041</td>
<td>1970(^c)</td>
</tr>
<tr>
<td>Br</td>
<td>2042</td>
<td>1973(^e)</td>
</tr>
<tr>
<td>I</td>
<td>2040</td>
<td>1975(^f)</td>
</tr>
</tbody>
</table>

\(^a\) From reference [43], recorded in heptane
\(^b\) Recorded in nujol
\(^c\) From reference [44], recorded in C\(_2\)Cl\(_4\)
\(^d\) From reference [36], recorded in nujol

2.4.3 X-Ray Crystal Structure Analysis of [OC-6-13][OsF\(_2\)(CO)\(_2\)(PPh\(_3\))\(_2\)] (29) [OC-6-13][OsF\(_2\)(CO)\(_2\)(PCy\(_3\))\(_2\)] (32) and [OC-6-13][RuF\(_2\)(CO)\(_2\)(PEtPh\(_2\))\(_2\)] (43)

There have been very few crystallographic structure determinations of low-valent transition-metal fluoride complexes.\(^{114}\) The structure determinations of [OC-6-13][OsF\(_2\)(CO)\(_2\)(PPh\(_3\))\(_2\)] (29) and [OC-6-13][OsF\(_2\)(CO)\(_2\)(PCy\(_3\))\(_2\)] (32) represent the first examples of crystallographic analyses of osmium(II) fluoride complexes. Crystals of (29), (32) and (43) suitable for X-ray diffraction were obtained from dichloromethane (29), (32) and from acetone (43) by slow evaporation of the solvent.
Table 2.6 Selected Bond Lengths (Å) and Angles(*) for the Complexes (29), (32), (42), (43) and (55).

<table>
<thead>
<tr>
<th>Compound</th>
<th>d(M-X) / Å</th>
<th>d(M-P) / Å</th>
<th>d(M-C) / Å</th>
<th>d(C-O) / Å</th>
<th>P-M-P / °</th>
<th>X-M-X / °</th>
<th>C-M-C / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OsCl₂(CO)₂(PEt₃)₂]</td>
<td>2.4442(11)</td>
<td>2.4053(11)</td>
<td>1.867(4)</td>
<td>1.134(5)</td>
<td>178.05(3)</td>
<td>88.61(4)</td>
<td>93.5(2)</td>
</tr>
<tr>
<td>(55)</td>
<td>2.4441(10)</td>
<td>2.4049(11)</td>
<td>1.870(5)</td>
<td>1.132(5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[OsF₆(CO)₆(PPh₃)₂]</td>
<td>2.023(5)</td>
<td>2.419(2)</td>
<td>1.844(9)</td>
<td>1.173(9)</td>
<td>177.51(10)</td>
<td>81.5(3)</td>
<td>90.6(5)</td>
</tr>
<tr>
<td>(29)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[OsF₆(CO)₆(PCy₃)₂]</td>
<td>2.023(4)</td>
<td>2.438(2)</td>
<td>1.841(8)</td>
<td>1.158(9)</td>
<td>166.41(5)</td>
<td>83.5(2)</td>
<td>86.6(3)</td>
</tr>
<tr>
<td>(32)</td>
<td>2.022(4)</td>
<td>2.423(2)</td>
<td>1.854(7)</td>
<td>1.154(8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[RuF₆(CO)₆(PPh₃)₂]</td>
<td>2.011(4)</td>
<td>2.406(1)</td>
<td>1.841(7)</td>
<td>1.135(9)</td>
<td>178.2(1)</td>
<td>84.4(2)</td>
<td>92.2(4)</td>
</tr>
<tr>
<td>(42)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[RuF₆(CO)₆(PPh₂Et₂)₂]</td>
<td>2.017(2)</td>
<td>2.3921(7)</td>
<td>1.855(3)</td>
<td>1.146(4)</td>
<td>171.82(2)</td>
<td>86.40(7)</td>
<td>91.9(2)</td>
</tr>
<tr>
<td>(43)</td>
<td>2.028(2)</td>
<td>2.3872(7)</td>
<td>1.853(3)</td>
<td>1.132(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* from reference [10].
The complexes are essentially pseudo-octahedral with the two phosphine ligands mutually trans and the fluoride ligands trans to the carbonyl groups, confirming the arrangement predicted by multinuclear NMR spectroscopy and IR spectroscopy, (Figures 2.10 - 2.12). Selected bond lengths (Å) and bond angles (°) in (29), (32) and (43) are presented in Table 2.6 along with those of \([\text{OC-6}\text{-13}]\text{RuF}_2(\text{CO})_2(\text{PPh}_3)_2\)^\[49\] and \([\text{OC-6}\text{-13}]\text{OsCl}_2(\text{CO})_2(\text{PEt}_3)_2\) for comparison.\[49\] The chloride complex \([\text{OC-6}\text{-13}]\text{OsCl}_2(\text{CO})_2(\text{PEt}_3)_2\) (55) (Figure 2.13), was prepared to enable comparisons between the fluoride and chloride complexes to be made. The chloride complex was synthesised from the reaction of the chloride bridged dimer \([\text{OsCl}_2(\text{CO})_6]_2\) with triethylphosphine, details of which can be found in the Experimental Section, Chapter Six. The fluoride complexes (29), (33), (43) and the chloride complex are isostructural with each other and the recently characterized ruthenium fluoride \([\text{OC-6}\text{-13}]\text{RuF}_2(\text{CO})_2(\text{PPh}_3)_2\) (42).\[49\] The metal-fluorine bond lengths are very similar to those of the only other crystallographically characterized carbonyl fluoride complexes of d⁶ transition metals, \([\text{ReF}_2(\text{CO})_3(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)]\), Re-F = 2.039(4) Å;\[164\] \([\text{RuF}_2(\text{CO})_3]_4\), Ru-F(terminal) = 1.99(7) Å, Ru-F(bridging) = 2.04(7)Å;\[152\] \([\text{IrF}(\text{CO})_2(\text{PEt}_3)_2][\text{BF}_4]_2\), Ir-F = 1.998(3) Å;\[147\] \([\text{IrFCl}(\text{NSF}_2)(\text{CO})(\text{PPh}_3)_2]\), Ir-F = 2.089(4) Å;\[148\] and \([\text{RuF}_2(\text{CO})_3(\text{PPh}_3)_2]\), Ru-F = 2.011(4) Å.\[110\] In all of these complexes the fluoride ligand is trans to a carbonyl group with the M-F bond lengths lying within the range 2.089 – 1.998 Å. The metal-phosphorus bond lengths are slightly longer than in other neutral d⁶ transition metal complexes, c.f. \([\text{RuF}_2(\text{CO})_3(\text{PPh}_3)_2]\). The phosphines with the smaller cone angle having the shorter M-P distance [2.3896(7) Å (mean) for PEtPh₂, 2.419(2) Å for PPh₃ and 2.430(2) Å (mean) for PPh₃]. This can be linked to the co-ordination chemical shift,\[131\] Δ¹³P (section 2.2.1), where the larger M-P bond length (for the fluoride complexes) gives rise to the smaller value of Δ¹³P. The metal-carbon bond distances for the fluoride complexes (29), (32) and (43) are very similar although slightly shorter than those observed for other osmium(II) and ruthenium(II) compounds (1.873 – 1.880 Å).\[49\] This may be an indication of the greater degree of back-bonding in the fluoride complexes to the empty π*-orbital of CO since fluoride is a better π-donor than chloride, which shortens the M-C bond and lengthens the C-O bond. This is
Figure 2.10 a) Molecular Structure of $[OC-6-13][OsF_2(CO)_2(PPh_3)_2]$ (29) with b) a View Down the P-Os-P axis
Figure 2.11 a) Molecular Structure of $[OC-6-13][OsF_2(CO)_2(PCy_3)_2]$ (32) with b) a View Down the P-Os-P axis
Figure 2.12 a) Molecular Structure of [OC-6-13][RuF₂(CO)₂(PEtPh₂)₂] (43) with b) a View Down the P-Ru-P axis and c) a Picture of the Intermolecular Interactions
Figure 2.13 a) Molecular Structure of $[OC-6-33][OsCl_2(CO)_3(PEt_3)_2]$ with b) a View Down the P-Os-P axis
particularly apparent when the Os-C distance in the osmium fluoride complexes (29) (1.844(9) Å) and (32) (1.848(8) Å (mean)) are compared to those of the chloride complex \([\text{OsCl}_2(\text{CO})_2(\text{PEt}_3)_2]\) (55) (1.869(5) Å (mean)). Similarly, there is a difference in the C-O bond length which is shorter in the chloride complex, [1.133 Å (mean) c.f. 1.173(9) Å (29) and 1.156(9) Å (mean) (32)], indicating a stronger C-O bond, this compares well with the CO stretching frequencies which are larger for the chloride complex [2029 cm\(^{-1}\) and 1953 cm\(^{-1}\), c.f. 2017 cm\(^{-1}\) and 1937 cm\(^{-1}\) for (29), 2005 cm\(^{-1}\) and 1925 cm\(^{-1}\) for (32)].

It is noteworthy that in the dihalide complexes (55), (29), (32) and (43) there is a considerable difference in the P-M-P angles, [178.05(3)\(^\circ\) (55), 177.51(10)\(^\circ\) (29), 166.41(5)\(^\circ\) (32), and 171.82(2)\(^\circ\) (43)] as the phosphine ligand is changed. The orientation of phosphines also varies, with the phosphines staggered with respect to one another in the chloride complex (Figure 2.13), (29), (Figure 2.10) and (42)\(^{100}\) and eclipsed in complexes (32) and (43) (Figures 2.11 and 2.12 respectively). The fluoride complexes (29), (32) and (43) all contain short intramolecular interactions between a hydrogen on the phosphine ligand and fluoride. In the complex (32) the PCY\(_3\) ligands are bent towards the fluoride ligands (P-\(\text{Os}-\text{P}\), 166.4\(^\circ\)) with non-bonding intramolecular H--F distances [H(21A) - F(1) 2.470 Å, H(26B) - F(1) 2.373 Å, H(42A) - F(1) 2.279 Å, H(46B) - F(1) 2.304 Å, H(26B) - F(2) 2.454 Å and H(32B) - (F2) 2.356 Å] all of which are shorter than the sum of the Van der Waals radii of hydrogen and fluorine (\(r_{\text{vdw}}\) H = 1.20 Å, \(r_{\text{vdw}}\) F = 1.35 Å\(^{100}\)), (Figure 2.11). Similarly, in the ruthenium complex (43) the ethyl groups of the diphenylethylphosphine ligands are coplanar and are bent towards the fluoride ligands, (P-\(\text{Ru}-\text{P}\), 171.82\(^\circ\)) (Figure 2.12), with non-bonding H--F interactions [H(6C) - F(1) 2.476 Å, H(32A) - F(2) 2.298 Å and H(16A) - F(2) 2.421 Å] shorter than the sum of the Van der Waals radii. Unlike the others, complex (43) has two different M-F bond lengths, 2.017(2) Å for Ru-F(1) and 2.028(2) Å for Ru-F(2) (Figure 2.12). The greater number of secondary, hydrogen bonding interactions to F(2) may account for the lengthening of Ru(1)-F(2). Although (29) has an essentially linear P-M-P arrangement (ca. 177.5\(^\circ\)), it still contains intramolecular non-bonded H--F interactions less than the sum of the Van der Waals radii (H(26B) - F(1) 2.253 Å, H(32B) - F(1) 2.238 Å, H(26B) - F(1A) 2.252 Å and H(32A) - F(1A) 2.238 Å). Unique among the structures of these
difluoride complexes is the short intermolecular non-bonded H—F interactions present in (43). The fluoride ligands were found to have secondary bonding interactions with hydrogens on the phenyl rings of two adjacent molecules in the unit cell, H(22A') - F(1) and H(43A") - F(2) of 2.235 Å and 2.378 Å respectively (Figure 2.12).

Details of data collection and refinements are given in the Appendix.

2.4.4 EXAFS Analysis of \([OC-6-13][OsF_2(CO)_2(PMe_3)_2]\) (31).

The high solubility of \([OC-6-13][OsF_2(CO)_2(PMe_3)_2]\) (31) precluded all attempts to obtain crystals suitable for X-ray crystallographic studies. However, extended X-ray absorption fine structure (EXAFS) spectroscopy, in combination with other spectroscopic techniques, has been widely used for structural identification in metal-phosphine-halide complexes when single crystals have been unavailable.\(^{[22]}\) In the first instance, osmium L\(_{\text{III}}\) edge EXAFS data were collected for the crystallographically characterized osmium fluoride complex \([OC-6-13][OsF_2(CO)_2(PPh_3)_2]\) (29), (see 2.3.3), which was used as a model system to test the reliability of data collection and treatment. The results are in satisfactory agreement with the single crystal X-ray data (Table 2.7). Transmission osmium L\(_{\text{III}}\) edge EXAFS data was collected for \([OsF_2(CO)_2(PMe_3)_2]\), (31), out to \(k = 15\) Å\(^{-1}\) (\(k = \) photoelectron wave vector). This was later truncated to 13.5 Å\(^{-1}\) due to increased noise at higher \(k\) values. Three data sets were averaged and the data multiplied by \(k^2\) to compensate for a decrease in intensity at higher \(k\). The AFAC and VPI values were taken from the analysis of the model compound \([OC-6-13][OsF_2(CO)_2(PPh_3)_2]\) (29).

No Fourier filtering was applied, and the fit discussed below was compared with the average raw (background subtracted) EXAFS data. As with the model compound, the data was modelled using EXCURV92\(^{[23]}\) to five shells of two carbon atoms at 1.83(4) Å, two fluorine atoms at 1.99(5) Å, two phosphorus atoms at 2.35(3) Å, two oxygen atoms at 2.95(4) Å and six carbon atoms at a non-bonded distance of 3.53(10) Å, (Figure 2.14). Each shell was tested for statistical significance.\(^{[24],[25]}\) The Os-P, Os-C and, more importantly, the Os-F bond lengths are in keeping with those obtained from the crystallographically determined fluoride complexes (29, 32, 42 and 43), Table 2.6.
Figure 2.14  a) The Background Subtracted EXAFS and b) the Fourier Transform of $[OC-6\cdot 13][OsF_2(CO)_{2}(PMe_3)_2]$ (31)

(dashed line theoretical)
Table 2.7  EXAFS and X-Ray crystal data for \([\text{OsF}_2(\text{CO})_2(\text{PPh}_3)_2]\) (29) and EXAFS data for \([\text{OsF}_2(\text{CO})_2(\text{PMe}_3)_2]\) (31)\(^a\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>([\text{OsF}_2(\text{CO})_2(\text{PPh}_3)_2])</th>
<th>([\text{OsF}_2(\text{CO})_2(\text{PMe}_3)_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X-Ray</td>
<td>EXAFS(^a)</td>
</tr>
<tr>
<td>d(Os-P) / Å</td>
<td>2.419(2)</td>
<td>2.39(0.008)</td>
</tr>
<tr>
<td>2σ(^a) / Å(^b)</td>
<td>-</td>
<td>0.015(0.002)</td>
</tr>
<tr>
<td>d(Os-F) / Å</td>
<td>2.023(5)</td>
<td>2.01(0.007)</td>
</tr>
<tr>
<td>2σ(^a) / Å(^b)</td>
<td>-</td>
<td>0.005(0.001)</td>
</tr>
<tr>
<td>d(Os-C) / Å</td>
<td>1.844(9)</td>
<td>1.88(0.009)</td>
</tr>
<tr>
<td>2σ(^a) / Å(^b)</td>
<td>-</td>
<td>0.003(0.002)</td>
</tr>
<tr>
<td>d(C-O) / Å</td>
<td>1.173(9)</td>
<td>1.09(0.007)</td>
</tr>
<tr>
<td>2σ(^a) / Å(^b)</td>
<td>-</td>
<td>0.007(0.002)</td>
</tr>
<tr>
<td>Fit index(^c)</td>
<td>-</td>
<td>1.4</td>
</tr>
<tr>
<td>R(^d)</td>
<td>-</td>
<td>13.9(^e)</td>
</tr>
</tbody>
</table>

\(^a\) standard deviations in parentheses. \(^b\) Debye-Waller factor. \(^c\) Fit index = \(\sum[(\chi^2 - \chi^0)^2]^{-1}\). \(^d\) R = \(\sum[\chi^2 - \chi^0]^2/\sum\chi^2\) \times 100\%. \(^e\) E0 9.55(0.30) eV, AFAC 0.71 and VPI -3.00. \(^f\) E0 15.05(0.30) eV, AFAC 0.71 and VPI -3.00. \(^g\) Additional non-bonded shell used in fit Os---C 3.54(0.0013), 0.014(0.004). \(^h\) Additional non-bonded shell used in fit Os---C 3.53(0.096), 0.019(0.027).

2.5 Reaction of \([\text{MF}_2(\text{CO})_3]\) with multidentate donor ligands, M = Ru and Os

In Section 2.3 the reaction of the carbonyl fluoride tetramers with monodentate ligands to give complexes of the type \([\text{OC}-5-i5]\)[\(\text{MF}_2(\text{CO})_2\)\(_2\)] where L = tertiary phosphine, arsine and nitrogen donor ligands is described. Here, the analogous reactions with multidentate donor ligands are outlined. The ruthenium halide polymers \([\text{RuX}_2(\text{CO})_2]\)_\(_n\), X = Cl, Br and I, have been reported to react with bidentate ligands (L") to give complexes of the type \([\text{RuX}_2(\text{CO})_2(L")\]) where L" = dppe, phen, bipy and dpae (dpae = Ph\(_2\)AsCH\(_2\)CH\(_2\)AsPh\(_2\)). Of the three possible isomers (A-C) only (B) and (C) have been reported (Figure 2.15).\(^{11}\) Similarly, \([\text{OsX}_2(\text{CO})_2]\)_\(_2\) and \([\text{OsX}_4(\text{CO})_2]\)_\(^b\) react with pmma and dppe to give \([\text{OsX}_2(\text{CO})_2(L")\]) with all three isomers (A-C) being isolated depending on the
reaction times (Figure 2.15). Tridentate and tetradentate ligands also known to co-ordinate to ruthenium and osmium to give substituted osmium and ruthenium halide complexes, \([\text{MX}_2(\text{CO})(\text{L}'''))\] and \([\text{MX}_2(\text{L}'''')\)] respectively, where \(\text{L}''' = \text{triphos}\) and \(\text{L}''' = \text{tetraphos}\).  

Reaction of the carbonyl fluoride tetramers with the tridentate phosphine ligand triphos(II), \(\text{PhP(}CH\text{CH}_2\text{PPh}_2\text{)}_2\), and the tetradentate ligand tetraphos(II), \(\text{P(}CH\text{CH}_2\text{PPh}_2\text{)}_3\), result in the evolution of CO(g). This suggests that the multidentate phosphine ligands were co-ordinating via displacement of CO as in the monodentate complexes. Unfortunately, no products from the reactions could be characterized and it is clear from the \(^{19}\text{F}\) NMR that no metal-bound fluoride ligands were present. However, the reaction with dppe gave a product which showed a mutually coupled quintet (\(\delta \approx \text{-}395.1\ M = \text{Os} : \delta \approx -400.5\ M = \text{Ru}\)) together with a doublet (\(\delta \approx 20.5\ M = \text{Os}\) : \(\delta \approx 40.3\ M = \text{Ru}\)) in the \(^{19}\text{F}\) and \(^{31}\text{P}\) (\(^{1}\text{H}\)) respectively. This suggests that the fluoride ligand is coupling to four equivalent phosphorus nuclei, with the phosphorus nuclei coupling to one fluorine. The coupling is characteristic of \(\text{cis} \ ^2\text{J(PF)}\) interactions (ca. 30 Hz for Os and 20 Hz for Ru) (see the section 2.2.1 on monodentate phosphine ligands).

**Figure 2.15 The three possible isomers of \([\text{MX}_2(\text{CO})(\text{L}-\text{L})]\)**

\[
\begin{align*}
\text{(A)} & \quad \text{CO} \quad \text{M} \quad \text{X} \\
\text{L} \quad \text{L} & \quad \text{CO} \\
\text{X} & \quad \text{X} \\
\text{(B)} & \quad \text{X} \quad \text{M} \quad \text{CO} \\
\text{L} & \quad \text{L} \\
\text{(C)} & \quad \text{X} \quad \text{M} \quad \text{CO} \\
\text{L} & \quad \text{L}
\end{align*}
\]

\(\text{M} = \text{Os or Ru}\)

\(\text{L-L} = \text{bidentate ligand}\)

\(\text{X} = \text{halide}\)

The chemical shifts for the fluorine resonances are in the region characteristic of a fluoride ligand \textit{trans} to a carbonyl group in a cationic complex. These data
suggest that two dppe ligands are co-ordinated to the metal centre along with one fluoride ligand and is consistent with the structure shown in Figure 2.16. The NMR data of the ruthenium complex corresponds exactly to the data reported for the cationic complex \( \text{trans-}[\text{RuF(CO)}(\text{dppe})_2][\text{BF}_4] \), formed during the reaction of the chloride complex \( \text{trans-}[\text{RuCl_2(dppe)}_2][\text{BF}_4] \) with \( \text{AgBF}_4 \) under a CO atmosphere.\(^{[11]}\)

Thus, one of the products from the reaction of \([\text{MF_2(CO)}_3]_4\) with dppe can be formulated as \( \text{trans-}[\text{MF(CO)}(\text{dppe})_2]^{[+]} \) where the fluoride ligand is in the apical position \( \text{cis} \) to four equivalent phosphorus nuclei (Figure 2.16). This formulation is confirmed by the mass spectra data which show parent ions at \( m/z \) 1035 for \( \text{trans-}[\text{OsF(CO)}(\text{dppe})_2]^{[+] \) and \( m/z \) 945 for \( \text{trans-}[\text{RuF(CO)}(\text{dppe})_2]^{[+] \). The \( ^{19}\text{F} \) NMR spectra contain both the BF\(_4^-\) (\( \delta \sim 150.0 \)) and SiF\(_6^{2-}\) (\( \delta \sim 130.0 \)) anions, the former being the most likely counterion due to its single charge and the fact that it is present in much larger amounts. The BF\(_4^-\) and SiF\(_6^{2-}\) are presumably formed as a result of attack of F\(^-\) on the glass reaction flask or attack of HF which could be formed if the F\(^-\) comes into contact with water. Unfortunately, the \( \nu(\text{CO}) \) stretching frequency of the complexes could not be determined due to the presence of a large number of carbonyl containing species. Although other fluorine containing species were present their characterization remains elusive due to the complex nature and number of signals present.

\[ \text{Figure 2.16} \]

![Structure](image)

\[ \text{P} = \text{dppe} \]

\[ \text{M} = \text{Os and Ru} \]
2.6 Summary

In summary, the addition of monodentate Lewis bases \( (L) \), (where \( L = \) phosphines, arsines and nitrogen donor ligands) to the ruthenium and osmium tetrameric carbonyl fluorides \([\text{MF}_2(\text{CO})_5]_4\) yield air-stable, pseudo-octahedral, compounds \([\text{OC-}6-13]\text{[MF}_2(\text{CO})_5(L)_2]\). In all of these complexes the fluoride ligand is \textit{trans} to the carbonyl group allowing synergic interactions between the fluoride, metal and the carbonyl group thereby stabilising the metal-fluoride bond. These results demonstrate that the fluoride ligand and low-valent transition-metals are not mutually incompatible. This work has also provided a wealth of new \(^{19}\text{F} \) NMR data for low-valent metal complexes.
Chapter Two References


CHAPTER THREE

Reactions of the Osmium and Ruthenium Fluoride Complexes [OC-6-13][MF₂(CO)₂(PR₃)₂]
3.1 Introduction

The chemistry of substituted osmium carbonyl halide (Cl, Br and I) complexes has been extensively studied and well documented. Their reactivity is often dictated by the nature of the halide and the ancillary ligands. Steric and electronic properties of these two components have often been used in homogeneous catalysis design. However, the chemistry of low-valent metal fluoride complexes remains relatively unexplored, although the number in the literature is increasing (ca. 135). Many compounds have only a single citation focusing mainly on preparation and identification. In fact, there have been only fifteen reports describing the chemical reactivity of these complexes. These reactions are discussed in Chapter One, where it was concluded that the chemistry of the fluoride complexes differed to that of the heavier halides.

A number of osmium(II) and ruthenium(II) fluoride complexes $\text{[OC-6-I3]}[\text{MF}_2(\text{CO})_2(\text{PR}_3)_2] \text{ M = Os and Ru, R = Ph}$ have been reported in Chapter Two. Due to the often unique reactivity of low-valent metal fluoride complexes and following the synthesis of these novel, air-stable, compounds, a detailed investigation of their reactivities with a variety of reagents has been undertaken.

3.2 Reactions of $\text{[OC-6-I3]}[\text{MF}_2(\text{CO})_2(\text{PR}_3)_2]$ with the Lewis acid Boron Trifluoride

Since the Lewis acid BF$_3$(g) is an established reagent for the abstraction of fluoride from ligands, at transition-metal complexes and metal-bound halogens, the reaction with $[\text{MF}_2(\text{CO})_2(\text{PR}_3)_2]$ M = Os and Ru, R = Ph was investigated. The difluoride complex $[\text{RuF}_2(\text{CO})_2(\text{PPh}_3)_2]$, contained in a 4mm outside diameter (O. D.) pre-fluorinated FEP tube, was dissolved in the non-co-ordinating solvent CH$_2$Cl$_2$ (ca. 0.3cm$^3$) and the reaction vessel charged with BF$_3$(g) at -78°C and sealed. The $^{19}$F NMR spectrum was recorded, revealing the formation of a BF$_3$ adduct (56) (Figure 3.1). At -89°C, four major $^{19}$F NMR resonances were observed at $\delta$ -149.5 (F$_a$), doublet; $\delta$ -151.3, a broad singlet; $\delta$ -237.6 (F$_b$), complex multiplet; and $\delta$ -330.0 (F$_c$), a doublet of multiplets, with the resonances F$_a$, F$_b$ and F$_c$ being in a 3 : 1 : 1 ratio. The broad resonance at $\delta$ -151.3 can be assigned to excess BF$_3$. The higher frequency doublet resonance of F$_a$ is typical of fluorine bound to a boron(III) centre.
and is in the region usually associated with BF₄⁻, with the doublet coupling of 78 Hz typical of ²J(FF) cis coupling. This implies that the BF₃ has removed a metal-bound fluoride to give BF₄⁻, but since the reaction was conducted in a non co-ordinating solvent, the BF₄⁻ is co-ordinated to the ruthenium centre via one of its fluorines (Figure 3.2). Thus, Fₐ and Fₖ are chemically inequivalent resulting in the doublet structure for Fₐ. The multiplicity of Fₖ is more complicated due to coupling to the three equivalent Fₐ’s, Fₖ and the mutually trans phosphine ligands which, even at this low temperature (-89°C) gives rise to a broad multiplet (Figure 3.1). The shift to higher frequency for Fₖ, from that typical for terminally bound metal-fluorides, is indicative of a fluoride bridging between ruthenium and boron.¹⁷ The expected doublet of triplets of quartets is not resolved as the ³J(PF) coupling constant is presumably small as in related adducts (ca. 10 Hz).¹⁸ The multiplet structure for Fₖ is also not well resolved but a ³J(FF) coupling constant of 87 Hz, typical of F cis F interactions in low-valent metal complexes can be seen,¹⁹,²⁰ for which the chemical shift is in the region associated with fluoride terminally bound to ruthenium (see Chapter Two). Similarly, the ³¹P{¹H} NMR spectrum was not resolved but gave a broad resonance at δ 23.4 at -70°C. The broadness of the NMR signals, even at low-temperature, may be as a result of intramolecular exchange of co-ordinated and non-co-ordinated fluoride atoms.

**Figure 3.2**

```
\[
\begin{align*}
\text{M} &= \text{Os} (56) \\
\text{M} &= \text{Ru} (57)
\end{align*}
\]
```

Removal of the solvent from the solution gave an off-white solid. The IR spectrum of this material recorded, in Nujol, gave two terminal ν(CO) bands of equal intensity at 2072 and 2002 cm⁻¹ as expected for a cis arrangement of carbonyls and
consistent with the cis-octahedral formulation for (56) (Figure 3.2). IR spectroscopy is particularly useful for identifying the co-ordination of $BF_4^-$ to a metal centre.\textsuperscript{60}\textsuperscript{12} Co-ordination of the highly symmetric $BF_4^-$ ($T_d$) anion leads to a significant lowering of the symmetry which results in characteristic splitting of the B-F stretching vibrations. The IR spectrum of $[OC-6-I3][RuF(FBF_3)(CO)_{2}(PPh_3)_{2}]$ (56) shows six $\nu$(BF) bands at $1204 \text{ m}, 1148 \text{ s}, 1127 \text{ s}, 944 \text{ w}, 918 \text{ s}$ and $895 \text{ s cm}^{-1}$. Four $\nu$(BF) bands are expected for the $C_3$ symmetry of the $M$-$F$-$BF_3$ group but, since there are two isotopes of boron $^{10}B$ (20 \%) and $^{11}B$ (80 \%), the number of $\nu$(BF) bands is expected to be eight. Only six absorptions are observed, since the $\nu(10B)$ bands are weak due to a lower natural abundance and because some of the stretches may be obscured by other vibrations in the molecule (Figure 3.3). Non co-ordinated, symmetrical, $BF_4^-$ is expected to show $\nu$(BF) at ca. 1050 cm$^{-1}$.\textsuperscript{60}

Metal complexes of weakly co-ordinated anions such as $BF_4^-$, $PF_6^-$, $AsF_6^-$ and $SbF_6^-$ are well known especially those of $BF_4^-$, and have been the subject of a review.\textsuperscript{12} The complex $[OC-6-I3][Ru(FBF_3)_{2}(CO)_{2}(PPh_3)_{2}]$ containing two weakly co-ordinating $BF_4^-$ groups has been reported.\textsuperscript{71} This was successfully synthesized from the dichloride complex $[OC-6-33][RuCl_2(CO)_{2}(PPh_3)_{2}]$ with AgBF$_4$ in a non co-ordinating solvent (CH$_2$Cl$_2$), and characterized by $^{19}F$ NMR and IR spectroscopies. The $^{19}F$ NMR spectrum recorded at -60$^\circ$C showed two resonances, a doublet at $\delta$ -143.3 and a mutually-coupled quartet at $\delta$ -272.7 with a $J$(FF) interaction of 89 Hz. Interestingly, no coupling to phosphorus was reported. The IR spectrum exhibited eight bands associated with $\nu(10B)$ and $\nu(11B)$ as expected for co-ordinated $BF_4^-$ ($\nu(11B) = 1171 \text{ s}, 1152 \text{ s}, 1145 \text{ s and 875 s cm}^{-1}$; $\nu(10B) = 1210 \text{ m}, 1200 \text{ m}, 1191 \text{ m and 904 m cm}^{-1}$).\textsuperscript{71} These data are in good agreement with those for $[RuF(FBF_3)(CO)_{2}(PPh_3)_{2}]$ reported here. The analogous reaction of $[OC-6-I3][OsF_2(CO)_{2}(PPh_3)_{2}]$ with $BF_3(g)$ is believed to result in a similar compound $[OC-6-I3][OsF(FBF_3)(CO)_{2}(PPh_3)_{2}]$ (57). However, this proved insoluble, precluding NMR studies, but the solid-state IR spectrum, recorded in Nujol exhibits a number of $\nu$(BF) bands (1212 m, 1154 s, 1140 s, 941 w, 902 m and 880 s cm$^{-1}$) showing that the $T_d$ symmetry of the free $BF_4^-$ anion has been removed, indicating co-ordination of $BF_4^-$. The complexes $[OC-6-I3][MF(FBF_3)(CO)_{2}(PMe_3)_{2}]$ where $M = Os, Ru$, also
show a similar number of bands in the ν(BF) region indicating that BF$_4^-$ is co-
ordinated.

Organometallic compounds of weakly co-ordinating anions are highly reactive. The co-ordinated anions are excellent leaving groups and can easily be replaced by other ligands under mild conditions and are known to catalyse a number of reactions.$^{[9]}$ For this reason the reactivity of the complexes [MF(FBF$_3$)(CO)$_2$(PR$_3$)$_2$] was investigated.

3.3 Displacement of Weakly Co-ordinated BF$_4^-$ in the Complexes [OC-6-12][MF(FBF$_3$)(CO)$_2$(PR$_3$)$_2$] with Tertiary Phosphines and Carbon Monoxide

The moisture-sensitive compounds [OC-6-13][MF(FBF$_3$)(CO)$_2$(PR$_3$)$_2$], M = Ru or Os and R = Ph or Me, were found to be insoluble in non-polar solvents. However, upon addition of tertiary phosphine, reaction occurs at room temperature and the metal complexes dissolve to give pale yellow solutions. Combinations of $^{19}$F and $^{31}$P NMR spectroscopies revealed the presence of one major complex in solution [OC-6-13][MF(CO)$_3$(PR$_3$)$_2$][BF$_4^-$] [(S8-61) Figure 3.4], [OC-6-13] denoting the cis,mer arrangement of ligands. The arrangement of ligands in the complexes correspond exactly to that of [MF(FBF$_3$)(CO)$_2$(PR$_3$)$_2$], with the weakly co-ordinating BF$_4^-$ ion replaced by a neutral tertiary phosphine ligand to give the cationic complexes (S8-61). Similarly, placing [MF(FBF$_3$)(CO)$_2$(PR$_3$)$_2$] under two atmospheres of CO(g) at room temperature in a non-polar solvent (CH$_2$Cl$_2$) affords [OC-6-13][MF(CO)$_3$(PR$_3$)$_2$][BF$_4^-$] (62-65) with a mer,trans arrangement of ligands the weakly co-ordinated anion being replaced by CO as evidenced by $^{19}$F and $^{31}$P NMR spectroscopies (Figure 3.5).
3.3.1 Discussion of the data for [MF(CO)₂(L)(PR₃)₂][BF₄] (58-65)

(a)¹⁹F and ³¹P{¹H] NMR Spectroscopy

The ¹⁹F spectra of complexes (58-61) (Table 3.1), each show one resonance with an apparent quartet structure, which is presumably an overlapping doublet of triplets with the metal-bound fluoride ligand coupling to the chemically unique P_b and the two mutually trans P_a nuclei (Figure 3.6). The chemical shifts of the fluoride resonances are in the region characteristic of a fluoride trans to a carbonyl ligand in a cationic complex with the coupling constants characteristic of cis ²J(PF) interactions (ca. 30 Hz for osmium and 20 Hz for ruthenium) (see section 2.2.1). The ³¹P{¹H] NMR spectra of (58), (60) and (61) (Table 3.1), each show two, mutually coupled, resonances, a doublet of doublets (P_a) and a doublet of triplets (P_b) (Figure 79).
3.6), in a 2:1 ratio respectively. The doublet of doublets structure for $\text{Pa}$ arises from coupling to $\text{Pb}$ and $\text{F}$, with the $\text{P}_a$-$\text{Pb}$ coupling (ca. 25 Hz) typical of cis $^2J(\text{PP})$ interactions (ca. 20 Hz). The doublet of triplets structure for $\text{Pb}$ results from coupling to $\text{F}$ and the two equivalent $\text{Pa}$ nuclei. The $^3\text{P}[^1\text{H}]$ NMR spectrum of \([\text{OsF(CO)}_2(\text{PPh}_3)_2][\text{BF}_4]\) (59) is not quite as straightforward and appears as a complex second-order multiplet at $\delta$ -14.5. This complex multiplet structure arises from the coincidence of $\delta(\text{Pa})$ and $\delta(\text{Pb})$. However, this second-order spectrum was successfully simulated using the Bruker PANIC (Parameter Adjustment in NMR by Iteration Calculation) program which gave a good fit between the observed spectrum and the theoretical spectrum (Figure 3.7). From this simulation a cis $^2J(\text{PP})$ coupling constant of 23 Hz was obtained. The $^{19}\text{F}$ and $^{31}\text{P}[^1\text{H}]$ NMR data for complexes (58-61) are presented in Table 3.1. The $^3\text{P}$ chemical shift for $\text{PR}_3\text{trans PR}_3$ ($\delta(\text{Pa})$) appears at a higher frequency than $\text{PR}_3\text{trans CO}$ ($\delta(\text{Pb})$) when the metal centre is ruthenium but the reverse is true when the metal is osmium.

Table 3.1 NMR Data for the Complexes \([\text{MF(CO)}_2(L)(\text{PR}_3)_2][\text{BF}_4]\)^a

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta(^{19}\text{F})$</th>
<th>$\delta(^{31}\text{P trans P})$</th>
<th>$\delta(^{31}\text{P trans CO})$</th>
<th>$^2J(\text{PF})$ / Hz</th>
<th>$^2J(\text{PP})$ / Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
<td>-405.0 (q)$^b$</td>
<td>-37.2 (d of d)</td>
<td>-33.7 (d of t)</td>
<td>44</td>
<td>28</td>
</tr>
<tr>
<td>59</td>
<td>-380.0 (q)$^b$</td>
<td>-14.7$^c$</td>
<td>-14.7$^c$</td>
<td>32$^d$</td>
<td>23$^d$</td>
</tr>
<tr>
<td>60</td>
<td>-398.2 (q)$^b$</td>
<td>-9.1 (d of d)</td>
<td>-5.5 (d of t)</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>61</td>
<td>-393.7 (q)$^b$</td>
<td>14.3 (d of d)</td>
<td>9.4 (d of t)</td>
<td>22</td>
<td>29</td>
</tr>
<tr>
<td>62</td>
<td>-433.7(t)</td>
<td>-30.0 (d)</td>
<td>-</td>
<td>42</td>
<td>-</td>
</tr>
<tr>
<td>63</td>
<td>-420.6 (t)</td>
<td>-8.9 (d)</td>
<td>-</td>
<td>31</td>
<td>-</td>
</tr>
<tr>
<td>64</td>
<td>-435.2 9t</td>
<td>0.1 (d)</td>
<td>-</td>
<td>22</td>
<td>-</td>
</tr>
<tr>
<td>65</td>
<td>-438.0 (t)</td>
<td>22.8 (d)</td>
<td>-</td>
<td>20</td>
<td>-</td>
</tr>
</tbody>
</table>

a Multiplicity in parentheses, (d) doublet, (t) triplet and (q) quartet.
b Apparent quartet (overlapping doublet of triplets).
c Overlapping second-order multiplet.
d Simulated value from PANIC.
e Mean Value.
Figure 3.6 a) $^{19}$F and b) $^{31}$P($^1$H) NMR Spectra of [OC-$^13$-13[RuF(CO)$_2$(PPh$_3$)$_3$][BF$_4$] (61)
Figure 3.7 a) Experimental and b) Simulated $^{31}\text{P}[^1\text{H}]$ NMR Spectra of [OC-6-$I_3$$\text{[OsF(CO)_{2}(PPh_3)](BF_4)}$ (59)
Figure 3.8 a) $^{19}$F and b) $^{31}$P[$^1$H] NMR Spectra of [OC-6-13][RuF(CO)$_3$(PPh$_3$)$_2$][BF$_4$] (65)
The $^{31}$P and $^{19}$F NMR spectra of complexes (62-65) were much simpler, each showing one resonance, a doublet and triplet respectively with mutual couplings (Figure 3.8). This indicates that the major species in solution contains two equivalent phosphine ligands coupling to one fluoride with the coupling characteristic of a cis $^{3}J$(PF) interaction. Once again, the $^{19}$F NMR chemical shifts of the fluoride ligands are in the region associated with fluorine trans carbonyl in a cationic complex, $^{33}$ which is shifted to lower frequency than that of the neutral metal fluoride complexes described in Chapter Two (ca. 8 -305 for [OsF$_2$(CO)$_2$(PPh$_3$)$_2$]). This can be rationalised in terms of the electron density at the metal centre. For complexes (63) and (65) these data correspond exactly to those reported recently for the octahedral complexes [OC-(5-(5)] [MF(CO)$_2$(PPh$_3$)$_2$][BF$_4$] obtained from the reaction of the acyl complexes [MF(CO)(CO)$_2$(PPh$_3$)$_2$] M = Os and Ru, with BF$_3$(g).$^{34}$ The $^{19}$F and $^{31}$P{$^{1}$H} NMR data for complexes (62-65) are presented in Table 3.1.

(b) Infrared and Mass Spectrometry

Removal of the solvent from the solutions afforded off-white solids. Positive ion FAB mass spectra of complexes (58-65) confirms the mononuclear nature of the complexes, with the parent ion with the correct isotope pattern often being observed, (Chapter Six, Table 6.3 and 6.4). The solid-state infrared spectra recorded in Nujol gave the expected two bands of equal intensity in the $\nu$(CO) region characteristic of cis carbonyls, for the complexes [MF(CO)$_2$(PR$_3$)$_2$][BF$_4$] (58-61). The values of $\nu$(CO) were higher than those of the neutral difluoride complexes [MF$_2$(CO)$_2$(PR$_3$)$_2$] (Chapter Two, Section 2.2.2). This can be attributed to the reduced electron density at the metal centre for the cationic complexes. This reduces the back-bonding from the metal to the $\pi$*-orbital of CO and hence the increase in $\nu$(CO) (Chapter Six, Table 6.3).

The solid-state infrared spectra of the tris carbonyl complexes, recorded in Nujol, gave the expected three bands for the mer arrangement of carbonyl ligands (Table 6.4, Chapter Six), with the $\nu$(CO) being much higher than the $\nu$(CO) of the difluoride complexes for the same reason as that outlined above.
3.4 Reaction of the Complexes [OC-6-13][MF(FBF₃)(CO)ₓ(PR₃)ₓ] with Olefins

So far, attempts to displace the weakly co-ordinated BF₄⁻ group in the complexes [OC-6-13][MF(FBF₃)(CO)ₓ(PR₃)ₓ] with unsaturated organic molecules such as ethylene has proved unsuccessful. However, the reaction of [RuF(FBF₃)(CO)ₓ(PR₃)ₓ] with ethyl vinyl ether resulted in polymerisation of the olefin to give a high molecular weight polymer with an average molecular weight of >40,000 and a polydispersity of six. This suggests that there are a number of polymeric chains of different chain lengths. This reduces the usefulness of this complex for catalysing the polymerisation of ethyl vinyl ether which is known to be readily polymerised by a number of cationic initiators to give polymers with low polydispersity.¹⁴

3.5 Metal Fluoride Complex Impurities in the Reaction of [OC-6-13][MF(FBF₃)(CO)ₓ(PR₃)ₓ] with Donor Ligands

In the reaction of [MF(FBF₃)(CO)ₓ(PR₃)ₓ] with PR₃ or CO, M = Os or Ru, R = Ph or Me, two additional minor species were observed in both the ³¹P and ¹⁹F NMR spectra. Attempts to separate these from (58-65) by column chromatography and crystallization failed. The cationic nature of the complexes (58-65) resulted in strong adhesion to the column material (alumina or silica) and eluting with highly polar solvents afforded no metal-bound fluoride complexes, presumably because of the solvolysis of the M-F bond. The two minor species are postulated to be the hydroxy compounds [MF(OH)(CO)ₓ(PR₃)ₓ] (66-69) (Figure 3.9), and the aquo species [MF(CO)ₓ(OH)ₓ(PR₃)ₓ][BF₄]⁻ (70-73) (Figure 3.10). The ³¹P{¹H} and ¹⁹F NMR spectra of both species each show one resonance with a doublet and triplet structure respectively with mutual couplings. This indicates that both contain one metal-bound fluoride ligand and two equivalent phosphine ligands with the coupling characteristic of cis ²J(PF) interactions.¹¹ The ¹⁹F NMR chemical shift for the fluoride resonance of the hydroxy species (66-69) is in the region characteristic of fluorine trans carbonyl (ca. δ -320). This suggests that the hydroxy complexes have the expected [OC-6-14] arrangement of ligands similar to the neutral difluoride complexes with one fluoride replaced by hydroxide. For the aquo complexes (70-73) the ¹⁹F NMR chemical shift for the fluoride resonances are at a much higher frequency
than expected (ca. δ -340) for a cationic complex (cf. [MF(CO)₅(PR₃)₂]⁺ (58-61) ca. δ -400 and [MF(CO)₅(PR₃)₂]⁺ (62-65) ca. δ -400). This is presumably due to strong intramolecular and possibly intermolecular hydrogen-bonding of the neutral H₂O ligand to the metal bound fluoride ligand. Similar hydrogen-bonding effects are thought to be responsible for the observation, in the ¹⁹F NMR spectrum, of free "F" at a higher frequency than expected. A difference of about 2000 ppm is expected between δ¹⁹F for F⁻ and F₂. However, δ¹⁹F for F occurs at only 542 ppm to lower frequency than that for F₂.¹⁷,¹⁸ This dramatic difference arises because it is impossible to obtain a fluoride ion that is not solvated or ion paired. Hydrogen-bonding is also responsible for some of the largest observed deshielding effects in ¹H NMR.¹⁸ This suggests that the stereochemistry of the aquo species is analogous to that of the hydroxy species (Figure 3.10). Although the hydroxy species (66-69) will also be subject to hydrogen bonding through the hydrogen of the hydroxy group and the metal-bound fluoride, the degree of this bonding is presumably less than in the aquo species since there is no dramatic shift in the ¹⁹F NMR resonances.

**Figure 3.9**

```
M = Os, R = Me (66)
M = Os, R = Ph (67)
M = Ru, R = Me (68)
M = Ru, R = Ph (69)
```
When M = Ru and PR₃ = PPh₃ the NMR data correspond exactly with those reported for the octahedral complexes [OC-6-14][RuF(OH)(CO)₂(PPh₃)₂] and [OC-6-14][RuF(CO)₂(OH₂)(PPh₃)₂][BF₄⁻], obtained from the reaction of water with [Ru(FBF₃)₂(CO)₂(PPh₃)₂]. The hydroxy and aquo species are believed to be in equilibrium, the equilibrium lying towards the aquo species. The aquo and hydroxy species are observed in a 3 : 1 ratio (Figure 3.11). A similar ratio of products being observed here. The ^{19}F and ^{1}P(¹H) NMR data for the complexes (66-73) can be seen in Table 3.2. Unfortunately, the proton resonances for the hydroxy group and coordinated water could not be distinguished from the bulk water in the ^{1}H NMR.
Table 3.2 NMR Data for the Complexes $[OC\cdot6\cdot14]^[MF(OH)(CO)\cdot2(PR\cdot3)\cdot2]$ and $[OC\cdot6\cdot14]^[MF(CO)\cdot2(OH\cdot2)(PR\cdot3)\cdot2][BF\cdot4]$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta$(19F)$^a$</th>
<th>$\delta$(31P)$^a$</th>
<th>$^2J$(PF) / Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>66</td>
<td>-327.8 (t)</td>
<td>-14.4 (d)</td>
<td>39</td>
</tr>
<tr>
<td>67</td>
<td>-322.7 (t)</td>
<td>2.0 (d)</td>
<td>30</td>
</tr>
<tr>
<td>68</td>
<td>-339.3 (t)</td>
<td>0.2 (d)</td>
<td>25</td>
</tr>
<tr>
<td>69</td>
<td>-344.7 (t)</td>
<td>21.5 (d)</td>
<td>22</td>
</tr>
<tr>
<td>70</td>
<td>-337.9 (t)</td>
<td>-17.3 (d)</td>
<td>37</td>
</tr>
<tr>
<td>71</td>
<td>-327.7 (t)</td>
<td>5.5 (d)</td>
<td>29</td>
</tr>
<tr>
<td>72</td>
<td>-341.5 (t)</td>
<td>2.4 (d)</td>
<td>25</td>
</tr>
<tr>
<td>73</td>
<td>-347.6 (t)</td>
<td>23.4 (d)</td>
<td>22</td>
</tr>
</tbody>
</table>

$^a$ Multiplicity in parentheses, (d) doublet and (t) triplet.

The source of water in these reactions must be the solvent, even though the solvents were rigorously dried prior to use. It appears that the Lewis acidic complexes formed before the addition of the donor ligand $[MF(FBF\cdot3)(CO)\cdot2(PR\cdot3)\cdot2]$ are extremely sensitive to moisture and scavenge it from every available source. The aquo and hydroxy species can be formed exclusively by the simple addition of BF\cdot3\cdotOEt\cdot2 to the difluoride complex dissolved in moist CH\cdot2Cl\cdot2 resulting in a ratio of aquo : hydroxy species of 3 : 1, similar to that obtained by Beck et al. in the hydrolysis of $[Ru(FBF\cdot3)(CO)\cdot2(PPh\cdot3)\cdot2]$. The aquo and hydroxy species $[RuF(CO)\cdot2(OH\cdot2)(PPh\cdot3)\cdot2]^+$ and $[RuF(OH)(CO)\cdot2(PPh\cdot3)\cdot2]$ were also observed in significant proportions when an attempt was made to form the difluoride complex $[OC\cdot6\cdot13][RuF(CO)\cdot2(PPh\cdot3)\cdot2]$ by the reaction of the chloride complex $[OC\cdot6\cdot33][RuCl\cdot3(CO)\cdot2(PPh\cdot3)\cdot2]$ with AgBF\cdot4 in CH\cdot2Cl\cdot2 followed by addition of N' Bu\cdot4F. Tertiarybutyl ammonium fluoride, which is extremely hygroscopic and holds water tenaciously even when dehydrated at 110°C under vacuum (0.1 mmHg) for three hours, is probably the source of water in this reaction. The formation of these complexes from four different reactions indicates that, in this system, water is a stronger nucleophile than fluoride.

The practically more convenient reactions of the difluoride complexes with BF\cdot3\cdotOEt\cdot2 [as opposed to BF\cdot3(g)], designed to abstract the fluoride ligand in the
presence of a donor ligand (CO or PR₃) also lead to the formation of the
[MF(CO)₃(PR₃)₂][BF₄] and [MF(CO)₃(PR₃)₂][BF₄] derivatives but, the aquo and
hydroxy species are also formed and in significantly greater quantities. This may be
attributed to the uptake of moisture by BF₃OEti.

3.6 Photolysis and Thermolysis of [OC-6-13][MF₂(CO)₃(PR₃)₂]

The cis,cis,trans ruthenium halide complexes [OC-6-33][RuX₂(CO)₂(L)₂], L =
tertiary phosphine or arsine, X = Cl, Br or I, are known to rearrange in solution under
the influence of UV radiation. The isomerisation to the all trans isomer [OC-6-
12][RuX₂(CO)₂(L)₂], via the loss and subsequent recombination of CO, was found to
be reversed by heating, reverting back to the cis isomer [OC-6-33] via the all cis
isomer [OC-6-32] (Figure 3.12). One carbonyl ligand of both the all trans isomer
and all cis isomer was found to be readily displaced by a number of ligands L’ to give
the complexes [OC-6-34][RuX₂(CO)(L)₂L’] in which L’ = NCMe, NCPH, C₂H₄,
SMe₂, OSMe₂ or PMe₂Ph and X = Cl, Br or I. Given the ease of isomerisation of
the heavier halide complexes of ruthenium, the effect of UV radiation and heat on the
difluoride complexes [OC-6-13][MF₂(CO)₃(PR₃)₂], M = Ru or Os and R = Me or Ph
have been studied.

Figure 3.12 Isomerisation of [OC-6-33][RuX₂(CO)₂(PR₃)₂]

\[
\begin{align*}
\text{OC} & \quad \text{PR₃} \\
\text{Ru} & \quad \text{X} \\
\text{PR₃} & \quad \text{OC} \\
\text{UV irradiation} & \quad \text{heat} \\
\end{align*}
\]

PR₃ = PMe₂Ph, X = Cl, Br or I
3.6.1 Photolysis of [OC-6-13][MF₂(CO)₃(PMe₃)₂]

UV irradiation of [OC-6-13][RuF²(CO)₃(PMe₃)₂] (44) in acetone or benzene solutions afforded no fluoride-containing product that could be attributed to either the all cis or all trans isomer. However, when the ruthenium fluoride complex is irradiated in the presence of free PMe₃ a number of species can be identified. Combinations of ¹⁹F, ³¹P{¹H} and ¹H NMR spectroscopies revealed the presence of two major complexes in solution, [OC-6-12][RuF₂(CO)(PMe₃)₃] (74) (Figure 3.13) and [OC-6-12][RuH(CO)(PMe₃)₃] (75) (Figure 3.14), along with starting material. The complex [OC-6-12][RuF₂(CO)(PMe₃)₃] (74) formed by the straightforward replacement of CO with PMe₃ is analogous to the displacement of CO by a phosphine ligand in the all trans and all cis isomers of the heavier halides. All the NMR data described below are from mixtures of (74) and (75) which could not be separated by conventional means. UV irradiation of the corresponding osmium complex [OsF₂(CO)₃(PMe₃)₂], both in the absence and presence of free PMe₃ resulted in no observed change. This suggests that the carbonyl groups are strongly bound to the osmium and are not displaced by UV irradiation.

3.6.1.1 Discussion of the Data for [OC-6-12][RuF₂(CO)(PMe₃)₃] (74)

The ¹⁹F NMR spectrum of [OC-6-12][RuF₂(CO)(PMe₃)₃] (74) revealed two resonances at 6 -301.3 (Fₐ) and 6 -312.8 (F₉) in a 1 : 1 ratio (Figure 3.15). The resonance associated with Fₐ is as a broad doublet, for which no coupling to phosphorus is resolved, whilst that of F₉ is a doublet of doublets of triplets with mutual ²J(Fₐ,F₉) cis coupling of 93 Hz. The remaining doublet of triplet couplings for F₉ arising from trans coupling to Fₐ with a ²J(P₉,F₉) coupling constant of 177 Hz and cis coupling to the two mutually trans phosphines (Pₐ) with a ²J(Pₐ,F₉) cis interaction of 25 Hz. This is consistent with the structure of (74) where the phosphine ligands are in a mer arrangement and the two fluorine ligands are chemically inequivalent (Figure 3.13). The assignment of the data to this structure was supported by ³¹P{¹H} NMR in which a mutually coupled doublet of triplets of doublets at 6 21.6 (Pₐ) and an apparent quartet at 6 1.7 (Pₐ) in a ratio of 1 : 2, with a cis ²J(Pₐ,P₉) coupling constant of 29 Hz was observed (Figure 3.15). The cis ²J(Pₐ,P₉) coupling constant, which was not resolved in the ¹⁹F NMR spectrum, was measured as 12 Hz. The observation of
an apparent quartet for $P_a$ is presumably due to the overlapping of the expected
doublet of doublets of doublets, in which $^2J(P_aF_b) = 25$ Hz, and $^2J(P_aP_b) = 29$ Hz are
already established which suggests that the coupling constant for $^2J(P_aF_a) = 27$ Hz. It
is noteworthy that the $^2J(P_bF_a)$ coupling constant is unusually small (ca. 12 Hz) which
implies that the phosphine ligand $trans$ fluoride is weakly bound. The complex (74)
represents a rare example of a neutral low-valent ruthenium fluoride complex where a
fluoride is $trans$ to a phosphine ligand. The arrangement of fluoride $trans$ phosphine is
thought to be unstable, based on electronic considerations, since the phosphine ligand,
especially a basic phosphine such as PMe$_3$ is unable to participate to any great extent
in back-bonding i.e. accepting electrons from the filled $p$ orbital of fluoride via the
metal centre, unlike CO where a considerable amount of back-bonding takes place
($vide$ $infra$ $v(CO)$ of the neutral metal difluoride complexes). Phosphine ligands are
able to accept electrons into the P-C $\sigma^*$-orbital however, this is thought to be weak.
This may account for the fact that the fluoride $trans$ to trimethylphosphine ($F_b$) is
shifted to lower frequency than fluoride trans to carbonyl ($F_a$), since the metal-
fluoride bond is weaker when trans to a weak $\pi$-acceptor ligand. A perusal of the
literature shows that the majority of the unambiguously characterized low-valent
metal fluoride complexes, especially those of the platinum group metals, contain a
fluoride ligand $trans$ to a carbonyl group.$^{[21]}

Figure 3.13

\[ \text{Figure 3.13} \]

\[ \text{(74)} \]

3.6.1.2 Discussion of the Data for [OC-6-12][RuH(CO)(PMe$_3$)$_4$]$^+$ (75)

The $^{31}$P($^1$H) NMR spectrum of [OC-6-12][RuH(CO)(PMe$_3$)$_4$]$^+$ (75) revealed
three resonances at $\delta$ -11.8 ($P_c$), $\delta$ -15.5 ($P_d$) and $\delta$ -21.0 ($P_b$) in a relative integrated
ratio of 2:1:1 respectively (Figure 3.16). The resonance associated with Pc was observed as a doublet of doublets coupling with Pd and Pe. That associated with Pd was observed as a doublet of triplets coupling with Pe and the mutually trans Pc nuclei, and that associated with Pe as a doublet of triplets coupling with Pd and Pc nuclei with mutual cis $^2J$(PdPc), $^2J$(PcPe) and $^2J$(PdPe) coupling constants of 40 Hz, 22 Hz and 36 Hz respectively. The $^{31}$P($^1$H)-$^{1}$H correlation spectrum can be seen in Figure 3.17. The multiplet structures (A2BC spin system) and couplings are consistent with the structure of (75). The presence of a metal bound terminal hydride ligand was confirmed by the low frequency resonance (ca. $\delta$ -9.3) in the $^1$H NMR spectrum. The resonance for the hydride ligand was observed as a doublet of quartets due to the similar H-P coupling of Pc and Pe [ca. 26 Hz cis $^2J$(HP) interaction] which causes the doublet of triplets expected to overlap to give a quartet which is then split further by the large trans $^2J$(HPd) interaction (ca. 74 Hz) (Figure 3.16). This hydride complex is isoelectronic and isostructural with the rhenium(I) hydride [ReH(CO)(PMe$_3$)$_4$] formed from the reaction of [ReH(PMe$_3$)$_4$] with CO.$^{122}$ It is unclear how the cationic complex (75) was formed wherein two fluoride ligands and one carbonyl have been replaced by two PMe$_3$ ligands and a hydride. The counterion for this complex is presumably BF$_4^-$ which was observed in the $^{19}$F NMR spectrum at $\delta$ -151.0. The formation of BF$_4^-$ arises from the fluorination of the borosilicate glass by F which was displaced from the metal centre during the reaction. The mononuclear nature of (75) was confirmed by positive FAB mass spectrometry which showed the correct isotope pattern for the parent ion at $m/z$ 435.

Figure 3.14

(75)
Figure 3.15  a) $^{19}$F and b) $^{31}$P($^1$H) NMR Spectra of 
[OC-6-12][RuF$_2$(CO)(PMe$_3$)$_3$] (74)
Figure 3.16  a) $^{31}$P($^1$H) and b) $^1$H NMR Spectra of 

$[OC-6-I2][RuH(CO)(PMe$_3$)$_4r$]’ (75)
Figure 3.17 $^3$P($^1$H) - $^3$P($^1$H) NMR COSY Spectrum of $[OC-6-12][RuH(CO)(PMe_3)_4]^+$ (75)
3.6.2 Thermolysis of \([OC-6-13][RuF_2(CO)_2(PMe_3)_2]\) (44) in the presence of PMe_3

The photolysis of \([OC-6-13][RuF_2(CO)_2(PMe_3)_2]\) (44) has already been shown to afford \([RuF_2(CO)(PMe_3)_3]\) via loss of CO. Therefore, the action of heat to remove a CO from the metal centre was investigated. However, no \([RuF_2(CO)(PMe_3)_3]\) was observed upon refluxing the ruthenium fluoride complex (44) in toluene in the presence of free PMe_3. Combinations of \(^1H, ^19F\) and \(^{31}P(1H)\) NMR spectroscopies revealed the presence of three major complexes in solution, the hydride complex (75) and two new species \(trans\)-\([RuF(CO)(PMe_3)_3]\)^+ (76) (Figure 3.18) and \([Ru(\eta^2-CO)_2-\text{OO}')(CO)(PMe_3)_3]\) (77) (Figure 3.19). All contain more than two PMe_3 ligands and only one carbonyl group. This indicates that one carbonyl group has indeed been replaced by PMe_3 but, due to the instability of fluoride \(trans\) phosphine (particularly at high temperature), further reaction has occurred. The NMR data described below are from mixtures of (75), (76) and (77).

**Figure 3.18**

![Diagram of complex 76](image)

(76)

**Figure 3.19**

![Diagram of complex 77](image)

(77)
Figure 3.20 a) $^{19}$F and b) $^{31}$P$^1$(H) NMR Spectra of trans-$\{RuF(CO)(PMe_3)_4\}^+$ (76)

a

b
3.6.2.1 Discussion of the Data for trans-[RuF(CO)(PMe$_3$)$_4$]$^+$ (76)

The $^{19}$F and $^{31}$P($^1$H) NMR spectra of trans-[RuF(CO)(PMe$_3$)$_4$]$^+$ (76) each show one resonance at $\delta$ -386.9 and $\delta$ -3.4 respectively with mutual quintet and doublet couplings and a $^2J(P_F)$ coupling constant of 30 Hz (Figure 3.20). This is consistent with the structure of (76) (Figure 3.18), where the four equivalent equatorial phosphorus nuclei are coupling to the metal-bound fluoride. The mononuclear nature of the complex was confirmed by positive ion FAB mass spectrometry which gave the characteristic pattern for [M - PMe$_3$]$^+$ at $m/z = 377$. The complex is isostructural to that of trans-[RuF(CO)(dppe)$_2$]$^+$, which according to the $^{19}$F and $^{31}$P($^1$H) NMR spectra has all four phosphorus atoms in the plane.$^{23}$ The formation of (76) shows that the labile CO has been replaced by PMe$_3$ but the complex formed, presumably [RuF$_2$(CO)(PMe$_3$)$_3$], must then be unstable at refluxing toluene temperatures. The fluoride trans carbonyl is less stable than fluoride trans carbonyl due to reduced synergic interactions, and since CO is a better $\pi$-acceptor, this fluoride ligand is then replaced by PMe$_3$ to give [RuF(CO)(PMe$_3$)$_4$]$^+$F$^-$. The $^1$F counterion reacts with the glass to give BF$_4$$^-$, which is observed in the $^{19}$F NMR at $\delta$ -151.0. A similar replacement of a metal-bound fluoride has been observed for the iridium(ni) aryl fluoride complexes [Cp'Ir(aryl)F(PMe$_3$)] which, upon reaction with PE$_3$ in the presence of trace amounts of water at room temperature, give the cationic complexes [Cp'Ir(aryl)(PE$_3$)(PMe$_3$)]$^+$F.xH$_2$O where Cp' = CsMes or CsMe$_2$Et and aryl = Ph or p-tolyl.$^{23}$

3.6.2.2 Discussion of the Data for [Ru(η$^2$-CO$_3$-OO')$^-(CO)(PMe$_3$)$_3$] (77)

The $^{31}$P($^1$H) NMR spectrum obtained for the carbonate complex (77) shows two resonances at $\delta$ 16.2 triplet (P$_0$) and $\delta$ 3.1 doublet (P$_0$) in a 1:2 ratio, with a cis $^2J(P_0P_0)$ coupling constant of 26 Hz. This corresponds exactly to the data reported for the compound [Ru(η$^2$-CO$_3$-OO')$^-(CO)(PMe$_3$)$_3$].$^{22}$ The formation of this carbonate species (77) infers that sometime during the reaction of [RuF$_2$(CO)$_2$(PMe$_3$)$_2$] with PMe$_3$ in refluxing toluene, CO$_2$(g) is produced. This may be generated from the CO(g) liberated during the course of the reaction interacting with moisture giving CO$_2$(g) and H$_2$(g).$^{23}$ The moisture present in the reaction may also account for the formation of the hydride species (75). The observation that [RuCl$_2$(PMe$_3$)$_4$] reacts...
with sodium sand amalgam under an atmosphere of CO\textsubscript{2}(g) to give the carbonate complex (77)\textsuperscript{[22]} may indicate that the formation of the carbonate complex from [RuF\textsubscript{2}(CO)\textsubscript{2}(PMe\textsubscript{3})\textsubscript{3}] proceeds via reaction of the unstable species [RuF\textsubscript{2}(PMe\textsubscript{3})\textsubscript{3}], the CO\textsubscript{2}(g), H\textsubscript{2}(g) and PMe\textsubscript{3} acting as the reducing agent rather than the sodium amalgam. The formation of the carbonate species from the difluoride complex was further confirmed by a single crystal X-ray structure determination.

3.6.2.3 Discussion of the Crystal Structure of [Ru(\eta^3-CO\textsubscript{2}-OO')\textsubscript{(CO)}(PMe\textsubscript{3})\textsubscript{3}] (77)

Single crystals of [Ru(\eta^3-CO\textsubscript{2}-OO')(CO)(PMe\textsubscript{3})\textsubscript{3}] (77) were grown from a toluene solution by slow evaporation. The crystal structure of complex (77) was then determined, details of data collection can be found in the Appendix. The molecular structure is shown in Figure 3.21 and confirms the predicted ligand arrangement.\textsuperscript{[22]} Selected bond lengths and angles are presented in Table 3.3. The carbonate ligand is essentially trigonal planar and bound in an \eta^3 fashion. The C(11)-O(4) bond retains marked double bond character [1.239(8) \textdegree\textsubscript{A}] and similarly C(11)-O(2) [1.304(8) \textdegree\textsubscript{A}] and C(11)-O(3) [1.313(8) \textdegree\textsubscript{A}] must also have some multiple bond nature [cf a typical C-O single bond of 1.43 \textdegree\textsubscript{A}]\textsuperscript{[23]} The dimensions of the carbonate ligand are within the expected range observed for other bidentate carbonates.\textsuperscript{[22,24]} The mutually trans phosphine ligands are bent toward the \eta^3-carbonate ligand with a P(1)-Ru(1)-P(3) bond angle of 164.66(7)\textdegree. The Ru(1)-P(1) [2.363(2) \textdegree\textsubscript{A}], Ru(1)-P(2) [2.294(2) \textdegree\textsubscript{A}] and Ru(1)-P(3) [2.389(2) \textdegree\textsubscript{A}] bond distances are within the expected range observed for other ruthenium(II) trimethylphosphine complexes.\textsuperscript{[25]} However, the Ru(1)-P(2) distance is significantly shorter (ca. 0.08 \textdegree\textsubscript{A} on average) than Ru(1)-P(1) and Ru(1)-P(3) which can be attributed to the weaker trans influence of CO\textsubscript{2}\textsuperscript{+} compared to that of PMe\textsubscript{3}. The Ru(1)-C(1) and C(1)-O(1) bond distances of 1.816(7) \textdegree\textsubscript{A} and 1.152(8) \textdegree\textsubscript{A} respectively lie within the range expected for terminal carboxyls bound to ruthenium.\textsuperscript{[27]} However, these bond lengths are towards the lower and higher end of the range respectively indicating the presence of significant back bonding from the metal which is in keeping with the low \nu(CO) observed (ca. 1935 cm\textsuperscript{-1}).
Table 3.3 Selected Bond Lengths (Å) and angles(°) for the Complex 
\([\text{Ru}(\eta^2-\text{CO}_3-\text{OO'})\text{(CO)}\text{(PMe}_3)_3]\) (77)

<table>
<thead>
<tr>
<th>Bond Lengths / Å</th>
<th>Bond Angles / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)-C(1)</td>
<td>1.816(7)</td>
</tr>
<tr>
<td>P(1)-Ru(1)-P(2)</td>
<td>94.60(7)</td>
</tr>
<tr>
<td>Ru(1)-O(2)</td>
<td>2.158(4)</td>
</tr>
<tr>
<td>P(1)-Ru(1)-P(3)</td>
<td>164.66(7)</td>
</tr>
<tr>
<td>Ru(1)-O(3)</td>
<td>2.115(4)</td>
</tr>
<tr>
<td>P(2)-Ru(1)-P(3)</td>
<td>100.73(7)</td>
</tr>
<tr>
<td>Ru(1)-P(1)</td>
<td>2.363(2)</td>
</tr>
<tr>
<td>O(2)-Ru(1)-O(3)</td>
<td>61.4(2)</td>
</tr>
<tr>
<td>Ru(1)-P(2)</td>
<td>2.294(2)</td>
</tr>
<tr>
<td>C(1)-Ru(1)-O(2)</td>
<td>111.8(2)</td>
</tr>
<tr>
<td>Ru(1)-P(3)</td>
<td>2.389(2)</td>
</tr>
<tr>
<td>C(1)-Ru(1)-P(2)</td>
<td>91.4(2)</td>
</tr>
<tr>
<td>C(1)-O(1)</td>
<td>1.152(8)</td>
</tr>
<tr>
<td>O(2)-C(1)-O(3)</td>
<td>113.1(6)</td>
</tr>
<tr>
<td>C(11)-O(2)</td>
<td>1.304(8)</td>
</tr>
<tr>
<td>C(11)-O(3)</td>
<td>1.313(8)</td>
</tr>
<tr>
<td>C(11)-O(4)</td>
<td>1.239(8)</td>
</tr>
</tbody>
</table>

Figure 3.21 Molecular Structure of \([\text{Ru}(\eta^2-\text{CO}_3-\text{OO'})\text{(CO)}\text{(PMe}_3)_3]\) (77)
3.6.3 Photolysis of \([OC-6-13][RuF_2(CO)_2(PPh_3)_2]\)

The photolysis of \([OC-6-13][RuF_2(CO)_2(PMe_3)_2]\) has been shown to afford \([OC-6-12][RuF_2(CO)(PMe_3)_2]\) (74) and \([OC-6-12][RuH(CO)(PMe_3)_2]\) (75). It was therefore of interest to study the photolysis of \([OC-6-13][RuF_2(CO)_2(PPh_3)_2]\). The UV irradiation of \([OC-6-13][RuF_2(CO)_2(PPh_3)_2]\) (42) in d^6-benzene solution in the presence or absence of free triphenylphosphine neither resulted in isomerisation, as observed with the heavier halides, nor in substitution of a carbonyl group for phosphine as observed in the photolysis of \([RuF_2(CO)_2(PMe_3)_2]\) in the presence of PMe_3. Combinations of ^19F and ^31P[^1H] NMR spectroscopic data revealed the presence of only one major complex in solution, namely the triply-bridged species \([Ru_2(u-F)_3(CO)_2(PPh_3)_4]^+\) (97) (Figure 5.7), along with unreacted starting material. The counterion is presumably HFa in the first instance, which is readily converted to BF_4 upon reaction with glass. The triply-bridged fluoride complex is described in Chapter Five along with its spectroscopic data and proposed mechanism of formation. The mechanism described in Chapter Five involves the loss of triphenylphosphine in the first step. The photolysis of \([OC-6-13][RuF_2(CO)_2(PPh_3)_2]\) is believed to follow the same reaction pathway with the loss of CO being the first step in this case.

3.6.4 Thermolysis of \([OC-6-13][RuF_2(CO)_2(PPh_3)_2]\)

The thermolysis of \([OC-6-13][RuF_2(CO)_2(PPh_3)_2]\) (42), with or without the presence of triphenylphosphine, leads only to isolation of unreacted starting material and phosphine oxide Ph_3P(O). The formation of triphenylphosphine oxide may suggest that reaction has taken place to give the triply bridged cationic species \([Ru_2(u-F)_3(CO)(PPh_3)_4]^+\) (97) which decomposes under these conditions.

3.6.5 Summary of the Photolysis and Thermolysis of \([OC-6-13][MF_2(CO)_2(PR_3)_2]\), where M = Os and Ru and R = Me or Ph

From these reactions it can be seen that a carbonyl ligand in the ruthenium fluoride complexes \([OC-6-13][RuF_2(CO)_2(PR_3)_2]\) where R = Me or Ph, is readily displaced by the action of heat or UV irradiation, to afford the complexes \([OC-6-12][RuF_2(CO)(PMe_3)_2]\) (74), \([OC-6-12][RuH(CO)(PMe_3)_2]\) (75), trans-[RuF(CO)(PMe_3)_2]^+ (76), [Ru(η^2-CO-OO')(CO)(PMe_3)_2] (77) and [Ru(u-
F)\textsubscript{3}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{4}\textsuperscript{+} (97). The loss of CO in the analogous chloride, bromide and iodide complexes is said to be the first step in the isomerisation of [OC-6-33][RuX\textsubscript{2}(CO)\textsubscript{2}(PR\textsubscript{3})\textsubscript{2}] to the all trans isomer [OC-6-12][RuX\textsubscript{2}(CO)\textsubscript{2}(PR\textsubscript{3})\textsubscript{2}].\textsuperscript{19,20}

However, no such isomer was observed in reaction of the fluoride complexes. This may be attributed to the instability of the all trans isomer, as fluorine trans to fluorine is inherently unstable when compared to fluorine trans to carbonyl because there are no longer any stabilising synergic interactions between the π-donor fluoride and the π-acid CO. This could result in rapid reaction, either by displacement of carbonyl with a tertiary phosphine, which has been shown to occur in the all trans isomers of the heavier halides which then revert back to the cis,mer isomers,\textsuperscript{20} or by reaction at the fluoride ligand bound to the metal, which presumably must occur since the formation of (75-77) and (97) requires loss of a metal-bound fluorine. It is, therefore, unclear as to whether the reactions that take place during the photolysis or thermolysis of the difluoride complexes proceed via the [OC-6-13] isomer or are a result of isomerisation to the more reactive all trans [OC-6-12].

3.7 Reaction of [OC-6-13][MF\textsubscript{2}(CO)\textsubscript{2}(PR\textsubscript{3})\textsubscript{2}] with MeLi and MeMgBr where R = Ph or Cy, M = Os or Ru

The novel difluoride complexes [OC-6-13][MF\textsubscript{2}(CO)\textsubscript{2}(PR\textsubscript{3})\textsubscript{2}], M = Os or Ru and R = Ph or Cy, react at room temperature with excess of the organometallic reagents MeLi and MeMgBr with retention of configuration to yield the air-stable compounds [OC-6-13][M(Me)\textsubscript{2}(CO)\textsubscript{2}(PR\textsubscript{3})\textsubscript{2}] (Figure 3.22). The di-alkyl complexes were characterized by \textsuperscript{13}C\textsuperscript{1}H, \textsuperscript{31}P\textsuperscript{1}H NMR and IR spectroscopies and mass spectrometry. Of the five possible isomers, analogous to those of the halides (Figure 2.3) where X now equals the organic moiety, only the [OC-6-13] isomer was isolated.

The complexes [OC-6-13][Os(CH\textsubscript{3})\textsubscript{2}(CO)\textsubscript{2}(PR\textsubscript{3})\textsubscript{2}], where R = Ph and Cy, were characterized further by X-ray crystallography. If the reactions of the difluoride complexes (where PR\textsubscript{3} = PPh\textsubscript{3}) with MeLi and MeMgBr are carried out in a 1 : 1 ratio a small amount of the species [OC-6-13][MF(Me)(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] (Figure 3.23) can be detected as identified by \textsuperscript{1}H \textsuperscript{19}F and \textsuperscript{31}P\textsuperscript{1}H NMR spectroscopies, along with the disubstituted compound [OC-6-13][M(Me)\textsubscript{2}(CO)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2}] and starting material.
This implies that the metal-bound fluoride in the mono substituted complex is more reactive to MeLi and MeMgBr than the difluoride complex.

**Figure 3.22**

\[
\begin{align*}
\text{OC} & \quad \text{PR}_3 \\
\text{OC} & \quad \text{M} - \text{F} + 2 \text{R'Li} / \text{R'MgBr} \rightarrow \text{OC} & \quad \text{PR}_3 \\
\text{OC} & \quad \text{M} - \text{R} + 2 \text{LiF} / \text{FMgBr} \\
\end{align*}
\]

\(M = \text{Os}, \text{R} = \text{Ph}, \text{R'} = \text{Me} \quad (78)\)

\(M = \text{Os}, \text{R} = \text{Cy}, \text{R'} = \text{Me} \quad (79)\)

\(M = \text{Ru}, \text{R} = \text{Ph}, \text{R'} = \text{Me} \quad (80)\)

\(M = \text{Ru}, \text{R} = \text{Cy}, \text{R'} = \text{Me} \quad (81)\)

**Figure 3.23**

\[
\begin{align*}
\text{OC} & \quad \text{M} - \text{F} + \text{MeLi} \rightarrow \text{OC} & \quad \text{PR}_3 \\
\text{OC} & \quad \text{M} - \text{Me} + \text{LiF} \\
\end{align*}
\]

\(M = \text{Os} \quad (82)\)

\(M = \text{Ru} \quad (83)\)

The osmium chloride complex \([\text{OC} - 6 - 33] \text{[OsCl}_2(\text{CO})_2(\text{PPh}_3)_2]\) was also found to react with MeLi to give the dimethyl complex \([\text{OC} - 6 - 13] \text{[Os(CH}_3)_2(\text{CO})_2(\text{PPh}_3)_2]\) but a longer reaction time and warming was needed. However, as previously reported the ruthenium chloride complex \([\text{OC} - 6 - 33] \text{[RuCl}_2(\text{CO})_2(\text{PPh}_3)_2]\) underwent no reaction with MeLi.\(^{[28]}\)

A wide range of alkyl complexes of ruthenium(II) and osmium(II) have been reported in the literature.\(^{[29]}\) Alkyl complexes have been postulated as intermediates in a number of reactions of organic compounds which involve osmium and in particular
ruthenium catalysts or reactants. The simplest divalent allcyl complexes cis-[OsH(R)(CO)₄] and [Os(R)₂(CO)₄] are prepared by alkylation of the anion [Na][OsH(CO)₄] with ROSO₂ and alkylation of the dianion [Na]₂[Os(CO)₄] with RX respectively where R = Me or Et and X = Cl or OTs. Photolysis of cis-[OsH(Me)(CO)₄] in the presence of PPh₃ in air affords cis-[OsH(Me)(CO)₃(PPh₃)] whilst reaction of cis-[OsH(Me)(CO)₄] with Me₃N·2H₂O and PPh₃ provides fac-[Os(Me)₂(CO)₃(PPh₃)]. cis-[M(Me)₂(CO)₃(PMe₃)]₄, where M = Ru and Os, have been prepared by reaction of either [Ru₂(C₂Me)₄Cl] or [Os(PhC₂Me)₂(PMe₃)]₄ with MgMe₂ in the presence of PMe₃. Protonation of the zerovalent ethene complex, [Os(Ti=C₂H₄)(CO)₂(PPh₃)₂], with HX (X = Cl, O₂CCF₃ or OCIO₃) yields the complexes cis,cis,trans-[Os(Et)X(CO)₃(PPh₃)] which are prone to migratory insertion reactions to give mer,trans-[Os(C(O)Et)(CO)₃(PPh₃)][X] when treated with suitable ligands such as CO. Alkyl and phenyl complexes of the type [OC-5-3i][RuCl(R)(CO)(PPh₃)]₂, R = Ph, Cy, have been prepared by the reaction of the all-trans, [OC-6-12], or all-cis-isomers, [OC-6-23], of [RuCl₂(CO)₄(L)] with HgR₂ or SnMe₄. However, [OC-6-33][RuCl₂(CO)₄(L)]₂, L = PMe₂Ph, PMePh₂, PPh₃, or PPh₅, formed no alkyl complexes upon reaction with organomercury reagents or with Grignard and lithium alkyl reagents. The hydrido complexes [OC-6-31][MH(Cl)(CO)(PPh₃)]₂, M = Os or Ru, were also found to react with organomercury compounds HgR₂ (R = Ph, p-tolyl, o-tolyl or trans-β-styryl) but, in these particular examples, the five co-ordinate σ-aryl and alkenyl complexes mer-[MCl(R)(CO)(PPh₃)]₂, were isolated. Bromide and iodide analogues of these five co-ordinate compounds can be prepared through reactions with silver perchlorate followed by addition of excess of bromide or iodide ions.

3.7.1 Discussion of the Data for [OC-6-13][M(Me)₂(CO)₃(PR₃)]₂, R = Ph, Cy

For the complexes [OC-6-13][M(Me)₂(CO)₃(PR₃)]₂ (78-81) the metal-bound methyl groups give rise to triplet resonances in both the ¹H and ¹³C(¹H) NMR, each to low frequency of TMS, ¹J(PH) = ca. 7 Hz, ¹J(PC) = ca. 7 Hz, whilst the ³¹P NMR spectra give rise to the expected singlet resonance. Removal of the solvent from the solutions afforded off-white solids. Positive ion FAB mass spectra of complexes (78-81) support the formulation, the most intense peak being assignable to the ion 104
The solid-state IR spectra, recorded in Nujol, show the expected two bands for the cis arrangement of carbonyls. The $^3P(1^H)$, $^1H$ and $^{13}C(1^H)$ NMR data are detailed in Table 6.5 Chapter Six.

3.7.2 Description of the Molecular Geometry of $[\text{Os}(\text{Me})_2(\text{CO})_2(\text{PPh}_3)_2]$ (78) and $[\text{Os}(\text{Me})_2(\text{CO})_2(\text{PCy}_3)_2]$ (79)

Crystals of (78) and (79) suitable for X-ray diffraction were obtained from benzene by slow evaporation of the solvent. The complexes (78) and (79) crystallize as discrete molecular units separated by normal Van der Waals distances with no abnormally short intermolecular contacts. Both complexes crystallize in the triclinic P-1 space group. Consequently, the molecules lie on a crystallographic inversion centre and are, therefore, disordered. However, this disorder manifests itself only in the scrambling of the mutually trans carbonyl and methyl ligands. A similar scrambling has been observed in the complexes trans-[Ir(Me)(CO)(PPh$_3$)$_2$] and trans-[OsH(Me)(CO)$_2$(PPr$_3$)$_2$] which also contain methyl trans to carbonyl. The complex trans-[Ir(Me)(CO)(PPh$_3$)$_2$] crystallizes in the same space group (P-1). The deconvoluted ordered structure of $[\text{Os}(\text{Me})_2(\text{CO})_2(\text{PPh}_3)_2]$ (78) and $[\text{Os}(\text{Me})_2(\text{CO})_2(\text{PCy}_3)_2]$ (79) are illustrated in Figures 3.24 and 3.25 respectively. Selected bond lengths and angles are presented in Table 3.4.

The osmium(II) metal centre in both complexes is six co-ordinate with no significant distortions from pseudo-octahedral geometry. The osmium-phosphorus bond lengths are comparable to those of other neutral d$^5$ transition metal complexes; the phosphine ligand with the smaller cone angle has the shorter M-P distance. The osmium-phosphorus distances in (78) are equivalent within experimental error, with Os(1)-P(1) = 2.379(4) Å and Os(1)-P(2) = 2.377(4) Å and $\angle$ P(1)-Os(1)-P(2) = 179.29(14)$^\circ$. Similarly, in complex (79), the osmium-phosphorus distances are equivalent with Os(1)-P(1) = Os(1)-P(1') = 2.446(2) Å and $\angle$ P(1)-Os(1)-P(1') = 180.00$^\circ$ (exactly). The carbon of the methyl and carbonyl groups in Figures 3.24 and 3.25 bear the suffix (*) which denotes that the carbon atom is a composite atom representing the disordered C(carbonyl) and C(methyl) atoms. Although both (78) and (79) are disordered about methyl and carbonyl it has been suggested that the individual M-CO and M-Me bond lengths can be readily estimated.
Figure 3.24 Molecular Structure of \([\text{OC-6-13}]\text{[Os(Me)}_2\text{(CO)}_2\text{(PPh}_3\text{)}_2]\) (78)

Figure 3.25 Molecular Structure of \([\text{OC-6-13}]\text{[Os(Me)}_2\text{(CO)}_2\text{(PCy}_3\text{)}_2]\) (79)
Table 3.4 Selected Bond Lengths (Å) and Angles(°) for the Complexes

<table>
<thead>
<tr>
<th></th>
<th>[Os(Me)₂(CO)₂(PPh₃)₂] (78)</th>
<th>[Os(Me)₂(CO)₂(PCy₃)₂] (79)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d[Os-C(Me)]° / Å</td>
<td>2.101(2)</td>
<td>2.055 (12)</td>
</tr>
<tr>
<td></td>
<td>2.100(2)</td>
<td></td>
</tr>
<tr>
<td>d[Os-C(CO)]° / Å</td>
<td>1.900(2)</td>
<td>2.082 (12)</td>
</tr>
<tr>
<td></td>
<td>1.902(2)</td>
<td></td>
</tr>
<tr>
<td>d[Os-P]° / Å</td>
<td>2.379(4)</td>
<td>2.446 (2)</td>
</tr>
<tr>
<td></td>
<td>2.377(4)</td>
<td></td>
</tr>
<tr>
<td>d[C-O']° / Å</td>
<td>0.950(2)</td>
<td>0.91 (2)</td>
</tr>
<tr>
<td></td>
<td>0.951(2)</td>
<td>1.05 (2)</td>
</tr>
<tr>
<td>d[Os---OJ]° / Å</td>
<td>2.950(2)</td>
<td>2.992(12)</td>
</tr>
<tr>
<td>Me-Os-Me °</td>
<td>82.7(10)</td>
<td>91.7(5)</td>
</tr>
<tr>
<td>CO-Os-CO °</td>
<td>82(2)</td>
<td>91.7(5)</td>
</tr>
<tr>
<td>P-Os-P / °</td>
<td>179.29(14)</td>
<td>180.0(-)</td>
</tr>
</tbody>
</table>

° Atom C is a composite C(carbonyl) / C(methyl). These distances must be interpreted carefully - see text.

This estimation relies on two assumptions: (a) the M-C-O system is essentially linear and is collinear with the M-C(methyl) vector; (b) the true carbon-oxygen bond length in the M-C-O system is 1.14 Å. Using these assumptions and the determined Os---O distance of 2.950(2) Å for (78) the estimated Os-C(carbonyl) distance is 1.810 Å (i.e. 2.950 - 1.14). Similarly (79) exhibits an Os---O distance of 2.992(12) Å which gives an estimated Os-C(carbonyl) bond length of 1.852 Å. Additionally, assuming that the composite atom (C*) represents the strict average position between the C(carbonyl) and C(methyl) atoms, the Os-Me distance can be estimated as 2.190 Å for (78) (i.e. 2 x 2.000 - 1.810) and 2.258 Å for (79). These values can be compared with known Os-CO (trans methyl) and Os-Me (trans carbonyl) distances [c.f. Os-CO 1.924(18) Å and Os-Me 2.198(17) Å for trans-[Os(Me)(CO)₃(NNCH₃)(PMe₃)₂][BPh₄] and Os-CO 1.895(16) Å and Os-Me
2.174(15) Å for trans-[Os(I)(Me)(CO)2(PMe3)2].\(^{[19]}\) The occurrence of disorder between the methyl ligands and their trans carbonyls makes the discussion of any variations between the estimated and literature values somewhat difficult since the error associated with the estimated figure is large. In contrast, the difluoride species (OC-6-13)[MF2(CO)2(PR3)2], where M = Os, PR3 = PPh3, PCy3 and M = Ru, PR3 = PPh3, PEtPh3, are perfectly ordered structures. This may be as a result of intramolecular and intermolecular hydrogen-bonding.

3.8 Reaction of [RuF2(CO)2(PR3)2] with Trimethylsilyle Reagents

Carboxylic acids and their conjugate bases, the carboxylate anions, feature extensively in homogeneous catalysis systems.\(^{[40-43]}\) The carboxylate anions are versatile ligands and can be monodentate or chelating, although many of the former type are susceptible to bridge formation due to the proximity effect and/or high basicity of the pendant oxygen.\(^{[40-43]}\)

Platinum group metal carboxylato complexes have attracted considerable interest, and several compounds have been shown to possess substantial catalytic activity. In particular, the ruthenium complex (OC-6-13)[Ru(O)(O)2(CO)2(PCy3)2] has been shown to be an extremely active catalyst precursor in the hydrogenation of dimethyl oxalate to ethylene glycol.\(^{[42]}\) Considering this interest in carboxylato complexes, an attempt was made to synthesize such a complex from the difluorides [RuF2(CO)2(PR3)2].

As already discussed in Chapter One, the most common reactions of metal fluoride complexes is the abstraction of the fluoride ligand from the metal centre. Trimethylsilyl reagents are known to attack metal fluoride complexes, resulting in displacement of the fluoride ion from the metal centre.\(^{[25]}\) Here, formal activation of an Si-O bond by the ruthenium fluoride complex (OC-6-13)[RuF2(CO)2(PCy3)2], has been observed. Reaction of the neutral fluoride complex [RuF2(CO)2(PCy3)2] with trimethylsilyletrifluoroacetate results in direct replacement of fluoride with trifluoroacetate to afford the bis-trifluoroacetate complex (OC-6-13)[Ru(O)(O)2(CO)2(PCy3)2] (84) (Figure 3.26). The driving force for the reaction is the formation of the strong Si-F bond in FSiMe6. If the reaction is repeated using the chloride complex (OC-6-33)[RuCl2(CO)3(PPh3)2], no activation of the Si-O bond

108
bond is observed, even at refluxing methanol temperatures. This can be attributed to
the greater strength of the Si-F bond (553 kJmol⁻¹), compared to Si-Cl (473 kJmol⁻¹),
which acts as a thermodynamic driving force for the reaction.

**Figure 3.26**

(84)

3.8.1 Discussion of the Data for [OC₆-6-13][Ru(OC(CF₃)2)(CO)₂(PCy₃)₂] (84)

The ³¹P and ¹⁹F NMR spectra of complex (84) revealed single resonances, with no multiplicity, at δ 31.3 and δ 73.7 respectively. The ¹³P resonance is very similar to that of the difluoride complex [OC₆-6-13][RuF₂(CO)₂(PCy₃)₂] (ca. δ 36.6). The infrared spectrum of (84) shows two bands of equal intensity in the ν(CO) region, 2049 and 1986 cm⁻¹, for the carbonyl ligands. These two bands are of much higher wavenumber than the ν(CO) in [RuF₂(CO)₂(PCy₃)₂] (ca. 2017 and 1936 cm⁻¹), suggesting that trifluoroacetate is a worse (σ + π) donor than fluoride, there being less back-bonding from the metal to the carbonyl ligands in the trifluoroacetate complex.

The carboxylate ligands show three ν(CO₂) bonds at 1683, 1448 and 1418 cm⁻¹. The highest frequency of these can be attributed to C=O, and is generally lower than in other trifluoroacetate complexes [cf. 1727 and 1700 cm⁻¹ for [Pt(OC₂CF₃)₂(PPh₃)₂] and 1690 cm⁻¹ for [Ru(OC₂CF₃)₂(CO)(PPh₃)₂]], implying a long C=O bond. Conversely, the C-O stretch is at a higher wave number (cf. 1401 cm⁻¹ for [Pt(OC₂CF₃)₂(PPh₃)₂] and 1400 cm⁻¹ for [Ru(OC₂CF₃)₂(CO)(PPh₃)₂]), suggesting a short C-O bond. This indicates that the trifluoroacetate ligands in (84) possess some degree of delocalisation of electron density between the C=O and the C-O. In order to confirm the structure and bonding of the carboxylate complex (84) in the solid state, a single crystal X-ray diffraction study was undertaken. Crystals of
(84), suitable for X-ray diffraction, were obtained from a toluene solution by slow evaporation of the solvent. The geometry of the monomeric complex is depicted in Figure 3.27. The complex is pseudo-octahedral, consisting of two mutually trans tricyclohexylphosphines and η-trifluoroacetates trans to carbonyl. The trifluoroacetate backbone O(2),C(3),O(3),C(2) is planar. Selected bond lengths (Å) and bond angles (°) are presented in Table 3.5. The Ru-P distance of 2.4837(7) Å, although slightly long, is comparable with similar bonds in the majority of other octahedral ruthenium complexes containing mutually trans tricyclohexylphosphine ligands, see Chapter Two.

The P-Ru-P angle is 172.80(3)°, the small deviation from linearity is most likely to be due to steric interactions associated with the bulky tricyclohexylphosphine ligands and the CF$_3$ groups of the trifluoroacetate in the equatorial plane. Within the tricyclohexylphosphine ligands themselves, the geometry is normal.

The bond distances and angles in the monodentate trifluoroacetate ligand are comparable with those found in other compounds. The carbon-oxygen "single" bond O(2)-C(3) distance of 1.222(4) Å is similar to those in [Ru(CO)$_2$(HgCF$_3$)(O$_2$CCF$_3$)]$^{[26]}$ and [Ir(O$_2$CCF)$_2$(NO)(PPh$_3$)$_2$]$^{[27]}$ of 1.230(30) Å and 1.22(2) Å respectively. The similarity of the O(2)-C(3) and C(3)-O(3) distances, within experimental error, is consistent with delocalisation of electron density over the two oxygens and carbon of the trifluoroacetate ligand. The Ru-O(2) distance of 2.105(2) Å is comparable with those found in other ruthenium trifluoroacetate complexes (cf. [Ru(CO)$_2$(HgCF$_3$)(O$_2$CF$_2$)] (ca. 2.153(16) Å) and [Ru(O$_2$CCF$_3$)$_2$(MeOH)$_2$(2s,4s)-BDPP] (ca. 2.16(1) Å) where 2s,4s-BDPP = 2s,4s-bis(diphenylphosphino)pentane).$^{[49]}$

The slight decrease may be attributed to a greater degree of π-bonding to the ruthenium in (84). The fluorine atoms display the high degree of anisotropic thermal motion frequently observed in structures containing trihalomethyl groups.$^{[49]}$ The bond distances and angles associated with the carbonyl ligands Ru(1)-C(1) 1.865(3) Å and C(1)-O(1) 1.131(4) Å are as expected for non-cluster monomeric ruthenium carbonyl complexes.$^{[27]}$ These distances however, are at the bottom and top of their ranges respectively. The short Ru-C bond length indicates a considerable degree of back-donation of π-electron density from the metal which correlates with the IR data.
reported earlier. This back-donation is somewhat less than that observed for the fluoride complexes, where even shorter M-C and longer C-O bonds are observed (see Chapter Two).

Table 3.5 Selected Bond Lengths (Å) and Angles(°) for the Complex \([OC-6-13][Ru(O(CO)CF_3)_2(CO)_2(PCy_3)_2]\) (84)

<table>
<thead>
<tr>
<th>Bond Lengths / Å</th>
<th>Bond Angles / °</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)-C(1)</td>
<td>1.865(3)</td>
</tr>
<tr>
<td>Ru(1)-O(2)</td>
<td>2.105(2)</td>
</tr>
<tr>
<td>Ru(1)-P(1)</td>
<td>2.4837(7)</td>
</tr>
<tr>
<td>C(1)-O(1)</td>
<td>1.131(4)</td>
</tr>
<tr>
<td>C(3)-O(2)</td>
<td>1.222(4)</td>
</tr>
<tr>
<td>C(3)-O(3)</td>
<td>1.230(4)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.549(5)</td>
</tr>
<tr>
<td>P-Ru-P</td>
<td>172.80(3)</td>
</tr>
<tr>
<td>C-Ru-C</td>
<td>84.7(2)</td>
</tr>
<tr>
<td>O-Ru-O</td>
<td>80.72(11)</td>
</tr>
</tbody>
</table>

Figure 3.27 Molecular Structure of \([OC-6-13]-[Ru(O(CO)CF_3)_2(CO)_2(PCy_3)_2]\) (84)
3.9 Summary

The results obtained here have outlined the usefulness of fluoride as a ligand in organometallic chemistry, unique reactivity often being observed. The di-alkyl complexes $[OC-6-13][M(\text{Me})_2(\text{CO})_2(P\text{R}_3)_2]$ were found to be readily formed from the corresponding fluoride complexes, whereas longer reaction times and warming are required with the heavier halide compounds. Similarly, the difluoride complex $[OC-6-13][\text{RuF}_2(\text{CO})_2(P\text{Cy}_3)_2]$ was found to activate the Si-O bond in trimethylsilyltrifluoroacetate whereas no formal activation was observed with the chloride complex $[OC-6-33][\text{RuCl}_2(\text{CO})_2(P\text{Ph}_3)_2]$. Fluoride complexes containing a weakly co-ordinated BF$_4^-$, a latent co-ordination site, have been synthesized by the straightforward reaction of the fluoride complexes with BF$_3(g)$, and offer the potential for some interesting chemistry. In particular, such complexes may prove catalytically useful, since complexes with weakly co-ordinated anions have been shown to catalyse a number of reactions. The photolysis and thermolysis of the difluoride complexes have resulted in a number of new compounds, in particular a rare example of a neutral complex with a fluoride ligand trans to a phosphine group.
Chapter Three References


1990, 541.

1981, 103, 3223 and references cited therein.

Polyhedron, 1982, 1, 97.

12478.


Trans., 1976, 961.

[29] See for Example “Comprehensive Organometallic Chemistry II”, E. W. Abel,
Complexes of Ruthenium and Osmium Containing η^1 Carbon Ligands”, A. F.


1978, 446.


CHAPTER FOUR

Fluorination of Ruthenium Carbonyl \([\text{Ru}_3(\text{CO})_{12}]\) with \(\text{XeF}_2\)

and Elemental Fluorine
4.1 Introduction to Platinum Group Metal Carbonyl Fluoride Complexes

The class of low-valent organo-transition-metal fluoride complexes first approached in any systematic way was that of the metal carbonyl complexes. A number of examples of such compounds have been reported in the literature but characterization of these species is often based primarily on IR and microanalysis.\(^1\) The unambiguous characterization of compounds of the type \([MF_x(CO)_y]\) is difficult without single crystal X-ray diffraction or multinuclear NMR spectroscopy, for example, \(^19\)F, \(^{13}\)C and \(^{19}\)M (where \(M = \text{transition-metal which has a nuclear spin and } x = \text{atomic number e.g. } ^{103}\text{Rh}\)).

For the platinum group metals, only low-valent compounds of iridium,\(^2\)\(^3\) osmium\(^4\)\(^6\) and ruthenium\(^5\) stabilised by only carbonyl and fluoride ligands, have been unambiguously characterized. The ruthenium carbonyl fluoride \([\{\text{RuF}_2(CO)_3\}_4]\) has been observed in the high-pressure, high-temperature carbonylation of \([\{\text{RuF}_5\}_4]\)\(^5\) and in the fluorination of \([\text{RuF}_5]_{12}\) with XeF\(_2\) in HF or the chlorofluorocarbon solvent, Genetron 113 (CF\(_2\)CICF\(_2\)).\(^6\) The structure of the complex, determined crystallographically,\(^5\) revealed the presence of both terminal and bridging fluoride ligands in an arrangement similar to that for \([\{\text{RuF}_5\}_4]\).\(^7\) Only two other X-ray crystal structures of complexes stabilised solely by carbonyl and fluoride ligands have been determined to date. That of \([\{\text{ReF}(CO)_3\}_4]\)\(^8\) which is also tetrameric, and the dimer \([\text{Re}(CO)_5(p,-F)\text{ReF}_2]\).\(^9\) Notable in all of these species is the presence of fluoride bridges.

Tetrairidium dodecacarbonyl reacts with a large excess of XeF\(_2\) in anhydrous HF to give the binary fluoride \([\text{IrF}_2]\). However, if the stoichiometry of the reaction is controlled and \([\text{Ir}_4(CO)_{12}]\) is reacted with XeF\(_2\) in a 1:6 ratio, fluorination affords the iridium(III) compounds \(\text{fac-}\) and \(\text{mer-}\)[\(\text{IrF}_2(CO)_3]\). Removal of the solvent and redissolution in HF affords only the \(\text{fac}\) isomer, the thermodynamic product.\(^2\)\(^3\) These were characterized by a combination of IR spectroscopy, \(^{13}\)C, \(^{13}\)C-\(^{19}\)F, \(^{19}\)F NMR spectroscopies \((\delta F = 310 \text{ for } \text{fac-}[\text{IrF}_2(CO)_3], \delta F_{\text{max}} = 238 \text{ (triplet)} \text{ and } \delta F_{\text{max}} = 476 \text{ (doublet)} \text{ for } \text{mer-}[\text{IrF}_2(CO)_3] \text{ with a } ^{1}J(\text{FF}) \text{ coupling constant of } 75 \text{ Hz})\) and EXAFS spectroscopy in HF solution. The IR spectrum of the \(\text{fac}\) isomer shows the expected two bands in the \(\nu(CO)\) region at 2213 and 2165 cm\(^{-1}\), (c.f. 2143 cm\(^{-1}\) in free carbon monoxide). The increase in \(\nu(CO)\) from that of free CO is explained in
terms of the strongly electron withdrawing effect of the fluoride ligands, which remove electron density away from the d^6 Ir(III) metal centre, significantly increasing the σ-acceptor ability of the metal. This increase in σ-acceptor ability is then responsible for σ-donation from the slightly antibonding 5σ lone pair on CO to the metal, which along with little or no π-back donation from the metal to the carbonyl, is believed to increase ν(CO) above that of free CO.

**Figure 4.1 Osmium Carbonyl Fluoride Complexes**

![Diagram of Osmium Carbonyl Fluoride Complexes](image)

The oxidative fluorination of [OsF_2(CO)_4] with XeF_2 in anhydrous HF affords, in solution, cis-[OsF_2(CO)_4] (85) as the major product with [OsF(CO)_3][HF_2] (86), [OsF_2(μ-F)(CO)_3] (87) and [OsF_2(μ-F)(CO)_3][HF_2] (88) as minor products, all of which have been characterized by ^1^H, ^19^F and ^13^C-{^19^F} NMR spectroscopies (Figure 4.1). The removal of the HF solvent yields the insoluble tetrameric species [[OsF_2(CO)_3]_4] based on IR spectroscopy and X-ray powder diffraction. In contrast
to fac- and mer-[IrF₃(CO)₃], these osmium(II) carbonyl fluoride complexes are stable to excess of fluorinating agent (XeF₂) at room temperature.

4.2 Reaction between [Ru₃(CO)₁₂] and F₂ in AHF

The fluorination of [Ru₃(CO)₁₂] with XeF₂ in Genetron 113 or AHF has previously been described.¹⁰ Different carbonyl fluoride complexes were formed depending on the ratio of the reactants and the temperature of the reaction. The room temperature reaction of [Ru₃(CO)₁₂] with XeF₂ in a 1:3 mole ratio affords [[RuF₂(CO)₃]₄] which as identified by its IR spectrum and X-ray powder diffraction pattern, is identical to that of the crystallographically characterized [[RuF₂(CO)₃]₄] formed by the reaction of [[RuF₃]₄] with CO.⁵ When the ratio is increased to 1: ≥4.5 the room temperature reaction is reported to yield the 17 e⁻ species, [RuF₃(CO)₃]. This formulation was supported by EPR spectroscopy, magnetic-susceptibility data and IR spectroscopy. The number and position of the ν(CO) bands are consistent with facial carbonyls, as observed for [[RuF₂(CO)₃]₄], although the IR spectra for the ruthenium(II) and ruthenium(III) complexes are suspiciously similar. The magnetic moment (at room temperature) of 1.92 BM, is the same as that expected for a Ru(III) species with its one unpaired electron. However, the EPR spectrum of this material in AHF at -196°C failed to reveal hyperfine coupling to the fluorine nuclei. Although this does not rule out the assignment [RuF₃(CO)₃][¹⁰] there are clearly doubts about the characterization of this species. When a large excess of XeF₂ is used and the temperature is increased to 100°C, based on its IR spectrum and microanalysis, the mixed oxidation-state adduct [[RuF₂(CO)₃[RuF₃]₂] is said to be obtained.

In an attempt to unambiguously characterize the carbonyl fluoride complexes of ruthenium in solution this reaction has been reinvestigated and a detailed NMR spectroscopic investigation has been carried out.

Triruthenium dodecacarbonyl was found to be insufficiently soluble in simple halocarbons to allow an investigation of its fluorination in these solvents. However, Hope et al. have shown that [Ru₃(CO)₁₂] dissolves slowly in AHF (ca. 24 hours) with protonation to yield [RuH(CO)₃][HF₂] and [Ru₃H(CO)₁₂][HF₂].[¹¹] Considering the success already achieved using AHF as a solvent in the fluorination reactions of
it was considered worthwhile to study the fluorination of [Ru₃(CO)₁₂] in this solvent also.

Fluorination of in AHF was studied in the molar ratios [Ru₃(CO)₁₂] : XeF₂ from 1 : 1 through to 1 : 6. Reaction occurred at ca. -60°C with the liberation of xenon gas and the generation of a number of HF-soluble ruthenium complexes. The reaction was controlled by judicious cooling and venting liberated gases. At ratios greater than 1 : 3, unreacted XeF₂ was identified in the HF solution by ¹⁹F NMR spectroscopy (δ¹⁹F : -197.8, J(XeF) = 5679.5 Hz), while at ratios of less than 1 : 3, ¹H NMR spectra showed the presence of unreacted [RuH(CO)₅] and [Ru₃H(CO)₁₂]. At the 1 : 3 molar ratio neither XeF₂ nor protonated ruthenium species were observed. Further addition of XeF₂ (up to 1 : 27) had no effect on the species present. These results are not in accord with those reported previously where it appeared that an increase in the mole ratio of [Ru₃(CO)₁₂] : XeF₂ from 1 : 3 resulted in further fluorination. The room temperature ¹⁹F NMR spectrum at the 1 : 3 ratio revealed a series of broad resonances which sharpened only slightly on cooling. EPR spectroscopy showed no evidence of paramagnetic species. However, if the species formed in the reaction were kept cool (ca. -60°C) throughout and after the reaction, resonances with multiplet structure could be resolved. This suggests that the species formed in the reaction are fluxional and / or unstable at room temperature.

In an attempt to control the fluorination of [Ru₃(CO)₁₂], fluorine gas was also used as the oxidative fluorinating agent. Since F₂(g) has a limited solubility in AHF, fluorination of protonated ruthenium carbonyl takes place at the gas-liquid interface. This reduces the rate of fluorination and renders the F₂ / AHF system a "milder" fluorinating agent than XeF₂ dissolved in AHF where the F-XeF.HF adduct is known to act as a catalyst in the reactions. Thus "XeF₂" in AHF is a more aggressive fluorinating agent than dissolved elemental fluorine. As in the case where XeF₂ was used as a fluorinating agent, reaction of [Ru₃(CO)₁₂] with F₂(g) at -78°C in a 1 : 3 ratio afforded a number of HF-soluble ruthenium complexes. The ¹⁹F NMR spectrum recorded in AHF solution at -78°C, Figure 4.2, was dominated by a large singlet at δ -349 (Fₐ) (as in the fluorination with XeF₂) and eight less intense resonances: a singlet at δ -429.5 (F₈), four doublets at δ -285.7 (F₆), δ -283.4 (F₈), δ -344.9 (F₇) and δ -345.8 (F₇); two triplets at δ -463.7 (F₈) and δ -500.8 (F₈) and a
doublet of triplets at δ -455.5 (F₁) were also observed. There are also a further seven minor resonances: a singlet at δ -294.1 (F₂); two doublets at δ -287.9 (F₃) and δ -495.9 (F₄) and three triplets at δ-272.4 (F₅), δ -279.6 (F₆) and δ -467.8 (F₇).

These resonances, highly shifted from the usual chemical shift region of the $^{19}$F NMR nucleus, are characteristic of a fluoride ligand bound directly to a low-valent transition-metal centre. The spectra of the 1 : 3 molar ratio, recorded at -78°C, showed a large number of signals (Figure 4.3) whose assignment was not possible without recording selective $^{13}$C-$^{19}$F NMR spectra, which has been shown to be effective in the assignment of structures for the carbonyl fluoride complexes of osmium and iridium. However, this requires specialist NMR spectrometers and unfortunately within the time span of this thesis it has not proved possible to gain access to the EPSRC ultra-high field NMR service at the University of Edinburgh to obtain $^{13}$C-$^{19}$F spectra for the ruthenium system. Consequently, the following assignments remain speculative.

By comparing the spectra with those of the products of the fluorination of osmium carbonyl, [Os₃(CO)₁₂], with XeF₂ and using relative intensities and coupling constants it has been possible to suggest assignments for the majority of the species present in AHF solution (ca. 99%) from the fluorination of [Ru₃(CO)₁₂].

The large singlet in the $^{19}$F NMR at δ -349.0 (F₈), is in a region characteristic of fluoride trans to carbonyl on a neutral d⁸ metal centre, and can be assigned to cis-[RuF₂(CO)₄] (89) (Figure 4.4). This is isostructural and isoelectronic with cis-[OsF₂(CO)₄] (85), the major species in the fluorination of [Os₃(CO)₁₂] in AHF with XeF₂ or F₂(g).

The singlet at δ -429.5 (F₉) is assigned to the cationic species [RuF(CO)₅]^⁺ (90) (Figure 4.4) which is analogous to [OsF(CO)₅]^⁺ (86) in which the low-frequency shift is typical of a cationic fluoride complex. A doublet at δ -344.9 (F₁₀) and a triplet at δ -500.8 (F₁₀), with a ratio of 2 : 1 and a mutual 2J(FF) cis coupling of 79 Hz, are assigned to [Ru₂F₂(μ-F)(CO)₈]^⁺ (91) (Figure 4.4). This corresponds to the binuclear osmium fluoride cationic complex [Os₂F₂(μ-F)(CO)₈]^⁺ (88). The extremely low-frequency resonance for F₁₀ (ca. δ -500.8) is one of the lowest $^{19}$F chemical shifts reported, but is not an unreasonable shift for a bridging fluoride ligand in a cationic complex. The doublets at δ -285.7 (F₁₁), δ -345.8 (F₁₂), and the doublet of triplets at δ -455.5 (F₁₃) by couplings of 61 and 85 Hz
Figure 4.3 $^{13}$C NMR Spectrum of the Products from the Reaction of $[\text{Ru}_2(\text{CO})_6]$ with Elemental Fluorine
respectively, and in a ratio of 2 : 1 : 1 are assigned to [Ru₂F₃(μ-F)(CO)₇] (92) (Figure 4.4). This is analogous to the binuclear osmium fluoride cationic complex [Os₂F₃(μ-F)(CO)₇] (87). These couplings are typical of cis \(^3J(FF)\) coupling constants, with the low-frequency resonance typical of a bridging fluoride. The \(^{19}F\) NMR data can be seen in Table 4.1 along with the data reported for the corresponding osmium complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\delta(^{19}F)^b)</th>
<th>cis (^3J(FF)) / Hz</th>
<th>Assignment (Ru only)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ru</td>
<td>Os</td>
<td>Ru</td>
</tr>
<tr>
<td>[MF₃(CO)₅]⁺</td>
<td>-349.0(s) -342.5(s)</td>
<td>-342.5(s)</td>
<td>Fₐ</td>
</tr>
<tr>
<td>(89)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[MF(CO)₅]⁺</td>
<td>-425.9(s) -433.0(s)</td>
<td>-342.5(s)</td>
<td>F₈</td>
</tr>
<tr>
<td>(90)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[M₂F₂(μ-F)(CO)₉]⁺</td>
<td>-344.9(d) -336.0(d)</td>
<td>73 112</td>
<td>F₉</td>
</tr>
<tr>
<td>(91)</td>
<td>-500.8(t) -465.0(t)</td>
<td>73 112</td>
<td></td>
</tr>
<tr>
<td>[M₂F₃(μ-F)(CO)₉]⁺</td>
<td>-285.7(d) -266.0(d)</td>
<td>61 86</td>
<td>F₁₁</td>
</tr>
<tr>
<td>(92)</td>
<td>-345.8(d) -340.0(d)</td>
<td>85 117</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-455.5(dt) -412.5(dt)</td>
<td>61,85 86,117</td>
<td></td>
</tr>
<tr>
<td>[MF(CO)₃(μ-F)M(CO)₅]⁺</td>
<td>-283.4(d) -463.7(t)</td>
<td>63 -</td>
<td>F₉</td>
</tr>
<tr>
<td>(93)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fac-[MF(CO)₅]⁻</td>
<td>-294.1(s) -</td>
<td>- -</td>
<td>F₁</td>
</tr>
<tr>
<td>(94)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mer-[MF(CO)₅]⁻</td>
<td>-272.5(t) -</td>
<td>55 -</td>
<td>F₁</td>
</tr>
<tr>
<td>(95)</td>
<td>-495.9(d) -</td>
<td>55 -</td>
<td></td>
</tr>
<tr>
<td>[{MF(CO)₅}]₄</td>
<td>-279.6(t) -</td>
<td>61 -</td>
<td>F₉</td>
</tr>
<tr>
<td>(96)</td>
<td>-467.8(t) -</td>
<td>61 -</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Recorded in AHF at -78°C with d\(^2\) acetone as external lock.
\(^b\) (s) singlet, (d) doublet, (t) triplet and (dt) doublet of triplets.
\(^c\) Number in parentheses corresponds to the ruthenium complexes.
Figure 4.4 Ruthenium Carbonyl Fluoride Complexes

\[ \text{Complex } 89 \]

\[ \text{Complex } 90 \]

\[ \text{Complex } 91 \]

\[ \text{Complex } 92 \]

\[ \text{Complex } 93 \]

\[ \text{Complex } 94 \]

\[ \text{Complex } 95 \]

\[ \text{Complex } 96 \]
The doublet at δ -283.4 (F₁₀) and triplet at δ -463.7 (F₁₁), with a ratio of 2 : 1, both showing a mutual \(^2\)J(FF) cis coupling of 63 Hz are assigned to [RuF₂(CO)₅(μ-F)Ru(CO)₅]\(^+\) (93) (Figure 4.4), where the two terminal fluoride ligands are on the same metal centre as opposed to adjacent metals as in [Ru₂F₅(μ-F)(CO)₅]\(^+\) (91). The high-frequency resonance of δ -285.7 is in keeping with the high-frequency shift observed when the number of fluoride ligands on a metal centre is increased [c.f. δ -266.0 (F₀), δ -340.0 (F₁) and δ -412.5(F₂) for [Os₂F₆(μ-F)(CO)₅] (87), Figure 4.5]. The lower value of the cis \(^2\)J(FF) coupling constant in [RuF₂(CO)₅(μ-F)Ru(CO)₅]\(^+\) (93) (ca. 63 Hz) compared to that of [Ru₂F₅(μ-F)(CO)₅]\(^+\) (91) (ca. 73 Hz) is also indicative of an increase in the number of fluoride ligands on the metal centre (c.f. \(^2\)J(F₀F₁) 86 Hz and \(^2\)J(F₁F₂) 117 Hz in [Os₂F₆(μ-F)(CO)₅] (Figure 4.5)]. Therefore the data are in keeping with the structure assigned to [RuF₂(CO)₅(μ-F)Ru(CO)₅]\(^+\) (93).

For the minor resonances, the singlet at δ -294.1 (F₁₂) is assigned to fac-[RuF₃(CO)₅]\(^-\) (94) and the doublet and triplet at δ -495.9 (F₁₃) and δ -272.4 (F₁₄) respectively, to mer-[RuF₃(CO)₅]\(^-\) (95). The complexes (94) and (95) are isostuctural and isoelectronic with the iridium carbonyl fluorides, fac-[IrF₃(CO)₅] and mer-[IrF₃(CO)₅], identified in the fluorination of [Ir₅(CO)₁₂] with XeF₂.\(^{[2,3]}\) The high-frequency resonance of F₁ and F₁₂ are in a region characteristic of fluoride trans to carbonyl where the metal centre has three fluoride ligands co-ordinated,\(^{[4]}\) and the low-frequency resonance of F₁₃ is characteristic of F trans F.\(^{[2,3]}\) The broad doublet and triplet at δ -279.6 (F₁₅) and δ -467.8 (F₁₆) respectively, are assigned to the crystallographically characterized\(^{[5]}\) tetrameric species [[RuF₂(CO)₅]₄] (96) which is known to be formed in the fluorination of [Ru₃(CO)₁₂].\(^{[6]}\) The broadness of the signals is due to the slight second-order nature of the resonances as the four bridging fluorides and four terminal fluorides are all magnetically inequivalent. The formation of [RuF(CO)₅]\(^+\) (90) and [Ru₂F₅(μ-F)(CO)₅]\(^+\) (92) which have more carbonyl ligands around the metal centre than in the starting material, suggests that carbonyl scrambling must have occurred. It has been suggested that metal-metal bond cleavage in [M₃(CO)₁₂] (M = Ru or Os) is associated with carbonyl scrambling.\(^{[18]}\) It is likely, therefore, that a similar process may be occurring during the fluorination of [Ru₃(CO)₁₂]. Similar reasoning has been put forward to explain the formation of
[OsF(CO)]^+ (86) in the fluorination of [OsF(CO)]^+. The assignment of these structures is inevitably tentative without ^13^C-{^19^F} NMR data. In particular, the assignments in respect of (93-96) have to be treated with some caution since the analogous osmium complexes have not been reported.

The precise nature of the counterions to the charged species is unclear, but the ratio of cationic to anionic ruthenium carbonyl fluorides is 2 : 1, and thus the remainder of the anions are presumably [HF]^−.

These NMR data indicate that there are number of HF-soluble ruthenium carbonyl fluoride complexes formed in the reaction of [RuF(CO)]^2 with F_2(g). These have been identified by a combination of chemical shift, relative intensities and coupling constants, and by comparison with reported data for osmium[^8] and iridium[^2,3] carbonyl fluoride complexes. The observation of more carbonyl fluoride complexes for ruthenium is a consequence of increased lability of carbonyl ligands in ruthenium halide complexes when compared to those of osmium.[^9,20] This study represents the first ^19^F NMR data reported for ruthenium(II) complexes stabilised by only carbonyl and fluoride ligands and shows that the earlier report[^6] of ([RuF_2(CO)]_3) in HF solution after the fluorination of [RuF(CO)]^2 is correct but the existence of higher oxidation state ruthenium species [RuF_3(CO)]^3 and ([RuF_2(CO)]_3,RuF_3)_2] in solution is in error. The experiments were found to be reproducible with only minor variations in the product ratios and, as with the osmium carbonyl fluorides,[^4] the ruthenium species are stable to further fluorination.

**Figure 4.5**

![Diagram of ruthenium complex](image)
This work extends the $^{19}$F NMR data available for low-valent metal fluoride complexes, the $^{19}$F chemical shift range for F trans CO now being δ - 272 to -500. The lowest frequency resonances are readily assigned to bridging-fluoride ligands, but care must be taken in the assignment of a particular resonance in a complicated $^{19}$F NMR spectrum as F trans F resonances also appear at this same low-frequency region (ca. δ - 496). It is interesting to note that F₅, F₆ and F₇ have very similar $^{19}$F NMR chemical shifts and have very similar chemical environments, i.e. they are bound to octahedral ruthenium(II) metal centres with cis-“F₂(CO)₄” ligand arrangements. Decreasing the number of fluoride ligands bound to the metal centre causes a low-frequency shift, δ - 425.9 for [RuF(CO)₅]⁺ compared with δ -349.0 for [RuF₂(CO)₄], while increasing the number of fluorines causes a high frequency shift, δ - 294.1 for [RuF₃(CO)₃]. Comparable shifts were observed in the carbonyl fluoride phosphine complexes described in Chapter Two and Three. It may, therefore, be postulated that the electron density at the metal centre has a significant effect on the $^{19}$F chemical shifts in these systems.

Removal of the HF solvent, at room temperature, from the products of fluorination of [Ru₃(CO)₁₂] with either XeF₂ or F₂ in a ratio of 1 : 3 affords a pale yellow, moisture-sensitive solid. The IR spectrum of this poorly crystalline material is identical to that reported for the X-ray crystallographically characterized [[RuF₃(CO)₃]₄]. This polymerisation of the major species cis-[RuF₂(CO)₄] (89) with the loss of CO is similar to that observed in the osmium carbonyl fluoride system which gives the analogous osmium tetrameric species, [[OsF₂(CO)₃]₄]. The fluorination of [Ru₃(CO)₁₂] to give mainly cis-[RuF₂(CO)₄] is comparable to oxidations with the heavier halogens (X₂; X = Cl, Br or I) which give cis-[RuX₂(CO)₄] which, in turn, readily polymerise to afford the oligomeric complexes [RuₓX₄(CO)₆], [Ru₃X₆(CO)₁₂] and the polymer [[RuX₂(CO)₃]₄]. The stability of the halide complexes of the type cis-[RuX₂(CO)₄] follows the order F < Cl < Br < I, since elevated temperatures are needed to polymerise the bromo and iodo complexes. This suggests that the fluoride complex has greater carbonyl lability.
Chapter Four References


CHAPTER FIVE

Reaction of Low-Valent Osmium and Ruthenium Hydride Complexes with Anhydrous HF
5.1 Introduction

A number of methods reviewed in Chapter One have been successfully used to introduce fluorine into low-valent transition-metal compounds. These reactions can be classified as halide exchange reactions, oxidative addition reactions, reactions involving displacement of weakly co-ordinating ligands or reactions of HF with metal hydride complexes (Table 5.1). However, the level of certainty in the identity of the metal fluoride compounds produced varies considerably, with characterization in many cases relying solely on elemental analysis and IR spectroscopy.

In this chapter the use of AHF as a route to low-valent metal fluorides via its reaction with metal hydride complexes is described. Although reactions involving HF and selected platinum group metals have been reported (Table 5.1) the products have been poorly characterized and in many cases, isolation of metal-fluoride complexes remains doubtful. However, the reaction with other metals has resulted in the occasional unambiguous characterization of a metal fluoride complex. The reaction of the tungsten(II) compound [WH(η^5-CH2PMe2)(PMe3)4] with aqueous HF results in protonation and isolation of the crystallographically characterized fluoride complex [WFH2(H2O)(PMe3)4]F, the anion being involved in hydrogen bonding with the H2O ligand. Dehydration with potassium hydride results in isolation of the difluoride complex [WF2H2(PMe3)4], as characterized by 1H, 19F and 31P NMR spectroscopies, a reaction which is reversible upon addition of H2O (Figure 5.1). Similar reactions of the hydrides with HCl have been reported, resulting in the loss of dihydrogen and the isolation of a number of chloride complexes. The unusual protonation of the chloride ligand in preference to hydride has also been observed in the reaction of [OsCl2H2L2] with triflic acid, which gives rise to the crystallographically characterized compound [Os2H4(μ-Cl)2(PPr3)4][CF3SO3].
### Table 5.1 Reaction of HF with a Range of Low-Valent Platinum Group Metal Complexes

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Reagents</th>
<th>Product</th>
<th>Characterisation</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ir(NCMe)(CO)(AsPh$_3$)$_2$]$^2$</td>
<td>HF$_{aq}$, NEt$_3$</td>
<td>[IrF(CO)(AsPh$_3$)$_2$]</td>
<td>IR</td>
<td>[1], [4]</td>
</tr>
<tr>
<td>Pd($\text{PPh}_3$)$_2$</td>
<td>AHF</td>
<td>[Pd$_2$F$_3$($\text{PPh}_3$)$_4$]F$_2$</td>
<td>EA</td>
<td>[5]</td>
</tr>
<tr>
<td>[PtCl($\text{PPh}_3$)$_2$], X = Cl, H</td>
<td>AHF</td>
<td>[PtFCl($\text{PPh}_3$)$_2$]</td>
<td>IR, EA</td>
<td>[5]</td>
</tr>
<tr>
<td>PtL$_4$, L = PPh$_3$, PMePh$_2$</td>
<td>AHF</td>
<td>[PtFL$_3$][HF$_2$], L = PPh$_3$, PMePh$_2$</td>
<td>IR, EA, $^{19}$F, $^{31}$P NMR</td>
<td>[5], [10]</td>
</tr>
<tr>
<td>[CpRuH$_2$L$_2$], L = PPh$_3$, AsPh$_3$, SbPh$_3$; L = (PPh$_3$)(AsPh$_3$)</td>
<td>HF$_{aq}$</td>
<td>[CpRuFL$_2$] L = PPh$_3$, AsPh$_3$, SbPh$_3$; L = (PPh$_3$)(AsPh$_3$)</td>
<td>EA, IR and $^1$H NMR</td>
<td>[6]</td>
</tr>
<tr>
<td>[RuH(cod)(PMe$_2$Ph)$_3$][PF$_6$]</td>
<td>HF$_{aq}$</td>
<td>[Ru$_2$($\mu$-F)$_3$(PMe$_2$Ph)$_6$][PF$_6$]</td>
<td>-</td>
<td>[7]</td>
</tr>
<tr>
<td>[IrX(CO)(L)$_2$] X = Cl, L = PPh$_3$; X = Br, L, L = PPh$_3$</td>
<td>HF$_{aq}$</td>
<td>[IrFHX(CO)L$_2$] X = Cl, L = PPh$_3$; X = Br, L, L = PPh$_3$</td>
<td>IR and XRPD</td>
<td>[8]</td>
</tr>
<tr>
<td>[Ir$_2$(CN-p-tol)(AsPh$_3$)$_2$]</td>
<td>ethanol soln of 5% HF</td>
<td>[IrF$_2$(CN-p-tol)(AsPh$_3$)$_2$]</td>
<td>IR$, EA$ and $^1$H NMR$^b$</td>
<td>[9]</td>
</tr>
</tbody>
</table>

---

*a* only one band present due to superposition of v(CO) and v(CN).

*b* Poorly resolved broad signal.
5.2 Reaction of Osmium and Ruthenium Hydrides with AHF

It has been demonstrated that the ruthenium and osmium complexes \([\text{OC-6-13}]\text{MH}_2(\text{CO})_2(L)_2\), \([\text{OC-6-13}]\text{MH}_2(\text{CO})(L)_3\) and \([\text{OC-6-32}]\text{MCl}_2(\text{CO})(L)_3\) react vigorously with \(\text{HCl(g)}\) to give dihydrogen and the dichloro-complexes \([\text{OC-6-13}]\text{Ma}_2(\text{CO})_2(L)_2\) and \([\text{OC-6-32}]\text{MCl}_2(\text{CO})(L)_3\) respectively, \(L = \text{tertiary phosphine}\). The dimeric compound \([\text{Ru}_2\text{Cl}(\mu-\text{Cl})_2(\text{CO})(\text{PPh}_3)_3]\) has also been reported to result from a similar reaction.\(^{17,18}\) Hydridoiridium(III) complexes of the type \([\text{IrHX}_3\text{L}_3]\), \(L = \text{tertiary phosphine or arsine}\), have a similarly labile hydride ligand and react with halogen acids \(\text{HY (Y = Cl, Br and I)}\) to give complexes of the type \([\text{IrX}_3\text{YL}_3]\) in which the ligand \(Y\) has replaced \(H\) without change in the configuration.\(^{19}\) It was, therefore, of interest to see if hydride complexes of osmium and ruthenium would react with AHF to give metal fluoride complexes, and whether the configuration of the fluoride complex remained the same as that of the hydride.
5.2.1 Reaction of the Hydrides $[\text{OC-6-13}][\text{MH}_2(\text{CO})_2(\text{PPh}_3)_2]$, $M = \text{Os}$ and $\text{Ru}$, with AHF

The hydrides $[\text{OC-6-13}][\text{MH}_2(\text{CO})_2(\text{PPh}_3)_2]$, $M = \text{Os}^{[20]}$ and $\text{Ru}^{[21]}$, were prepared as previously described in the literature. AHF was slowly condensed on to the solid hydrides, contained in pre-fluorinated FEP reaction vessels at -196°C, as described in the Experimental Section, Chapter Six. The reaction mixture was slowly warmed to -50°C, at which time a reaction took place as evidenced by the evolution of dihydrogen. After effervescence had ceased, the HF solvent was removed to give off-white air-stable solids in each case. For $M = \text{osmium}$, the $^{31}P(^{1}H)$ and $^{19}F$ NMR spectra, recorded in $d^5$-acetone, each contain one resonance with mutual triplet coupling at $\delta$ 1.0 and $\delta$ -304.0 respectively with a $^2J(\text{PF})$ coupling constant of 30 Hz. Similar triplet resonances were obtained for $M = \text{ruthenium}$, $\delta$ 22.0 and $\delta$ -325.0 for $^{31}P(^{1}H)$ and $^{19}F$ respectively with $^2J(\text{PF}) = 20$ Hz. This indicates that only a single species exists in solution as a result of both reactions. These data correspond exactly to those for $[\text{OC-6-13}][\text{M}(\text{CO})_2(\text{PPh}_3)_2]$ obtained as the final products from the reactions of $[\text{M}(\text{CO})_3(\text{PPh}_3)_2]$ with $\text{XeF}_2^{[23]}$, and to the data from the reaction of the tetrameric species $[(\text{M}(\text{CO})_2)_4(\text{PPh}_3)_4]$ with $\text{PPh}_3$, $M = \text{Os}$ and $\text{Ru}$, described in Chapter Two, 2.1.. The IR and mass spectral data (Chapter Six) further confirm the characterization of $[\text{OC-6-13}][\text{M}(\text{CO})_2(\text{PPh}_3)_2]$ with the ligands in the expected cis,cis,trans arrangement.

During the course of the reaction, the AHF solution changed from colourless to a deep red which persists until the HF solvent is removed. A problem noted previously is that if an eighteen electron complex $L_n\text{MH}$ undergoes hydride loss, which is observed as dihydrogen evolution, it will give a sixteen electron species $L_{n-2}\text{M}^+$ species that will rarely be stable if the metal is not nickel, platinum, palladium, iridium or rhodium. In the present case two hydride ligands are lost which will give rise to an extremely reactive co-ordinatively unsaturated intermediate which could explain the intense red colour observed during the reaction. It is this co-ordinative unsaturation that is said to encourage the reduced substrate, in this case F, to bind to the metal centre. In this particular reaction both the solvent and reactant are HF, as opposed to the HCl reactions in which HCl gas is passed through an organic solvent containing the hydride complex. The F formed after the loss of dihydrogen can either bind
directly to the metal to give the difluoride complex \( \text{LnMF}_2 \) or react with the bulk HF to form HF\(_2\) which may co-ordinate weakly to the metal centre forming \( \text{LnM-}(\text{FH}_2)_2 \) or \( \text{LnFM-}(\text{FH}_2) \) The formation of the HF adduct is more probable as the red colour persists for an indefinite period of time until the HF solvent is removed, where upon the difluoride species is isolated (Figure 5.2).

**Figure 5.2**

\[
\text{LaM} + 2 \text{HF} \rightarrow \text{La}^2+ + \text{H}_2(g) + 2 \text{F} \rightarrow \text{LaMF}_2
\]

### 5.2.2 Reaction of the Hydrides \([\text{OC-6-13}]\text{[MH}_2(\text{CO})(\text{PPh}_3)_2]\), \( \text{M} = \text{Os} \) and \( \text{Ru} \), with AHF

The hydrides \([\text{OC-6-13}]\text{[MH}_2(\text{CO})(\text{PPh}_3)_2]\), \( \text{M} = \text{Os} \) and \( \text{Ru} \), were prepared as previously described in the literature.\(^{120}\) As with the reactions of \([\text{MH}_2(\text{CO})(\text{PPh}_3)_2]\), AHF was slowly condensed on to the solid hydrides at -196°C, contained in pre-fluorinated FEP reaction vessels. Upon warming, reaction occurred at -50°C. After evolution of dihydrogen had ceased, the HF solvent was removed, to give in both cases, off-white air-stable solids.

The \(_{19}\text{F}\) NMR spectra of the products dissolved in d\(^5\)-thf exhibit two multiplets in a 2 : 1 ratio in the region characteristic of a metal-bound fluorine\(^{12,21}\) for \( \text{M} = \text{Ru} \) at \( \delta -305.2 \) and \(-332.8 \) and for \( \text{M} = \text{Os} \) \( \delta -280.2 \) and \(-299.8 \) (Figure 5.3). However, the spectra are second-order. Attempts to resolve additional couplings at lower temperatures were unsuccessful, with the signals remaining relatively unchanged in appearance. However, \(_{19}\text{F}-_{19}\text{F}\) NMR COSY experiments revealed that the two resonances were coupled, as evidenced by the off-diagonal peaks in the spectrum (Figure 5.4). The \(_{31}\text{P}(^{1}\text{H})\) NMR spectra of the two compounds were also complicated but similar to one another, suggesting that analogous products had been formed in both the osmium and ruthenium reactions (Figure 5.5). Each \(_{31}\text{P}(^{1}\text{H})\) spectrum contains a complex multiplet, at \( \delta 51.0 \) for \( \text{M} = \text{Ru} \) and \( \delta 2.2 \) for \( \text{M} = \text{Os} \), along with an apparent doublet of doublets at \( \delta 47.2 \) for \( \text{M} = \text{Ru} \) and \( \delta 4.4 \) for \( \text{M} = \text{Os} \), with the two resonances in a 1 : 1 ratio. Interestingly, the \(_{31}\text{P}(^{1}\text{H})\) NMR spectra of both complexes showed the presence of free PPh\(_3\) which was not present in the starting
Figure 5.3 $^{19}$F NMR Spectrum of [Ru$_2$(μ-F)$_2$(CO)$_2$(PPh$_3$)$_4$][BPh$_4$]
Figure 5.4 $^{19}$F - $^{19}$F COSY NMR Spectrum of [Ru$_2$(μ-F)$_2$(CO)$_2$(PPh$_3$)$_4$][BPh$_4$]
material. This indicates that PPh$_3$ has been displaced from the metal centre during the course of the reaction. Although unexpected this is not surprising as it has been well established that the phosphine trans to the hydride ligand in the complex [OC-6-32][MClH(CO)(PPh$_3$)$_3$] is preferentially displaced to afford the complex [MCIH(CO)(L)(PPh$_3$)$_3$] upon reaction with a range of phosphines, phosphites, phosphonites and phosphinites (L = PPh$_3$R; P(OR)$_x$R; R = Me, Et and x = 1-3). Acetonitrile and dmf are also known to replace PPh$_3$ from this complex. The loss of PPh$_3$ in the reactions of mer-[MH$_2$(CO)(PPh$_3$)$_3$] with AHF, and the ease of displacement of the phosphine ligand trans to hydride in the complexes [MClH(CO)(PPh$_3$)$_3$], M = Os and Ru, is in accord with the high trans labilising influence of the hydride ligand. In this present case it is unclear what has displaced the phosphine ligand but, because the reaction was carried out in AHF with no other ligands present, it can be assumed that HF is weakly co-ordinated to the metal centre. The formation of either [MF$_2$(CO)(HF)(PPh$_3$)$_2$] or [MF$_2$(CO)(PPh$_3$)$_3$] can be ruled out as they would give first-order $^1$H NMR spectra and the two chemically inequivalent fluorines would give rise to two resonances in a 1 : 1 ratio, as opposed to the 2 : 1 ratio observed. This suggests that the reaction has proceeded further than expected.

When recording the $^1$F NMR spectra in glass NMR tubes it was evident that BF$_4^-$, $\delta$(F) -151, and trace amounts of SiF$_6^{2-}$, $\delta$(F) -136, were always present. However these anions were not observed when the off-white solid isolated from the reactions was allowed to react with NaBPh$_4$ in dry thf in pre-fluorinated FEP reactors, before being exposed to the glass NMR tubes. This suggested that the complexes formed are cationic with the initial counterion being HF$_2^-$, which undergoes anion exchange upon reaction with NaBPh$_4$. The presence of BF$_4^-$ and SiF$_6^{2-}$ in the initial reactions is due to fluorination of the borosilicate glass by the initial counterion HF$_2^-$. In light of the complexes being cationic and having presumably at least three fluorines on the metal centre with two of these being chemically equivalent, as determined from the integrals in the $^1$F NMR spectra, the complexes were thought to be oligomeric. That is, assuming there has been no change in the oxidation state of the metal. The binuclear nature of the products was confirmed by electrospray mass spectrometry, using dry thf as the solvent. This gave the parent ion isotope pattern for the ruthenium complex [Ru$_2$F$_3$(CO)$_2$(PPh$_3$)$_4$]$^+ m/z$ 1363 (for $^{103}$Ru) (Figure 5.6), while no signal was
Figure 5.5 $^{31}$P($^1$H) NMR Spectrum of [Ru$_2$(μ-F)$_2$(CO)$_9$(PPh$_3$)$_4$][BPh$_4$]
observed in the electrospray mass spectrum of the corresponding osmium complex. The positive ion FAB mass spectrum showed the correct isotope pattern for the parent ion \([\text{Os}_2\text{F}_3(\text{CO})_2(\text{PPh}_3)_4]^+\) \(m/z\) 1541 (for \(^{192}\text{Os}\)). On the basis of the observation of \([\text{M}_2\text{F}_3(\text{CO})_2(\text{PPh}_3)_4]^+\) in the mass spectra, and the fact that the \(^{19}\text{F}\) NMR shows two second order multiplets in a 2 : 1 ratio, the products from the reaction of the hydrides \([\text{OC}^-\text{H}][\text{MH}_2(\text{CO})(\text{PPh}_3)_3]\) with AHF are formulated as \([\text{M}_2\text{F}_3(\text{CO})_2(\text{PPh}_3)_4]^+(\text{HF}_2)^-\) (Figure 5.7). The \(^{19}\text{F}\) chemical shift of a fluoride ligand bridging two metal centres in a cationic complex is usually at a very low frequency [cf. \(\text{cis}\)-\(\text{Os}_2\text{F}_3(\text{CO})_4\) \(\delta(\text{F})\) -465.0\(^\text{1}\)] but the resonances for the triply-bridged cationic fluoride complex \([\text{M}_2(\mu-\text{F})_3(\text{CO})_2(\text{PPh}_3)_4]^+\), \(M = \text{Os}\) or \(\text{Ru}\), were observed at a significantly higher frequency. Since it has been observed by Hope\(^2\) that the frequency of the chemical shift increases as the number of fluoride ligands on the metal centre increases [cf. \(\text{cis}\)-\(\text{Os}_2\text{F}_2(\text{CO})_4\) \(\delta(\text{F})\) -342.0, \(\text{cis}\)-\(\text{Os}_2\text{F}_3(\text{CO})_4\) \(\delta(\text{F})\) -266.0 for the terminal fluoride \(\text{cis}\) to two other fluorides], this anomaly can be attributed to the unusual environment of the fluorides and also that there are three fluorine atoms bound to the metal centre.

Figure 5.7

\[
\begin{array}{c}
\text{P} \\
\text{M} \\
\text{F}_1 \\
\text{F}_2 \\
\text{F}_3 \\
\text{M} \\
\text{P} \\
\text{CO}
\end{array}
\]

\(M = \text{Ru} \ (97)\)

\(M = \text{Os} \ (98)\)

\(P = \text{PPPh}_3\)

The complicated \(^{19}\text{F}\) and \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra can be rationalised in terms of the triply-bridged cations (97) and (98) which contain seven magnetically inequivalent 100% spin 1/2 nuclei (Figure 5.7). The triply-bridged cations have two distinct sets of
fluoride ligands ([Fa, Fa] and Fb) and two sets of phosphine ligands [(Pc, Pd) and (Pe, Pf)]. The two fluoride ligands Fa and Fa are chemically equivalent as they are both trans to one carbonyl group and one phosphine ligand. However, they are magnetically inequivalent due to their different coupling to Pc (as Fa is cis to Pc whereas Fa is trans to Pd). The third fluoride ligand Fb is chemically unique as it is trans to two phosphine groups, hence two distinct multiplets are observed in a 2:1 ratio in the $^{19}$F NMR spectra. The phosphorus nuclei labelled Pc and Pd are chemically equivalent as they are both trans to one fluorine (Fa and Fa respectively) which are in turn trans to one carbonyl. However, Pc and Pd are magnetically inequivalent by virtue of their different coupling to Fa (as Pc is cis to Fa whereas Pd is trans to Fb). Similarly, the phosphorus nuclei labelled Pb and Pc are chemically equivalent as they are both trans to one fluorine (Fb) but magnetically inequivalent as they couple differently to Pc, ($^J$ and $^J$ coupling respectively), hence two distinct multiplets are observed in the $^{31}$P($^1$H) NMR spectra in a 1:1 ratio.

The second-order $^{31}$P($^1$H) and $^{19}$F NMR spectra were simulated using this model, using the Bruker PANIC (Parameter Adjustment in NMR by Iteration Calculation) program. This gave a good fit between the observed and theoretical spectra (Figures 5.8 and 5.9), suggesting that the NMR spectra can be rationalised in terms of the triply-bridged complexes, although other NMR acceptable solutions could also exist. However, these solutions do not fit the data obtained from IR spectroscopy and mass spectrometry. The simulated coupling constants for [Ru$_2$(μ-F)$_3$(CO)$_2$(PPh$_3$)$_4$]$^+$ can be seen in Table 5.2.

The combination of the two metal fragments can result in two geometrical isomers, one with the two carbonyls syn (C), (Figure 5.10) and the other where the carbonyls are in an anti arrangement, (A). The anti isomer (A) is a chiral molecule (C$_2$ symmetry) as it has a non-superimposable mirror image, (B). The syn isomer is symmetrical (C$_{$2V} symmetry) and is therefore achiral. Only the chiral anti isomer, presumably present as a racemic mixture, is observed in solution as evidenced by $^{19}$F and $^{31}$P NMR spectroscopies. The syn isomer (C) can be ruled out on the basis of the $^{31}$P NMR spectra. While Fa and Fa remain magnetically inequivalent and chemically equivalent with Fb remaining chemically unique, the four phosphorus nuclei become chemically equivalent although still magnetically inequivalent. Hence, the $^{31}$P($^1$H) NMR would show only one phosphorus environment. It is clear from the spectra that
there are two phosphorus chemical environments, hence the *anti* isomers (A) and (B) are the sole products.

A similar *anti* arrangement of a terminal chloride and CS ligand (rather than two carbonyls) is found in the neutral complex \([\text{Ru}_2\text{Cl}(_\mu\text{-Cl})_3\text{(CS)(PPh}_3)_4]\), which has been crystallographically characterized.\(^{27}\) The same arrangement is also found in the crystal structure of \([\text{Ru}_2\text{Cl}(_\mu\text{-Cl})_3\text{(PPh}_3)_4]\), a ruthenium(II)-ruthenium(III) complex with the terminal chloride ligands in an *anti* arrangement.\(^{28}\) The *syn* isomer, \([\text{M}_2(\mu-_F}_3\text{(CO)}_2\text{(PPh}_3)_4]\)^* [Figure 5.10(C)], with the phosphine ligands on adjacent metals coplanar, cannot be ruled out on steric grounds. Upon comparison with \([\text{Ru}_2\text{Cl}(_\mu\text{-Cl})_3\text{(CO)(PPh}_3)_3]\) (Figure 5.11), where the structure has been crystallographically determined,\(^{29}\) one can see that the triphenylphosphine ligand (P3) and the second ruthenium atom (Ru2) lie *syn* to the triphenylphosphine ligand (P2) bound to the first ruthenium centre (Ru1). The isolation of the sterically disfavoured *syn* isomer suggests that in complexes with the M\(_2(\mu\text{-X})_3\) fragment, the triphenylphosphine ligands on adjacent metal centres are not subject to steric interactions. Molecular modelling on this chloride complex and the fluoride complexes \([\text{M}_2(\mu-_F}_3\text{(CO)}_2\text{(PPh}_3)_4]\)^*, \(\text{M} = \text{Ru and Os}\), with the bonded and non-bonded distances taken from EXAFS data (see below) confirms this observation. Rotation of one of the octahedra by \(\pm 120^\circ\) about the M—M axis to form the *syn* isomer (C) from the *anti* isomer (A) or its mirror image (B), results in no significant Van der Waal clashes of the phenyl rings on the phosphine ligands from adjacent metal centres which cannot be overcome by small rotation about the P-C bond. The *syn* isomer (C) must therefore be disfavoured on electronic grounds. In isomer (C) two of the bridging fluoride ligands would be *trans* to two phosphines and the third fluoride *trans* to two CO groups, whilst in the *anti* isomers (A) and (B) only one fluoride is *trans* to two phosphorus nuclei, with the third fluoride ligands *trans* to one phosphorus nuclei and one carbonyl group. These data indicate that since the *syn* isomer (C) is not observed, the greater number of bridging fluoride ligands stabilised by synergic interactions between the F π-donor and CO π-acceptor is very important.
Figure 5.10 Possible isomers of (97) and (98)

\[ \text{(A)} \]

\[ \text{(B)} \]

Newman projection of (A) along M-M axis

Newman projection of (B) along M-M axis

\[ \text{(C)} \]

\[ M = \text{Ru (97)} \]
\[ M = \text{Os (98)} \]
\[ P = \text{PPh}_3 \]
\[ C = \text{CO} \]

Newman projection of (C) along M-M axis
In forming the triply-bridged cationic species, the initial mononuclear complex [OC-6-13][MH₂(CO)(PPh₃)₂] has presumably lost the triphenylphosphine trans to the hydride ligand, owing to its strong trans influence, leaving the two remaining phosphines trans to one another. The next step may be the formation of a cis-difluoride complex with concomitant loss of dihydrogen, which has been shown to be facile in the reaction of the bisphosphine complexes [MH₂(CO)₂(PPh₃)₂] with HF, section 5.2.1. This produces a mer arrangement of the fluorides and the latent site (created by loss of PPh₃) which is presumably occupied by weakly co-ordinating solvent (Figure 5.12). To obtain the triply bridged fluoride species the two fluoride ligands and the latent site must be in a facial arrangement, therefore intramolecular reorientation must occur to force the phosphine ligands cis to one another (Figure 5.12). This facial species can then interact with a second facial species to give the doubly bridged species [M₂F₂(μ-F)₂(CO)₂(PPh₃)₄] which then goes on to form the triply bridged cationic species via intramolecular attack of fluoride with loss of F. A similar mechanism has been proposed by Stephenson et. al. for the formation of the triply bridged chloride complex [Ru₂(Cl(μ-Cl))₂(CS)(PPh₃)₄] with the M₂(μ-Cl)₂ unit being formed by attack of a terminal chloride onto the adjacent metal centre with loss of CS. The final step in the mechanism which involves loss of “F” may be assisted by F---HF interactions, labilising the M-F bond and ultimately leading to HF₂ formation. With the loss of this fluoride ligand the more strongly bound terminal fluoride trans to a carbonyl group, which is presumably resistant to protonation due to favourable synergic interactions with the carbonyl, readily fills the vacant or latent site to give the co-ordinatively saturated triply bridged fluoride complex. The terminal fluoride trans to the phosphine is preferentially removed as opposed to the terminal fluoride trans to CO as the F-M π-donation will be diminished due to little or no synergic interactions with the phosphine.
Table 5.2 Simulated Coupling Constants for \([\text{Ru}_2(\mu-F)_3(\text{CO})_2(\text{PPh}_3)_2]^+\) (97)

<table>
<thead>
<tr>
<th>Coupling</th>
<th>Value in Hz</th>
<th>Coupling</th>
<th>Value in Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2J(\text{AA'}))</td>
<td>180.00</td>
<td>(2J(\text{BC}))</td>
<td>5.44</td>
</tr>
<tr>
<td>(2J(\text{AC}))</td>
<td>4.00</td>
<td>(2J(\text{BD}))</td>
<td>173.48</td>
</tr>
<tr>
<td>(2J(\text{AD}))</td>
<td>4.03</td>
<td>(2J(\text{BC'}))</td>
<td>5.44</td>
</tr>
<tr>
<td>(2J(\text{AC'}))</td>
<td>160.00</td>
<td>(2J(\text{BD'}))</td>
<td>173.48</td>
</tr>
<tr>
<td>(2J(\text{AD'}))</td>
<td>4.03</td>
<td>(2J(\text{CD}))</td>
<td>29.31</td>
</tr>
<tr>
<td>(2J(\text{A'C}))</td>
<td>160.00</td>
<td>(4J(\text{CC'}))</td>
<td>0.00</td>
</tr>
<tr>
<td>(2J(\text{A'D}))</td>
<td>4.00</td>
<td>(4J(\text{CD'}))</td>
<td>0.00</td>
</tr>
<tr>
<td>(2J(\text{A'C'}))</td>
<td>4.00</td>
<td>(2J(\text{C'D'}))</td>
<td>29.31</td>
</tr>
<tr>
<td>(2J(\text{A'D'}))</td>
<td>4.00</td>
<td>(4J(\text{DC'}))</td>
<td>0.00</td>
</tr>
<tr>
<td>(2J(\text{BA}))</td>
<td>160.00</td>
<td>(4J(\text{DD'}))</td>
<td>0.00</td>
</tr>
<tr>
<td>(2J(\text{BA'}))</td>
<td>160.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.11 Molecular Structure of \([\text{Ru}_2\text{Cl}_3(\mu-\text{Cl}_3)(\text{CO})(\text{PPh}_3)_3]^+\)
Figure 5.12 Proposed Mechanism for the Formation of $[M_2(\mu-F)\text{CO}(\text{PPh}_3)_4]^+$

(i) Rearrangement.
(ii) Dimerisation via displacement of the weakly co-ordinated HF solvent.
(iii) Displacement of the weakly bound fluoride $trans$ phosphine via protonation and formation of the third fluorine bridge.

M = Ru (97)
M = Os (98)
This increases the Brönsted basicity of the fluoride which, coupled with the high acid strength of AHF, may be sufficient to effect protonation. The protonation step of the fluoride ligand can be likened to the protonation of chloride in the complex [OsH2Cl2(PPr3)2] when treated with triflic acid, CF3SO3H.\textsuperscript{115} The product of reaction has been shown by single crystal X-ray diffraction to be [Os2H4(μ-Cl)2(PPr3)2][CF3SO3], with the hydrides remaining unaffected by the addition of acid, and the chloride ligand lost as HCl.\textsuperscript{113} The intense red colour that is observed upon reaction of the colourless hydride with HF could be due to the unsaturated species proposed in the mechanism. The solution remains red until the HF solvent is removed.

This may imply that the species with the latent co-ordination (which is effectively a sixteen electron metal centre solvated by HF) is stable in HF solution but, upon removal of the HF, dimerisation occurs.

Head and Nixon\textsuperscript{31} have reported the reaction of [OC-6-75][RuH2(CO)(PPh3)2] with HCl(g) and have proposed the formation of a neutral triply-bridged chloride complex [Ru2Cl(μ-Cl)3(CO)2(PPh3)2] of which there are three isomers. All are isolated in the reaction of [OC-6-34][RuCl2(CO)(dmf)(PPh3)2] with [RuCl2(PPh3)2] and have been identified by \(^{31}\)P\{^1H\} NMR spectroscopy.\textsuperscript{117} The isostructural chloride complex [Ru2(μ-Cl)3(CO)3(PPh3)2][BPh4] has been prepared directly from the rearrangement of [RuCl2(CO)(MeOH)(PPh3)2] in polar solvents and from the addition of NaBPh4 and PPh3 to [Ru2Cl(μ-Cl)3(CO)2(PPh3)2].\textsuperscript{117} This facile rearrangement of the solvato complex supports the proposition that an HF-stabilised intermediate [MF2(CO)(HF)(PPh3)2] is involved in the formation of the triply fluorine bridged cations. A number of triply-bridged halide complexes have been reported in the literature.\textsuperscript{115,132} Compounds of the type [Ru2(μ-Cl)3(PR3)2]Y, Y = Cl, ClO4, SCN or BPh4 have been prepared from RuCl3.xH2O and PR3 in alcoholic media.\textsuperscript{113,132} The confacial bicapped octahedral geometry being verified by single crystal X-ray diffraction for PR3 = PF3, Ph, PMe2Ph and PMe3, Y = mer-[RuCl3(PMe3Ph)2]^+. PF6^- and BF4^- have also been synthesised by treatment of [RuH3(cod)(PMe3Ph)2] with water, and has been structurally characterized by X-ray crystallography.\textsuperscript{112} Treatment of this hydroxy compound with HX provides a convenient high yield route to [Ru2(μ-X)3(PMe3Ph)2]\textsuperscript{+} where X = Cl, Br and I.\textsuperscript{120} The ruthenium complex [RuH3(cod)(PMe3Ph)2]\textsuperscript{+} has also
been reported to react with HF(aq), to give the triply bridged fluoride complex 
[Ru₂(μ-F)₃(PMe₂Ph)₆]⁺ but no corroborating spectroscopic data or elemental analysis
have been given.[12] However, there has been a report of an unambiguously
characterized triply bridged fluoride complex of molybdenum.[17] The formation of
[Mo₂H₄(μ-F)₃(PMe₂Ph)₆][BF₄] from the reaction of [MoH₄(PMe₂Ph)₄] with HBF₄,
represents the first crystallographically confirmed case of a transition-metal compound
containing an M₂(μ-F)₃ group.[17] This suggests that the formulation of the triply
bridged complexes [M₂(μ-F)₃(CO)₂(PPh₃)₄][BF₄], M = Os and Ru
is not unreasonable and not without precedent in the literature. However, the mechanism of its formation is somewhat
tentative.

5.2.2.1 EXAFS Analysis of [M₂(μ-F)₃(CO)₂(PPh₃)₄][BPh₄], M = Os and Ru

The instability of the triply-bridged compounds in solution over long periods
of time has precluded attempts to obtain crystals suitable for X-ray crystallographic
studies. However, the usefulness of EXAFS spectroscopy in obtaining structural
information has already been described in Section 2.3.4, Chapter Two. Spectroscopic
investigations of (97) and (98), suggest the formation of binuclear complexes
containing the M₂(μ-F)₃ unit. In order to obtain further structural information and
ascertain whether the complexes are binuclear, an EXAFS study was instigated.

In the first instance, the ruthenium K-edge EXAFS data for the structurally
characterized chloride complex [Ru₂(μ-Cl)₃(PMe₂Ph)₆][Cl₂] were obtained to provide a
model system to test the reliability of data collection and treatment. The results are in
satisfactory agreement with the single crystal X-ray data (Table 5.3). The Fourier
transform of the EXAFS data is dominated by the back-scattering from the bonded
phosphorus and chloride atoms, which give the Ru-P distance as 2.284(0.002) Å as
compared to 2.29 Å (mean) from the crystallographic study, and the Ru-Cl distance as
2.473(0.002) Å compared to 2.49 Å (mean). More importantly, the non-bonded
Ru--Ru distance (3.418(0.006) Å) is comparable with 3.39(1) Å from the X-ray
single crystal study, confirming the dimeric structure of the complex. Transmission
ruthenium K-edge EXAFS and osmium L₃-edge EXAFS were then collected for
[M₂(μ-F)₃(CO)₂(PPh₃)₄][BPh₄], M = Ru and Os respectively, out to k = 15 Å⁻¹ (k =
photoelectron wave vector) beyond the edge, which was later truncated to 13.5 Å⁻¹
Figure 5.13  a) The Background Subtracted EXAFS and b) the Fourier Transform of [Ru₂(μ-F)₃(CO)₃(PPh₃)₄][BPh₄]
(dashed line theoretical)
Figure 5.14  a) The Background Subtracted EXAFS and b) the Fourier Transform of \([\text{Os}_2(\mu-F)_2(\text{CO})_3(\text{PPh}_3)_4][\text{BPh}_4]\)

(dashed line theoretical)
Table 5.3 EXAFS data for [Ru2(μ-Cl)(PMe2Ph)3][BPh4], [Ru2(μ-F)(CO)3(PPh3)3][BPh4] and [Os2(μ-F)(CO)3(PPh3)3][BPh4]a

<table>
<thead>
<tr>
<th>Compound</th>
<th>[Ru2(μ-Cl)(PMe2Ph)3][BPh4]</th>
<th>[Ru2(μ-F)(CO)3(PPh3)3][BPh4]</th>
<th>[Os2(μ-F)(CO)3(PPh3)3][BPh4]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X-Ray EXAFS</td>
<td>EXAFS</td>
<td>EXAFS</td>
</tr>
<tr>
<td>d(M-P) / Å</td>
<td>2.29(mean) 2.284(2)</td>
<td>2.292(6)</td>
<td>2.440(2)</td>
</tr>
<tr>
<td>2σ² / k Å²</td>
<td>- 0.0081(3)</td>
<td>0.0095(15)</td>
<td>0.0060(3)</td>
</tr>
<tr>
<td>d(M-X) / Å</td>
<td>2.49(mean) 2.473(2)</td>
<td>2.078(16)</td>
<td>2.073(2)</td>
</tr>
<tr>
<td>2σ² / k Å²</td>
<td>- 0.0110(4)</td>
<td>0.0145(36)</td>
<td>0.0095(4)</td>
</tr>
<tr>
<td>d(M-C) / Å</td>
<td>- 1.812(7)</td>
<td>1.805(4)</td>
<td></td>
</tr>
<tr>
<td>2σ² / k Å²</td>
<td>- 0.0023(13)</td>
<td>0.0044(8)</td>
<td></td>
</tr>
<tr>
<td>d(C-O) / Å</td>
<td>- 1.087(38)</td>
<td>1.158(3)</td>
<td></td>
</tr>
<tr>
<td>2σ² / k Å²</td>
<td>- 0.0402(234)</td>
<td>0.0029(4)</td>
<td></td>
</tr>
<tr>
<td>d(M-M) / Å</td>
<td>3.39(1) 3.418(6)</td>
<td>2.973(12)</td>
<td>3.115(19)</td>
</tr>
<tr>
<td>2σ² / k Å²</td>
<td>- 0.0165(15)</td>
<td>0.0111(22)</td>
<td>0.0230(27)</td>
</tr>
<tr>
<td>Fit indexb</td>
<td>- 3.00</td>
<td>2.39</td>
<td>2.39</td>
</tr>
<tr>
<td>R²</td>
<td>- 19.0b</td>
<td>22.0</td>
<td>23.8</td>
</tr>
</tbody>
</table>

a standard deviations in parentheses. b Debye-Waller factor. c Fit index = Σ[(χ²−χk)²]k. d R = [σχ²−χk²dk / σχ²dk] × 100 %. e E0 15.60(0.33) eV, AFAC 0.86 and VPI -4.14. f E0 18.78(1.80) eV, AFAC 0.86 and VPI -4.14. g E0 3.51(0.29) eV, AFAC 0.57 and VPI -4.14. h Additional non-bonded shell used in fit Ru–P 4.428(0.011), 0.0211(0.0032).
due to poor signal / noise at high k. Three data sets were averaged and the data multiplied by $k^2$ to compensate for a decrease in intensity at higher k. The AFAC and VPI values were taken from the analysis of the model compound [Ru$_2$(μ-Cl)$_3$(PMe$_2$Ph)$_3$][BPh$_4$]. No Fourier filtering was applied, and the fits discussed below were all compared with the average raw (background subtracted) EXAFS data (Figures 5.13 and 5.14). As with the model compound, the data was modelled using EXCURV92, but due to the presence of a carbonyl ligand on each metal centre, as opposed to the third phosphine ligand on the model compound, the complexes were modelled to five shells, with the M-C-O bond angle fixed to 180° for multiple scattering. Each shell was added stepwise, iterated in the usual way, and the best fits tested for statistical significance. The five shells consisted of two phosphorus atoms at ca. 2.292(0.006) Å for M = Ru; ca. 2.440(0.002) Å for M = Os, three fluorine atoms at ca. 2.078(0.016) Å for M = Ru; ca. 2.073(0.002) Å for M = Os; one carbon atom at ca. 1.812(0.007) Å for M = Ru, ca. 1.805(0.004) Å for M = Os; one oxygen atom at ca. 1.087(0.037) Å for M = Ru; ca. 1.158(0.003) Å for M = Os and one metal atom at 2.973(0.012) Å for M = Ru and 3.115(0.020) Å for M = Os (Table 5.3). The M-P, M-C and C-O bond lengths are all consistent with the values determined from the single crystal X-ray diffraction studies of the mononuclear fluoride complexes [OC-6-I3][MF$_2$(CO)$_2$(PR$_3$)$_2$] described in Chapter Two, 2.3.3. In particular, the metal-metal separation in the ruthenium complex, 2.973(0.012) Å, is not inconsistent with a non-bonded Ru—Ru distance [c.f 3.08 Å for [Ru$_2$(μ-F)$_3$(PMe$_2$Ph)$_3$][BPh$_4$]], although others have suggested a Ru—Ru bond distance of 2.96 Å to have a bond order of 1.0. The Ru—Ru distance of 2.973(0.012) Å neither implies nor excludes the presence of a metal-metal bond. However, the eighteen electron rule does not require the existence of a metal-metal bond in these triply bridged fluoride complexes. The same is true for the osmium complex. The non-bonded Os—Os distance of 3.115(0.020) Å, determined by EXAFS, is typical of other reported non-bonded Os—Os distances determined by single crystal X-ray diffraction. In the binuclear complex [M$_2$(μ-F)$_3$(CO)$_2$(PPh$_3$)$_3$][BPh$_4$] the M-F-M bridging angle, as calculated from the M-F bond length and the metal-metal separation, is on average 91° for M = Ru and 97° for M = Os. Hence, the metal centres are further apart than they would be in a regular cofacial bicocahedron [two
regular octahedra sharing one face have a bridging angle $\theta$ of 70.5°, derived from the equation $\cos(\theta/2) = (2/3)^{\frac{1}{3}}$.

The reaction of ruthenium and osmium hydride complexes with anhydrous HF shows the importance of the presence of $\pi$-acceptor ligands (such as carbonyl ligands) in the formation of stable low-valent metal fluoride complexes. The fluoride ligand is usually trans to the $\pi$-acceptor in the final product to maximise synergic interactions. For example, the reaction of the hydrido complex [RuH$_2$(tetraphos)], which contains a weak $\pi$-acceptor phosphine ligand, with AHF leads only to decomposition. Similarly, problems of stability were encountered in the attempted synthesis of [PtF$_2$(PR$_3$)$_2$] complexes.$^{[4]}$ A survey of the literature shows that the majority of the low-valent metal fluoro complexes contain fluoride ligand trans to carbonyl and, indeed, in all the crystallographically characterised compounds of this type, it is this arrangement which is found.$^{[5]}$ The formation of only the anti isomers of the triply bridged cations (97) and (98) is due to this stabilising influence.
Chapter Five References


[26] Parameter Adjustment in NMR by Iterative Calculation; NMR Program
Library, Quantum Chemistry Program Exchange.
[29] V. M. Barbosa, A. A. Batista, O. R. Nascimento, G. Oliva and O. M. Porcu,
Trans.* 1974, 1134.
Chp 45.
[36] No Ru---Ru non-bonded distance listed.
7302.
[38] N. Binsted, S. J. Gurman and J. W. Campbell, EXCURV92, SERC Daresbury
1907.
CHAPTER SIX

Experimental
General Procedures and Techniques

All reactions have been carried out either on a metal vacuum line with facilities to connect glass or plastic reaction vessels, via Teflon™ couplings, or under dinitrogen on a glass vacuum line using standard Schlenk techniques.

6.1 Analytical Techniques

6.1.1 Nuclear Magnetic Resonance Spectroscopy

The NMR measurements were made on a Bruker AM300 spectrometer operating at 300.13, 75.47, 282.41, and 121.50 MHz for $^1$H, $^{13}$C, $^{19}$F and $^{31}$P respectively and on a Bruker ARX250 operating at 250.13, 235.34 and 101.26 MHz for $^1$H, $^{19}$F and $^{31}$P respectively. $^1$H and $^{13}$C NMR spectra were referenced to external TMS, $^{19}$F NMR spectra to external CFCl$_3$ and $^{31}$P to 85% H$_3$PO$_4$, using the high-frequency positive convention.

6.1.2 Infrared Spectroscopy

Infrared spectra were recorded for solid samples either as dry powders or dispersed in Nujol mulls compressed between KBr plates on a Digilab FTS40 FTIR spectrometer. For air-sensitive materials sample preparation was performed in the dry box. Solution spectra were recorded in dry CH$_2$Cl$_2$ using KBr cells with a path length of 0.01 cm.

6.1.3 Mass Spectrometry

Mass spectra were obtained using a Kratos Concept 1H double focusing forward-geometry mass spectrometer using 3-nitrobenzyl alcohol as the matrix when operating in positive ion FAB mode and dry thf as the solvent in electrospray mode.

6.1.4 Extended X-Ray Absorption Fine Structure (EXAFS) Spectroscopy

Osmium L$_{III}$ edge EXAFS data were collected at the Daresbury synchrotron radiation source operating at 2GeV (ca. $3.2 \times 10^{10}$ J) with an average ring current of 190mA on station 7.1 using an order sorting Si(111) monochromator, offset to 50% of the rocking curve for harmonic rejection. Ruthenium K-edge EXAFS data were

158
collected under the same conditions in transmission mode on station 9.2 using a double-crystal Si(220) monochromator offset to 50% of the rocking curve for harmonic rejection. The EXAFS data were collected in the transmission mode for the solid samples diluted with boron nitride and mounted between Sellotape strips in 1mm aluminium spacers. The EXAFS data treatment utilised the programs EX[1] and EXCURVE 92.[2] Several data sets were collected for each sample in k space ($k = \text{photoelectron wavevector}/\AA^{-1}$), and averaged to improve the signal to noise ratio. The pre-edge background was removed by fitting the spectrum to a quadratic 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 minimising the intensity of chemically insignificant shells at low radial distance from the primary absorbing atom in the Fourier transform. The data were multiplied by $k^2$ to compensate for the decreased intensity at higher k.

Curie fitting used multiple-scattering curved-wave theory with phase shifts and back scattering factors calculated using normal ab initio methods.

6.1.5 X-Ray Crystal Structure Determinations

- Crystals of [OsF$_2$(CO)$_2$(PPh$_3$)$_2$] (29), [OsF$_2$(CO)$_2$(PCy$_3$)$_2$] (32), [RuF$_2$(CO)$_2$(PEt$_3$)$_2$] (43), [OsCl$_2$(CO)$_2$(PEt$_3$)$_2$] (55), [Ru($\eta^1$-CO$_2$-OC)(CO)(PMe$_3$)$_2$] (77), [Os(Me)$_2$(CO)$_2$(PPh$_3$)$_2$] (78), [Os(Me)$_2$(CO)$_2$(PCy$_3$)$_2$] (79) and [Ru(OC(O)CF$_3$)$_2$(CO)$_2$(PCy$_3$)$_2$] (84) suitable for single crystal X-ray crystallographic studies were grown by slow evaporation of the appropriate solvent at room temperature in all cases. All crystals were glued to the end of thin glass-fibres using epoxy resin. Intensity data were measured on a Siemens P4 diffractometer at 295K or 190K, using Mo-Kα radiation ($\lambda = 0.71073 \ \AA$). Unit cell parameters were determined from the optimised setting angles of 20 - 40 reflections in the range 10.0° < 2θ < 25.0°. Semi-empirical absorption corrections were applied based on psi scans and the data for each structure corrected for Lorentz and polarisation effects. All of the structures were solved using SHELXTL-pc[3] and refined using the program package SHELXL-93[4] with crystal stability monitored by the observation of the intensities of three standard reflections.
The structures of the complexes were solved by Patterson and Fourier methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions (C-H 0.96 Å) with a fixed isotropic thermal parameter. Details of crystal data, collection and refinement are described in Table A in the Appendix.

6.1.6 Microanalysis
Elemental analyses were carried out by Butterworth Laboratories Ltd.

6.1.7 Electron Paramagnetic Resonance Spectroscopy
EPR spectra were recorded using a Bruker ER 200 on samples frozen in AHF solution at -196°C, contained in 4mm O.D. FEP tubes.

6.2 Metal Vacuum Line
The metal vacuum line consisted of 316-stainless steel or Monel Autoclave Engineers valves (AE-30 series) connected via Autoclave Engineers high-pressure connectors. Argon arc welded 'U' traps were incorporated to permit separation and condensation of gases in the metal manifold. Inlets for argon and fluorine gas were positioned as shown in Figure 6.1. Rough pump outlets were connected via a stainless steel soda-lime chemical scrubber unit (to neutralise the fluorine gas and HF) to a rotary pump which provided a vacuum of 10^2 mmHg. High vacuum was achieved using a mercury diffusion pump which was attached to a rotary pump (Edwards High Vacuum International, model RV5). This provided a vacuum in the region of 10^5 mmHg. A glass trap cooled to -196°C was used to protect the pumping system and a second glass trap at -78°C placed between the mercury diffusion pump and the rotary pump to prevent any mercury vapour passing through the rotary pump. Pressures of 0 - 1500 mmHg were measured by Bourdon tube gauges.

6.3 Glass Vacuum Line (Schlenk Line)
This apparatus was used in the preparation of materials which were slightly less sensitive to oxygen and moisture. The glass line consisted of a vacuum and nitrogen manifold fitted with greased vacuum taps. Reaction vessels were connected
Figure 6.1 Metal Vacuum Line
to the outlets by Neoprene tubing. Vacuum (0.1 mmHg) was achieved using a rotary pump (Model PSR/2 NGN Ltd), protected by a glass trap cooled to -196°C.

### 6.4 Inert Atmosphere Dry-Box

Involatile air- and moisture-sensitive materials were manipulated in an autorecirculating positive-pressure dry box (Vacuum Atmosphere Co., VAC NE 42-2 Dri Lab.), which provided a dry dinitrogen atmosphere with an oxygen and water content of less than 5ppm. The quality of the atmosphere was maintained via circulation through columns of manganese oxide and molecular sieves which remove oxygen and water respectively. The dry-box was equipped with a Sartorius balance (Model 1601 MP). Powdered samples were weighed in small glass boats prior to loading into the reaction vessels. Static charge build-up was found to affect weighings and therefore, a Zerostat 3 anti-static gun was used before weighing.

### 6.5 Reactions on the Metal Vacuum Line

Reactions that were believed to be extremely sensitive to air and moisture or involved the use of AHF, \( F_2(g) \), BF\(_3\)(g) or other gases were performed on the metal vacuum line. These reactions involved the use of glass and / or FEP reactors. Glass reaction vessels were fitted with Youngs' greaseless taps and used for storage of dried and degassed organic solvents. The FEP reactors, in which all the reactions took place, consisted of a straightened 4mm O.D. x 25cm (0.05cm wall thickness) FEP tube (Production Techniques Ltd.) sealed at one end by heat moulding into a 5mm O.D. NMR tube. The sealed FEP reactors were then connected to Chemcon™ coarse-control needle valves [Type STD/VC-4, Production Techniques] by a PTFE 'O' ring compression union. The FEP reactors were passivated before use. This involved evacuating the system to 10\(^{-7}\) mmHg to ensure a vacuum-tight seal and then placing the system under 500 mmHg of \( F_2(g) \), for approximately 0.5h. The \( F_2(g) \) was then removed using the rough pump and the system re-evacuated to high vacuum. After passivation was complete, either non-volatile reagents were loaded in the dry-box and / or volatile materials were transferred under static vacuum into the evacuated FEP reactor. (Figure 6.2).
Figure 6.2 Apparatus Used for the Transfer of Volatile Reagents

- Autoclave engineer valve of vacuum line.
- Autoclave engineer connector with 6mm adaptor.
- Chemcon tee coupling.
- 6mm glass connector.
- Chemcon needle valve.
- Young's greaseless tap.
- PTFE tubing (6mm o.d.; 2mm i.d.).
- Glass vessel.
- Molecular sieves.
- Solvent.
- FEP tubing (4mm o.d.; 2mm i.d.).
After reaction, the solvent was either removed to allow the solid to be manipulated, or the reactor sealed for NMR studies. The FEP reactors were sealed by placing them under vacuum and heating the top of the tube with a small heater whilst keeping the product in solution frozen at -196°C. NMR spectra were recorded with the 4mm O.D. FEP tubes held coaxially in 5mm precision glass NMR tubes which contained a small quantity of D$_2$O as a lock substance, as shown in Figure 6.3.

Reactions involving AHF were performed with extreme care, the AHF was contained in Kel-F tubes and all of the connectors and couplings were either PTFE or FEP.

6.6 Solvents

Diethylether, tetrahydrofuran, hexane and toluene (BDH Ltd., Spectroscopic Grade) were all dried by refluxing over sodium and benzophenone. Dichloromethane (BDH Ltd., Spectroscopic Grade) was dried by refluxing over calcium hydride, benzene was dried over sodium and acetone was dried over calcium sulphate. All were vacuum-distilled prior to use into glass storage vessels closed by Youngs' PTFE valves.

Solvents used on the metal vacuum line required a more rigorous drying method and additional purification. Dichloromethane was further purified and dried by shaking with portions of conc. H$_2$SO$_4$ until the acid layer remained colourless, washed with water, aq. 5% Na$_2$CO$_3$ and then water again. The solvent was then pre-dried with CaCl$_2$, distilled from P$_2$O$_5$ and finally distilled from CaH$_2$ under dinitrogen.
Figure 6.3 NMR Sample in 4 mm FEP Tubing

FEP Tube (4 mm o.d., 3 mm i.d.).

Cap.

Precision Glass NMR Tube (5 mm o.d.).

deuterated solvent

Sample.
### 6.7 Chemical Reagents

<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>SOURCE</th>
<th>PURIFICATION / SPECIAL STORAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecacarbonyl triruthenium, ([\text{Ru}<em>9(\text{CO})</em>{12}])</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Dodecacarbonyl triosmium, ([\text{Os}<em>9(\text{CO})</em>{12}])</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Trimethylphosphine, (\text{PM}_{3})</td>
<td>1</td>
<td>B</td>
</tr>
<tr>
<td>Triethylphosphine, (\text{PE}_{3})</td>
<td>1</td>
<td>B</td>
</tr>
<tr>
<td>Ethyldiphenylphosphine, (\text{PEtPh}_2)</td>
<td>1</td>
<td>B</td>
</tr>
<tr>
<td>Methylidiphenylphosphine, (\text{PMePh}_2)</td>
<td>1</td>
<td>B</td>
</tr>
<tr>
<td>Dimethylphenylphosphine, (\text{PMe}_3)</td>
<td>1</td>
<td>B</td>
</tr>
<tr>
<td>Triphenylphosphine, (\text{PPh}_3)</td>
<td>2</td>
<td>A</td>
</tr>
<tr>
<td>Diethylphenylphosphine, (\text{PEtPh}_2)</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Tris(4-fluorophenyl)phosphine, (\text{P}(p-F-C_6\text{H}_{4})_3)</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Tri-p-tolylphosphine, (\text{P}(p-\text{MeC}_6\text{H}_4)_3)</td>
<td>1</td>
<td>C</td>
</tr>
<tr>
<td>Tricyclohexylphosphine, (\text{PC}_{12})</td>
<td>1</td>
<td>C</td>
</tr>
<tr>
<td>Diphenylpentfluoro-phenylphosphine, (\text{P}(\text{C}_6\text{F}_5)_2)</td>
<td>5</td>
<td>A</td>
</tr>
<tr>
<td>Bis(diphenylphosphino)-ethane, (\text{dppe})</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>1,1,1-Tris(diphenylphosphinomethyl)ethane, (\text{triphos(II)})</td>
<td>1</td>
<td>C</td>
</tr>
<tr>
<td>Tris[2-(diphenylphosphino-ethyl)]phosphino, (\text{tetraphos(II)})</td>
<td>1</td>
<td>C</td>
</tr>
<tr>
<td>Triphenylarsine, (\text{AsPh}_3)</td>
<td>1</td>
<td>C</td>
</tr>
<tr>
<td>Pyridine, (\text{py})</td>
<td>6</td>
<td>E</td>
</tr>
<tr>
<td>Disodium hexachlorooximate, ([\text{Na}_2\text{OsCl}_6])</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Dipotassium hexachlorooximate, ([\text{K}_2\text{OsCl}_6])</td>
<td>6</td>
<td>A</td>
</tr>
<tr>
<td>Boron trifluoride, (\text{BF}_3)</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Carbon monoxide, (\text{CO})</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Fluorine, (\text{F}_2)</td>
<td>4</td>
<td>A</td>
</tr>
<tr>
<td>CHEMICAL</td>
<td>SOURCE</td>
<td>PURIFICATION / SPECIAL STORAGE</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>--------</td>
<td>-----------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Xenon, Xe</td>
<td>7</td>
<td>A</td>
</tr>
<tr>
<td>Bismuth pentafluoride, BiF₅</td>
<td>5</td>
<td>C</td>
</tr>
<tr>
<td>Xenon difluoride, XeF₂</td>
<td></td>
<td>Prepared by the static fluorination of xenon gas under UV radiation at room temperature[^3]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sublimed before use and stored in pre-fluorinated FEP vessels in the dry-box</td>
</tr>
<tr>
<td>Hydrogen fluoride, HF</td>
<td>5</td>
<td>Doubly vacuumed distilled, dried by repetitive fluorination at room temperature and stored in a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pre-fluorinated Kel-F tube over dry BiF₅</td>
</tr>
<tr>
<td>Osmium trichloride hydrate, [OsCl₃·3H₂O]</td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Silver fluoride, AgF</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Dichlororotricarbonylosmium (II) dimer,</td>
<td></td>
<td>Prepared according to the literature method[^6]</td>
</tr>
<tr>
<td>([OsCl₂(CO)₉]₂)</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Dicarbonylbis(triphenylphosphine)ruthenium(II)-</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>chloride, [OC-6-33][RuCl₅(CO)₃(PPh₃)₂]</td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Dicarbonylbis(triphenylphosphine)osmium(II)-</td>
<td></td>
<td>Prepared according to the literature method[^7]</td>
</tr>
<tr>
<td>hydride, [OC-6-13][OsH₃(CO)₃(PPh₃)₂]</td>
<td></td>
<td>D</td>
</tr>
<tr>
<td>Dicarbonylbis(triphenylphosphine)ruthenium(II)-</td>
<td></td>
<td>Prepared according to the literature method[^8]</td>
</tr>
<tr>
<td>hydride, [OC-6-13][RuH₃(CO)₃(PPh₃)₂]</td>
<td></td>
<td>D</td>
</tr>
<tr>
<td>Carbonyltris(triphenylphosphine)osmium(II)-</td>
<td></td>
<td>Prepared according to the literature method[^7]</td>
</tr>
<tr>
<td>hydride, [OC-6-14][OsH₃(CO)(PPh₃)₃]</td>
<td></td>
<td>D</td>
</tr>
<tr>
<td>Carbonyltris(triphenylphosphine)ruthenium(II)-</td>
<td></td>
<td>Prepared according to the literature method[^8]</td>
</tr>
<tr>
<td>hydride, [OC-6-14][RuH₃(CO)(PPh₃)₃]</td>
<td></td>
<td>D</td>
</tr>
<tr>
<td>Tris[2-(diphenylphosphinomethyl)ethene]-</td>
<td></td>
<td>Prepared according to the literature method[^9]</td>
</tr>
<tr>
<td>ruthenium(II)hydride, [RuH₃(Tetraphos)]</td>
<td></td>
<td>D</td>
</tr>
<tr>
<td>Boron trifluoride etherate, BF₃·OEt₂</td>
<td>2</td>
<td>A</td>
</tr>
</tbody>
</table>

[^3]: Prepared by the static fluorination of xenon gas under UV radiation at room temperature. Sublimed before use and stored in pre-fluorinated FEP vessels in the dry-box. (2023-01-16)
<table>
<thead>
<tr>
<th>CHEMICAL</th>
<th>SOURCE</th>
<th>PURIFICATION / SPECIAL STORAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium hydride, CaH₂</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Tertiarybutyl ammonium fluoride, N'Bu₃F</td>
<td>1</td>
<td>F</td>
</tr>
<tr>
<td>tris(triphenylphosphine)-ruthenium(II)chloride, [RuCl₃(PPh₃)₃]</td>
<td>Prepared according to the literature method.[66]</td>
<td>D</td>
</tr>
<tr>
<td>Sodium borohydride, NaBH₄</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Phosphorus pentoxide, P₂O₅</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Calcium sulphate, CaSO₄</td>
<td>1</td>
<td>E</td>
</tr>
<tr>
<td>Sodium, Na</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Sodium tetrphenylborate, NaBPh₄</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Ruthenium trichloride, RuCl₃</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Methyl lithium, MeLi, 1.4M in diethyl ether</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Methyl magnesium bromide, MeMgBr, 1.0M in thf</td>
<td>1</td>
<td>A</td>
</tr>
<tr>
<td>Trimethylsilyl-trifluoroacetate, Me₃SiOC(OF₃)</td>
<td>1</td>
<td>A</td>
</tr>
</tbody>
</table>

(1) Aldrich Chemical Company Ltd, (2) Lancaster Chemical Company Ltd, (3) Air Products, (4) Fluorochem, (5) Johnson Matthey, (6) FSA Laboratory Supplies, (7) BOC Gasses, (A) used as supplied, (B) stored in a glass ampoule fitted with a Youngs’ tap and degassed prior to use, (C) used as supplied, stored in the dry-box, (D) recrystallized prior to use, (E) dried prior to use, (F) dried prior to use and stored in the dry box.
The complexes $[\text{MF}_2(\text{CO})_3]_4$ (M = Os or Ru) were synthesised in almost quantitative yield from the oxidative fluorination of $[\text{M}_3(\text{CO})_{12}]$ with either XeF$_2$ or fluorine gas. For large-scale preparations, fluorine gas was used for economic reasons and to avoid a large evolution of xenon gas which is a by-product from the XeF$_2$ reactions.

**a) Reactions using F$_2$(g).**

In a large scale preparation a weighed amount of $[\text{M}_3(\text{CO})_{12}]$ (M = Os or Ru) typically 5g, was loaded, in a dry-box, into a pre-fluorinated 400 cm$^3$ Teflon™ reaction vessel containing a 2.5cm PTFE magnetic stirrer bar and fitted with Chemcon™ connectors. The reaction vessel was connected to the metal vacuum line and the connectors passivated. The reactor was evacuated and AHF (ca. 10 cm$^3$) condensed into the reaction vessel at -196°C under a static vacuum. The AHF was allowed to warm to room temperature and the reaction mixture stirred for 24h to ensure that all of the $[\text{M}_3(\text{CO})_{12}]$ had dissolved. The solution was cooled to -78°C and placed under one atmosphere of fluorine gas, and stirred for a further 12h during which the deep orange colour became less intense. The reaction mixture was then cooled to -78°C and the vessel opened to the metal vacuum line to monitor the consumption of fluorine gas. If all the fluorine gas had been consumed, the reaction was placed under an additional atmosphere of fluorine gas and allowed to warm to room temperature. This process was repeated until the uptake of fluorine gas had ceased, suggesting complete reaction.

The AHF solvent was then removed in vacuo to leave a white / buff solid or pale yellow solid for osmium or ruthenium respectively. The solid was placed under high vacuum for 24h to remove any residual AHF to give the carbonyl fluoride tetrarters, $[\text{MF}_2(\text{CO})_3]_4$, in an almost quantitative yield (ca. >90%). The compounds were stored in the dry box. The authenticity and purity of the material was checked by comparison of the infrared spectra with the reported literature values.$^{[11,12]}$
b) Reactions using XeF$_2$.

Following the literature method,$^{[12]}$ a weighed amount of [M$_3$(CO)$_2$] (M = Os or Ru) (ca. 0.10 g), was loaded, in a dry-box, into a 6 mm pre-fluorinated FEP tube along with 3.5 molar equivalence of XeF$_2$. The two solids were kept separate, to avoid uncontrolled reaction, by means of a kink in the reactor. The FEP tube was re-connected to the metal vacuum line and the connectors passivated. The reactor was cooled to -196°C and evacuated to approximately 10$^4$ mmHg; cooling to -196°C is necessary to prevent the removal of the volatile XeF$_2$. The AHF solvent (ca. 0.3 cm$^3$) was distilled into the reaction tube under a static vacuum at -196°C. The reaction mixture was allowed to warm to -60°C whereupon reaction occurred with the rigorous evolution of xenon gas. WARNING, allowing the initial reaction to warm above -60°C can cause a violent reaction with a massive increase in pressure due to the evolution of xenon gas. This, in turn, can result in the FEP tube being blown off the vacuum line and lead to exposure to AHF. The xenon gas evolved in the reaction was, therefore, vented regularly to avoid a dangerous build up of pressure by cooling the reactor to -78°C and pumping away the volatile gas. After vigorous reaction had ceased, the pale orange solution was cautiously allowed to warm to room temperature and left overnight to ensure complete reaction.

After this period the AHF solvent was removed *vaccum* to leave a white/buff solid for M = Os and a pale yellow solid for M = Ru. The solid was placed under high vacuum for 24 hours to remove residual AHF to give the carbonyl fluoride tetramers, [MF$_2$(CO)$_3$)$_4$] in an almost quantitative yield (ca. >90%). The compounds were stored in the dry box. The authenticity and purity of the material was checked by comparison of the infrared spectra with the reported literature values.$^{[10,11]}$

6.8.1 Reaction of [Ru$_3$(CO)$_2$]$_2$ with XeF$_2$ in AHF: Preparation of NMR Samples

As described in Chapter Four, the reactions between various ratios of [Ru$_3$(CO)$_2$]$_2$ : XeF$_2$ were investigated in an attempt to identify any reaction intermediates. A weighed amount of [Ru$_3$(CO)$_2$]$_2$ (ca. 0.05 g) was introduced into a 4 mm O.D. pre-fluorinated FEP reaction tube along with the appropriate amount of XeF$_2$ using a dry-box. The reaction was carried out as above, and the FEP vessels heat sealed upon completion of reaction for NMR studies.
6.8.2 Reaction of [Ru₃(CO)₁₂] with Fluorine gas in AHF: Preparation of NMR Samples

In an attempt to investigate reaction intermediates these reactions were carried out in a similar manner to those described above. A weighed amount of [Ru₃(CO)₁₂], (ca. 0.15g), was loaded into a 4mm O.D. pre-fluorinated FEP tube in a dry-box. AHF solvent (ca. 0.3 cm³) was distilled into the reaction tube under a static vacuum at -196°C and the reaction mixture was allowed to warm to room temperature and left overnight to ensure the [Ru₃(CO)₁₂] had dissolved. The reactor was cooled to -78°C and the appropriate amount of fluorine gas was introduced. The needle valve on the FEP reactor was left open to the metal vacuum line to allow close monitoring of the fluorine gas. After complete reaction (ca. 8h) the FEP tube was heat sealed and stored at -196°C prior to NMR studies.

6.9 Preparation of [MF₂(CO)₃(L)₂], where M = Os, Ru

A weighed amount of [MF₂(CO)₃]₄ (ca. 0.10g) was loaded into a Schlenk flask in the dry-box along with, for the solid reagents, a slight excess of the ligand (8 molar equivalence). The Schlenk was then attached to the glass vacuum line and the tubing degassed. After degassing (i.e. three successive cycles of pumping and introducing dry dinitrogen) freshly distilled dichloromethane (for M = Os) or acetone (for M = Ru) (ca. 20 cm³) was transferred on to the reagents via a cannular. Reaction ensued immediately as evidenced by gas evolution. The reaction mixture was then degassed and stirred under dinitrogen for 3h to ensure complete reaction to give a yellow solution in all cases. The solvent was removed under reduced pressure and the pale yellow/white solid recrystallized from dichloromethane (or benzene) and petrol (40°-60°) to give complexes of the type [MF₂(CO)₃(L)₂] in ~ 90% yield.

Liquid phosphines and pyridine were syringed under dinitrogen into the Schlenk flask in a slight excess after the addition of the solvent to [MF₂(CO)₃]₄ rather than being placed directly onto [MF₂(CO)₃]₄ in the dry-box.

NMR and IR data for all the products are described in Chapter Two.
Table 6.1 $^1$H NMR and Mass spectrometry Data for [OC-6-F][MF$_2$(CO)$_2$L$_2$]

<table>
<thead>
<tr>
<th>L</th>
<th>$\delta(^1$H) / ppm</th>
<th>m/z</th>
<th>L</th>
<th>$\delta(^1$H) / ppm</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPh$_3$ (29)</td>
<td>7.5 (m)</td>
<td>791$^a$</td>
<td>PPh$_3$ (42)</td>
<td>7.6 (m)</td>
<td>701$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>763$^b$</td>
<td></td>
<td></td>
<td>673$^b$</td>
</tr>
<tr>
<td>PPh$_3$(C$_6$F$_3$)$_2$ (33)</td>
<td>7.6 (m)</td>
<td>971$^a$</td>
<td>PPh$_3$(C$_6$F$_3$) (45)</td>
<td>7.5 (m)</td>
<td>881$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>943$^b$</td>
<td></td>
<td></td>
<td>853$^b$</td>
</tr>
<tr>
<td>P(p-tolyl)$_3$ (34)</td>
<td>2.4 (s)$^a$</td>
<td>827$^a$</td>
<td>P(p-tolyl)$_3$ (47)</td>
<td>2.1 (s)$^a$</td>
<td>757$^b$</td>
</tr>
<tr>
<td>P(p-F-C$_6$H$_4$)$_3$ (35)</td>
<td>7.1 (m)</td>
<td>899$^a$</td>
<td>P(p-F-C$_6$H$_4$)$_3$ (48)</td>
<td>7.5 (m)</td>
<td>809$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>871$^b$</td>
<td></td>
<td></td>
<td>781$^b$</td>
</tr>
<tr>
<td>P(p-tolyl)$_3$ (36)</td>
<td>1.3 (m)$^a$</td>
<td>502$^a$</td>
<td>PPh$_3$ (49)</td>
<td>1.2 (m)$^a$</td>
<td>413$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>475$^b$</td>
<td></td>
<td></td>
<td>385$^b$</td>
</tr>
<tr>
<td>PMe$_2$Ph$_2$ (37)</td>
<td>2.0 (m)$^a$</td>
<td>657$^a$</td>
<td>PMe$_2$Ph$_2$ (50)</td>
<td>1.9 (m)$^a$</td>
<td>549$^b$</td>
</tr>
<tr>
<td>PMe$_2$Ph (38)</td>
<td>1.7 (m)$^a$</td>
<td>543$^a$</td>
<td>PMe$_2$Ph (51)</td>
<td>1.8 (m)$^a$</td>
<td>453$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>515$^b$</td>
<td></td>
<td></td>
<td>425$^b$</td>
</tr>
<tr>
<td>PEt$_3$Ph (39)</td>
<td>1.0 (m)$^a$</td>
<td>599$^a$</td>
<td>PEt$_3$Ph (52)</td>
<td>1.1 (m)$^a$</td>
<td>481$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>571$^b$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_5$N (40)</td>
<td>7.7 (m)</td>
<td>425$^a$</td>
<td>C$_6$H$_5$N (53)</td>
<td>7.8 (m)</td>
<td>335$^a$</td>
</tr>
<tr>
<td>AsPh$_3$ (41)</td>
<td>7.5 (m)</td>
<td>851$^b$</td>
<td>AsPh$_3$ (54)</td>
<td>7.5 (m)</td>
<td>789$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>761$^b$</td>
</tr>
</tbody>
</table>

$^a$[M - F]$^a$

$^b$[M - F - CO]$^b$

$^c$[M - 2F - CO]$^c$

$^d$CH$_3$ protons,

$^e$CH$_2$ protons

$^f$aryl protons

$^{19}$F NMR data for the para fluorine ca. $\delta$ -108

$^{19}$F NMR data for the C$_6$F$_3$ ring ca. $\delta$ -122 (ortho), $\delta$ -146 (para) and $\delta$ -161 (meta)
Table 6.2 Microanalytical Data* for [OC-6-13][MF₂(CO)₂L₂], Calculated Values in Parentheses

<table>
<thead>
<tr>
<th></th>
<th>Microanalysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>M = Os, L = PPh₃ (29)ᵇ</td>
<td>56.36 (56.43)</td>
</tr>
<tr>
<td>M = Os, L = PMe₃ (31)ᵇ</td>
<td>22.07 (22.02)</td>
</tr>
<tr>
<td>M = Os, L = PCy₃ (32)ᵇ</td>
<td>54.14 (54.01)</td>
</tr>
<tr>
<td>M = Ru, L = PPh₃ (42)</td>
<td>63.09 (63.42)</td>
</tr>
<tr>
<td>M = Ru, L = PEtPh₂ (43)</td>
<td>57.90 (57.78)</td>
</tr>
<tr>
<td>M = Ru, L = P(p-F-C₆H₄)₃ (48)</td>
<td>54.84 (55.15)</td>
</tr>
<tr>
<td>M = Ru, L = AsPh₃ (54)ᵇ</td>
<td>55.92 (56.52)</td>
</tr>
</tbody>
</table>

* unsatisfactory analysis was obtained for the majority of the difluoride complexes due to incomplete combustion.

ᵇ tungstic oxide added to aid combustion.

6.10 Reaction of [M(F₂CO)₃] with dppe

This reaction was carried out as described above but with 4 molar equivalence of dppe. The reaction gave a mixture of products and is discussed in more detail in Chapter Two.

6.11 Preparation of [OC-6-13][MF₂(CO)₂(PPh₃)₂] (56-57), where M = Os, Ru

A weighed amount (ca. 0.03g) of [OC-6-13][M(CO)₂F₂(PPh₃)₂] was loaded, in the dry-box, into a pre-fluorinated 4mm FEP tube. The FEP tube was connected to the metal vacuum line and the connectors passivated. Dichloromethane (ca. 0.3cm³) was condensed into the tube at -196°C under a static vacuum. The contents were allowed to warm to -78 °C and placed under one atmosphere of boron trifluoride gas giving a yellow solution. The tube was heat sealed for NMR studies or the solvent removed to give an off-white solid (ca. > 90%) which was manipulated in the dry-box for recording IR spectra.
6.12 Preparation of \([OC-6-13] [MF(CO)_2(PR_3)_3][BF_4]\), where \(M = \text{Os, Ru and PR}_3 = \text{PPh}_3, \text{PMe}_3\)

A weighed amount (ca. 0.10g) of \([MF(FBp_3)(CO)_2](PPh_3)_2]\) was loaded, in the dry-box, into a pre-fluorinated 6mm FEP tube along with slightly greater than one molar equivalent of triphenylphosphine. The FEP tube was connected to the metal vacuum line and the connectors passivated. Dichloromethane (ca. 0.80cm\(^3\)) was condensed into the reaction tube at -196°C under a static vacuum. The mixture was allowed to warm to room temperature and left for two hours, with occasional agitation. The solvent was then removed under reduced pressure to give off-white solids in all cases, excess of phosphine being removed by washing with warm hexane to give the complexes \([MF(CO)_2(PR_3)_3][BF_4]\) in yields greater than 80%.

The complex \([MF(CO)_2(PMe_3)_3][BF_4]\) was prepared in an analogous manner, \(\text{PMe}_3\) being vacuum transferred to the reaction flask at -196°C.

\(^{31}\text{P} (\text{\textsuperscript{1}H})\) and \(^{19}\text{F} \text{NMR data are described in Chapter Three.}\)

Table 6.3 \(^{1}H\), IR and Mass Spectrometry Data for the Complexes \([OC-6-13] [MF(CO)_2(PR_3)_3][BF_4]\)

<table>
<thead>
<tr>
<th></th>
<th>(\delta^{1}H)</th>
<th>(\nu(\text{CO}) / \text{cm}^{-1})</th>
<th>(m/z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M = Os, PR(_3) = PPh(_3) (58)</td>
<td>7.5 (m)</td>
<td>2043 (s), 1970 (s)</td>
<td>1053 (\text{[M]}^+), 791 (\text{[M - PPh}_3]^+)</td>
</tr>
<tr>
<td>M = Os, PR(_3) = PMe(_3) (59)</td>
<td>1.6 (m)</td>
<td>2040 (s), 1970 (s)</td>
<td>495 (\text{[M]}^+), 419 (\text{[M - PMe}_3]^+)</td>
</tr>
<tr>
<td>M = Ru, PR(_3) = PPh(_3) (60)</td>
<td>7.4 (m)</td>
<td>2054 (s), 1985 (s)</td>
<td>963 (\text{[M]}^+), 701 (\text{[M - PPh}_3]^+)</td>
</tr>
<tr>
<td>M = Ru, PR(_3) = PMe(_3) (61)</td>
<td>1.6 (m)</td>
<td>2048 (s), 1975 (s)</td>
<td>405 (\text{[M]}^+), 329 (\text{[M - PMe}_3]^+)</td>
</tr>
</tbody>
</table>

* Recorded in d\(^6\)-acetone.
6.13 Preparation of \([OC-6-13][MF(CO)_3(PR_3)_2][BF_4]\) (62-65) where \(M = Os, Ru\) and \(PR_3 = PPh_3, PMe_3\)

A weighed amount (ca. 0.10g) of \([MF(FBF_3)_2(CO)_2(PR_3)_2]\), \(PR_3 = PPh_3\) or \(PMe_3\) was loaded, in the dry-box, into a pre-fluorinated 6mm FEP tube. The FEP tube was connected to the metal vacuum line and the connectors passivated. Dichloromethane (ca. 0.8cm³) was condensed into the reaction tube at -196°C under a static vacuum. The reactor was allowed to warm to -78 °C and placed under two atmospheres of carbon monoxide gas and slowly warmed to room temperature. The tube was left to stand for 3h with occasional agitation after which all the solid appeared to have dissolved. The solvent and excess of carbon monoxide were then removed under reduced pressure to give an off-white solid of \([MF(CO)_3(PR_3)_2]\) in an almost quantitative yield (ca. >85%).

\(^{31}\)P[\(1\)H] and \(^{19}\)F NMR data are described in Chapter Three.

Table 6.4 \(^{1}\)H, IR and Mass Spectrometry Data for the Complexes
\([OC-6-13][MF(CO)_3(PR_3)_2][BF_4]\)

<table>
<thead>
<tr>
<th></th>
<th>(\delta^{1})H</th>
<th>(\nu(CO) / \text{cm}^{-1})</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M = Os, PR_3 = PMe_3) (62)</td>
<td>1.7 (m)</td>
<td>2112 (m) 2038 (s) 1963 (s)</td>
<td>419 [(M - CO)]⁺, 391 [(M - 2CO)]⁺</td>
</tr>
<tr>
<td>(M = Os, PR_3 = PPh_3) (63)</td>
<td>7.5 (m)</td>
<td>2151 (m) 2070 (s) 2035 (s)</td>
<td>791 [(M - CO)]⁺, 763 [(M - 2CO)]⁺ 744 [(M - 2CO-F)]⁺</td>
</tr>
<tr>
<td>(M = Ru, PR_3 = PMe_3) (64)</td>
<td>1.7 (m)</td>
<td>2065 (m) 2013 (s) 1970 (s)</td>
<td>357 [(M)]⁺, 329 [(M - CO)]⁺, 301 [(M - 2CO)]⁺</td>
</tr>
<tr>
<td>(M = Ru, PR_3 = PPh_3) (65)</td>
<td>7.6(m)</td>
<td>2163 (m) 2103 (s) 2077 (s)</td>
<td>701 [(M - CO)]⁺, 673 [(M - 2CO)]⁺ 653 [(M - 2CO-F)]⁺</td>
</tr>
</tbody>
</table>

\(^{a}\) Recorded in \(d^2\)-acetone.
6.14 Reaction of Metal Hydrides with AHF

In a typical reaction, the solid metal-hydride complex (ca. 0.05g) was weighed out, in the dry-box, into a 4mm pre-fluorinated FEP tube. The FEP tube was re-connected to the metal vacuum line and the connectors passivated. The reactor was evacuated to approximately 10⁻³ mmHg and the AHF solvent distilled into the reaction tube under a static vacuum at -196°C. The reaction mixture was allowed to warm to -50°C whereupon reaction occurred with the vigorous evolution of hydrogen gas. WARNING, allowing the initial reaction to warm above -50°C can result in a violent reaction with a large increase in pressure due to the evolution of hydrogen gas. This, in turn, can result in the FEP tube being blown off the vacuum line and lead to exposure of AHF. The hydrogen gas evolved in the reaction was vented regularly to avoid a dangerous build up of pressure by cooling the reactor to -78°C and pumping away the volatile gas. After the vigorous reaction had ceased, the blood-red solution was cautiously allowed to warm to room temperature and left overnight to ensure complete reaction. The AHF solvent was removed in vacuo to give off-white solids.

Anion exchange reactions were carried out on the cationic complexes by adding NaBPf₄ (in the dry-box) to the solid samples and condensing dry thf (ca. 0.3 cm³) into the reaction vessels. The solutions were agitated (1h) and any unwanted solid material removed by filtration. The solvent was then removed to give off-white solids. NMR and mass spectrometry for the complexes are described in Chapter Five.

No elemental analysis for the triply bridged fluoride complexes could be obtained due to the release of PPh₃ in the reaction which could not be efficiently removed before decomposition of the product.

ν(CO) 1877 (s) cm⁻¹ for [Os₂(μ-F)₃(CO)(PPh₃)₄][BPh₄] and 1961 (s) cm⁻¹ for [Ru₂(μ-F)₃(CO)(PPh₃)₄][BPh₄].

6.15 Preparation of [OC-6-J][M(Me)₆(CO)₆(PR₃)₃], where M = Os, Ru, PR₃ = PPh₃, P(η₅-C₅Me₅)

Typically, [OC-6-J][MF₆(CO)₆(PR₃)₃] (ca. 0.20g), was loaded into a Schlenk flask in a dry box. The flask was then evacuated and filled with dry dinitrogen and dry, freshly distilled diethyl ether or thf (ca. 20ml) was transferred into the flask via a cannular. Under an atmosphere of dry dinitrogen, 6 molar excess of the alkylating
agent [MeLi (1.4M in diethyl ether solution) / MeMgBr (1.0 M in thf)] was added via a syringe. The reaction mixture was stirred for two hours. Excess of alkylating agent was destroyed by careful addition of water-saturated diethyl ether, the solvent was removed in vacuo and the metal complexes extracted using benzene and recrystallized from a mixture of benzene / hexane to give beige solids in yields of ca. >60%. $^1$H, $^{13}$C($^1$H), $^{31}$P($^1$H) NMR, IR and mass spectrometry data are presented in Table 6.5.

Table 6.5 NMR, IR and Mass Spectrometry Data for the Complexes [OC-6-13][M(Me)$_2$(CO)$_2$(PR$_3$)$_2$]$^a$

<table>
<thead>
<tr>
<th></th>
<th>$\delta^{13}$C($^1$H)$_{\text{a}}$</th>
<th>$\delta^1$H$_{\text{d}}$</th>
<th>$\delta^{31}$P($^1$H)$_{\text{a}}$</th>
<th>$\nu$(CO)/ cm$^{-1}$</th>
<th>m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>M = Os</td>
<td>PR$_3$ = PPh$_3$ (78)</td>
<td>-13.4</td>
<td>-0.8</td>
<td>6.6</td>
<td>1977 (s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2$^2$(PC) = 8 Hz</td>
<td>$^2$(PH) = 8 Hz</td>
<td>1910 (s)</td>
<td></td>
</tr>
<tr>
<td>M = Os</td>
<td>PR$_3$ = PCy$_3$ (79)</td>
<td>-21.0</td>
<td>-0.3</td>
<td>-13.4</td>
<td>1967 (s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2$^2$(PC) = 9 Hz</td>
<td>$^2$(PH) = 7 Hz</td>
<td>1890 (s)</td>
<td></td>
</tr>
<tr>
<td>M = Ru</td>
<td>PR$_3$ = PPh$_3$ (80)</td>
<td>-2.5</td>
<td>0.0</td>
<td>29.4</td>
<td>1960 (s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^2$(PH) = 7 Hz</td>
<td></td>
<td>1816 (s)</td>
<td></td>
</tr>
<tr>
<td>M = Ru</td>
<td>PR$_3$ = PCy$_3$ (81)</td>
<td>not observed</td>
<td>0.1</td>
<td>46.5</td>
<td>1973 (s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^3$(PH) = 7 Hz</td>
<td></td>
<td>1902 (s)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Recorded in CDCl$_3$

$^b$ Recorded in C$_6$D$_6$

$^c$ Methyl group only

$^d$ Triplet Resonance

$^e$ Singlet Resonance

177
6.16 Reaction of \([\text{OC-6-13}][\text{MF}_2(\text{CO})_2(\text{PPh}_3)_2]\) with MeLi in a 1 : 1 ratio

This reaction was carried out as described above with the reagents in a 1 : 1 ratio. \(^{19}\text{F}, \quad ^{31}\text{P}(\text{'H})\) and \(^1\text{H}\) NMR data are presented in Table 6.6.

Table 6.6 NMR Data for the Complexes \([\text{OC-6-13}][\text{MF}(\text{Me})(\text{CO})_2(\text{PPh}_3)_2]\)^a

<table>
<thead>
<tr>
<th>M = Os (82)</th>
<th>(\delta^{19}\text{F})</th>
<th>(\delta^{31}\text{P}(\text{'H}))</th>
<th>(\delta^1\text{H})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-346.8) (t)</td>
<td>(-4.3) (d)</td>
<td>(-0.1) (t)</td>
<td></td>
</tr>
<tr>
<td>(3J(\text{PF}) = 30) Hz</td>
<td>(2J(\text{PF}) = 30) Hz</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>M = Ru (83)</th>
<th>(\delta^{19}\text{F})</th>
<th>(\delta^{31}\text{P}(\text{'H}))</th>
<th>(\delta^1\text{H})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-368.2) (t)</td>
<td>(22.2) (d)</td>
<td>(-0.3) (t)</td>
<td></td>
</tr>
<tr>
<td>(2J(\text{PF}) = 18) Hz</td>
<td>(2J(\text{PF}) = 18) Hz</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Recorded in \(\text{C}_6\text{D}_6\).

\(^b\) Multiplicity in parentheses, (d) doublet and (t) triplet.

\(^c\) Methyl group only.

6.17 Preparation of \([\text{OC-6-13}][\text{M}(	ext{OC}(_{\text{CF}})\text{CF}_{\text{CF}})_{\text{CO}}(\text{CO})_2(\text{PCy}_3)_2]\) (84)

A mixture of \([\text{OC-6-13}][\text{Ru}(_{\text{CF}})\text{CO}(_{\text{OC}})\text{CO}(_{\text{PCy}_3}_2)]\) (0.10g, 0.12mmol), and \(\text{Me}_3\text{SiOC(OC)CF}_3\) (0.05 cm³, 0.58mmol) in dry, freshly-distilled, methanol (30 cm³) was degassed and refluxed under dry dinitrogen for 3h. The mixture was allowed to cool. A small amount of unreacted starting material remained, and this was removed by filtration. Slow evaporation of the solvent affords colourless crystals in a yield of 60%. \(^{19}\text{F}, \quad ^{31}\text{P}(\text{'H})\) NMR and IR data is described in Chapter Three. \(\delta(\text{'H})\) 2.1 (m), \(m/z = 831 [\text{M} - \text{OC(OC)CF}_3]^+\). Microanalysis, found: C, 53.59; H, 7.04. Calc. for \([\text{M}(_{\text{OC}})\text{OC}(_{\text{CF}})\text{CF}_{\text{CF}})_{\text{CO}}(\text{CO})_2(\text{PCy}_3)_2]\): C, 53.44; H, 7.05.

6.18 Photolysis of \([\text{OC-6-13}][\text{MF}_2(\text{CO})_2(\text{PR}_3)_2]\), \(\text{M} = \text{Os}, \text{Ru}\) and \(\text{PR}_3 = \text{PMe}_3, \text{PPPh}_3\)

A weighed amount (ca. 0.02g) of \([\text{MF}_2(\text{CO})_2(\text{PR}_3)_2]\) was loaded into a 5mm Pyrex NMR tube, and dissolved in 0.5 cm³ of \(d_6\)-benzene. The solution was irradiated with UV light (350 nm) for 3h. \(^{19}\text{F}\) and \(^{31}\text{P}(\text{'H})\) NMR data are described in Chapter Three. \(m/z = 453 \quad [\text{RuF(CO)(PMe}_3)_4]^+, \quad 435 \quad [\text{RuH(CO)(PMe}_3)_4]^+, \quad 377 \quad [\text{RuF(CO)(PMe}_3)_2]^+\) and 357 \([\text{Ru(CO)(PMe}_3)_3]^+\).
6.19 Thermolysis of \([OC-6-13][MF_2(CO)_2(PR_3)_2]\). \(M = Os, Ru\) and \(PR_3 = PMes, PPh_3\)

A suspension of \([MF_2(CO)_2(PR_3)_2]\) (ca. 0.05g) in dry, freshly distilled toluene was degassed and refluxed under dry dinitrogen for 3h. NMR data is described in Chapter Three.

6.20 Reaction of \([OC-6-33][RuCl_2(CO)_2(PPh_3)_2]\) with silver tetrafluoroborate, followed by \(N^+BuF\)

Silver tetrafluoroborate (0.05g, 0.27mmol) was added to a solution of \([RuCl_2(CO)_2(PPh_3)_2]\) (0.10g, 0.13mmol) in dry, freshly distilled dichloromethane (20 cm³) at room temperature. The reaction mixture was then stirred under dry dinitrogen. After 24hrs silver salts were removed by filtration under nitrogen. The fluoride ion donor \(N^+BuF\) (0.1g, 0.38 mmol) was added to the filtrate under dry dinitrogen, and the mixture degassed and stirred under nitrogen for a further 24h. Insoluble salts were removed by filtration and the filtrate evaporated to give a white solid, which was a mixture of \([OC-6-13][RuF_2(CO)_2(PPh_3)_2]\), \([OC-6-13][RuF(OH)(CO)_2(PPh_3)_2]\) and \([OC-6-13][RuF(CO)_2(OH)_2(PPh_3)_2]\]⁺. This reaction is discussed further in Chapter Three.

6.21 Preparation of \([OC-6-33][OsCl_4(CO)_3(PPh_3)_2]\) (65)

Triethylphosphine (0.10cm³, 0.67mmol) was added under dry dinitrogen to a solution of \([OsCl_4(CO)_3]\) (0.12g, 0.17mmol) in dry, freshly distilled dichloromethane (ca. 20 cm³). The reaction mixture was degassed and stirred under nitrogen for 3h. The solvent was removed under vacuum to give a pale yellow oil. Excess of triethylphosphine was removed by washing with warm hexane, and the sticky solid recrystallized from CH₂Cl₂ / hexane to give pale yellow crystals in a yield of 65%. δ¹H, 1.23 (m) (CH₃), 2.22 (m) (CH₂), 8¹P(¹H) -9.3 (s): ν(CO) 2029 (s), 1953 (s) cm⁻¹.
6.22 Reaction of \( \text{IOC-C}_{6} \text{H}_{13} \text{IMe} \text{F}_{5} \text{(CO)}_{4} \text{(PR}_{3})_{2} \) with BF\(_{3}\)OEt\(_{2}\), where PR\(_{3}\) = PPh\(_{3}\) and PMe\(_{3}\).

To a degassed solution of [RuF\(_{2}\)(CO)\(_{2}\)(PR\(_{3}\))\(_{2}\)] (ca. 0.05g) in dry dichloromethane (ca. 20 cm\(^{3}\)) a 2 molar equivalent of BF\(_{3}\)OEt\(_{2}\) was added under dry dinitrogen. The reaction was stirred for 1h under dinitrogen followed by removal of the solvent and excess of BF\(_{3}\)OEt\(_{2}\) under vacuum to give beige solids. The NMR data for the mixture of complexes formed are discussed in Chapter Three.
Chapter Six References


[8] Prepared from the reaction of [RuCl$_2$(CO)$_2$(PPh$_3$)$_2$] with LiAIH$_4$ in thf.


APPENDIX
Table A  X-Ray Crystal Data Collection, Solution and Refinement Details for the Complexes (29), (32), (43), (55), (78), (79) and (84).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(29)</th>
<th>(32)</th>
<th>(43)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{3}$H$</em>{2}$Cl$<em>{2}$O$</em>{2}$EtF$_{2}$</td>
<td>C$<em>{3}$H$</em>{2}$Cl$<em>{2}$F$</em>{3}$O$<em>{2}$EtF$</em>{2}$</td>
<td>C$<em>{3}$H$</em>{2}$F$<em>{2}$O$</em>{2}$P$_{2}$Ru</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>893.69</td>
<td>929.97</td>
<td>623.55</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293</td>
<td>190</td>
<td>193</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2c</td>
<td>P-1</td>
<td>P$<em>{2}$$</em>{1}$n</td>
</tr>
<tr>
<td>Unit cell dimensions (Å and °)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a = 17.197(2)</td>
<td>a = 10.732(2)</td>
<td>a = 9.7510(10)</td>
<td></td>
</tr>
<tr>
<td>b = 10.791(2)</td>
<td>b = 12.519(2)</td>
<td>b = 13.0220(10)</td>
<td></td>
</tr>
<tr>
<td>c = 20.034(3)</td>
<td>c = 17.228(4)</td>
<td>c = 22.415(2)</td>
<td></td>
</tr>
<tr>
<td>α = 90</td>
<td>α = 81.14</td>
<td>α = 90</td>
<td></td>
</tr>
<tr>
<td>β = 102.94</td>
<td>β = 76.12</td>
<td>β = 100.93</td>
<td></td>
</tr>
<tr>
<td>γ = 90</td>
<td>γ = 71.13</td>
<td>γ = 90</td>
<td></td>
</tr>
<tr>
<td>Volume / Å$^3$</td>
<td>3623.4(10)</td>
<td>2118.9(7)</td>
<td>2794.6(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Density (calc.)</td>
<td>1.638 Mg/m$^3$</td>
<td>1.458 Mg/m$^3$</td>
<td>1.482 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient (μ mm$^{-1}$)</td>
<td>3.799</td>
<td>3.250</td>
<td>0.714</td>
</tr>
<tr>
<td>F(000)</td>
<td>1760</td>
<td>952</td>
<td>1272</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.38 x 0.18 x 0.11</td>
<td>0.60 x 0.56 x 0.55</td>
<td>0.70 x 0.40 x 0.28</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-1 ≤ h ≤ 20</td>
<td>-1 ≤ h ≤ 12</td>
<td>-1 ≤ h ≤ 12</td>
</tr>
<tr>
<td></td>
<td>-1 ≤ k ≤ 12</td>
<td>-14 ≤ k ≤ 14</td>
<td>-1 ≤ k ≤ 16</td>
</tr>
<tr>
<td></td>
<td>-23 ≤ l ≤ 23</td>
<td>-20 ≤ l ≤ 20</td>
<td>-28 ≤ l ≤ 28</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>4071</td>
<td>8688</td>
<td>7820</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3184 (Rint = 0.0294)</td>
<td>7406 (Rint = 0.0301)</td>
<td>6100 (Rint = 0.0245)</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least squares on F$^2$</td>
<td>Full-matrix least squares on F$^2$</td>
<td>Full-matrix least squares on F$^2$</td>
</tr>
<tr>
<td>data / restraints / parameters</td>
<td>3184 / 0 / 210</td>
<td>7405 / 0 / 442</td>
<td>6100 / 0 / 334</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>0.963</td>
<td>1.045</td>
<td>1.041</td>
</tr>
<tr>
<td>Final R indices</td>
<td>R1 = 0.0485</td>
<td>R1 = 0.0447</td>
<td>R1 = 0.0359</td>
</tr>
<tr>
<td></td>
<td>wR2 = 0.1170</td>
<td>wR2 = 0.1083</td>
<td>wR2 = 0.0840</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0682</td>
<td>R1 = 0.0576</td>
<td>R1 = 0.0513</td>
</tr>
<tr>
<td></td>
<td>wR2 = 0.1236</td>
<td>wR2 = 0.11650</td>
<td>wR2 = 0.0921</td>
</tr>
<tr>
<td>Largest diff. peak and hole (eÅ$^3$)</td>
<td>0.924 and -1.03</td>
<td>1.910 and -2.093</td>
<td>0.536 and -0.391</td>
</tr>
<tr>
<td>Compound</td>
<td>(55)</td>
<td>(77)</td>
<td>(78)</td>
</tr>
<tr>
<td>----------</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Formula</td>
<td>C₁₁H₂₆Cl₂O₅P₂</td>
<td>C₁₁H₂₆O₅P₂Ru</td>
<td>C₁₂H₂₆O₅P₂</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>553.42</td>
<td>471.35</td>
<td>800.83</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>190</td>
<td>190</td>
<td>293</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>orthorhombic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
<td>Pbcn</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions (Å and °)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a = 8.2860(10)</td>
<td>a = 19.347(4)</td>
<td>a = 10.208(2)</td>
<td></td>
</tr>
<tr>
<td>b = 20.210(3)</td>
<td>b = 13.113(2)</td>
<td>b = 12.457(2)</td>
<td></td>
</tr>
<tr>
<td>c = 12.7170(10)</td>
<td>c = 16.156(4)</td>
<td>c = 14.485(6)</td>
<td></td>
</tr>
<tr>
<td>α = 90</td>
<td>α = 90</td>
<td>α = 97.61</td>
<td></td>
</tr>
<tr>
<td>β = 107.50</td>
<td>β = 90</td>
<td>β = 103.89</td>
<td></td>
</tr>
<tr>
<td>γ = 90</td>
<td>γ = 90</td>
<td>γ = 106.430(10)</td>
<td></td>
</tr>
<tr>
<td>Volume / Å³</td>
<td>2031.0(4)</td>
<td>4099(2)</td>
<td>1674.9(8)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>Density (calc.)</td>
<td>1.810 Mg/m³</td>
<td>1.528 Mg/m³</td>
<td>1.588 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient (µ mm⁻¹)</td>
<td>6.700</td>
<td>1.024</td>
<td>3.937</td>
</tr>
<tr>
<td>F(000)</td>
<td>1080</td>
<td>1952</td>
<td>796</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.60 × 0.21 × 0.17</td>
<td>0.68 × 0.51 × 0.14</td>
<td>0.46 × 0.32 × 0.16</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-1 ≤ h ≤ 10</td>
<td>-1 ≤ h ≤ 23</td>
<td>-1 ≤ h ≤ 11</td>
</tr>
<tr>
<td></td>
<td>-1 ≤ k ≤ 25</td>
<td>-1 ≤ k ≤ 15</td>
<td>-13 ≤ k ≤ 13</td>
</tr>
<tr>
<td></td>
<td>-16 ≤ l ≤ 15</td>
<td>-1 ≤ l ≤ 19</td>
<td>-16 ≤ l ≤ 16</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>5050</td>
<td>4484</td>
<td>6037</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3964 (Rint = 0.0347)</td>
<td>3602 (Rint = 0.0581)</td>
<td>4924 (Rint = 0.0516)</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least squares on F²</td>
<td>Full-matrix least squares on F²</td>
<td>Full-matrix least squares on F²</td>
</tr>
<tr>
<td>data / restraints / parameters</td>
<td>3964 / 0 / 190</td>
<td>3592 / 0 / 195</td>
<td>4905 / 20 / 326</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.072</td>
<td>1.040</td>
<td>1.029</td>
</tr>
<tr>
<td>Final R indices</td>
<td>R1 = 0.0278</td>
<td>R1 = 0.0580</td>
<td>R1 = 0.0696</td>
</tr>
<tr>
<td></td>
<td>wR2 = 0.679</td>
<td>wR2 = 0.1485</td>
<td>wR2 = 0.1896</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0330</td>
<td>R1 = 0.0804</td>
<td>R1 = 0.1031</td>
</tr>
<tr>
<td></td>
<td>wR2 = 0.0703</td>
<td>wR2 = 0.1771</td>
<td>wR2 = 0.2826</td>
</tr>
<tr>
<td>Largest diff. peak and hole (eÅ⁻³)</td>
<td>1.181 and -1.302</td>
<td>2.009 and -1.230</td>
<td>3.068 and -1.804</td>
</tr>
<tr>
<td>Compound</td>
<td>(79)</td>
<td>(84)</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Formula</td>
<td>C_{20}H_{32}O_{12}P_{2}</td>
<td>C_{20}H_{32}O_{12}P_{2}Ru</td>
<td></td>
</tr>
<tr>
<td>Formula Weight</td>
<td>837.12</td>
<td>943.96</td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>190</td>
<td>293</td>
<td></td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
<td>monoclinic</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>C_{2n}</td>
<td></td>
</tr>
<tr>
<td>Unit cell dimensions (Å and °)</td>
<td>a = 10.085(1) b = 10.405(4) c = 11.092(2) α = 62.18(2) β = 71.51(1) γ = 89.72(2)</td>
<td>a = 11.040(2) b = 17.021(2) c = 24.011(3) α = 90 β = 96.35 γ = 90</td>
<td></td>
</tr>
<tr>
<td>Volume / Å³</td>
<td>961.9(4)</td>
<td>4484.3(11)</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Density (calc.)</td>
<td>1.445 Mg/m³</td>
<td>1.398 Mg/m³</td>
<td></td>
</tr>
<tr>
<td>Absorption coefficient (µm⁻¹)</td>
<td>3.429</td>
<td>0.490</td>
<td></td>
</tr>
<tr>
<td>F(000)</td>
<td>434</td>
<td>1976</td>
<td></td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.49 × 0.26 × 0.23</td>
<td>0.70 × 0.66 × 0.64</td>
<td></td>
</tr>
<tr>
<td>Index ranges</td>
<td>-1 ≤ h ≤ 9 -10 ≤ k ≤ 10 -12 ≤ l ≤ 13</td>
<td>-1 ≤ h ≤ 14 -1 ≤ k ≤ 21 -30 ≤ l ≤ 30</td>
<td></td>
</tr>
<tr>
<td>Reflections collected</td>
<td>3417</td>
<td>6022</td>
<td></td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2845 (R_{int} = 0.0521)</td>
<td>4866 (R_{int} = 0.0158)</td>
<td></td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least squares on F²</td>
<td>Full-matrix least squares on F²</td>
<td></td>
</tr>
<tr>
<td>data / restraints / parameters</td>
<td>2845 / 0 / 214</td>
<td>4865 / 0 / 258</td>
<td></td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.062</td>
<td>0.778</td>
<td></td>
</tr>
<tr>
<td>Final R indices</td>
<td>R1 = 0.0409 wR2 = 0.1103</td>
<td>R1 = 0.0392 wR2 = 0.1110</td>
<td></td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0410 wR2 = 0.1104</td>
<td>R1 = 0.0482 wR2 = 0.1222</td>
<td></td>
</tr>
<tr>
<td>Largest diff. peak and hole (eÅ⁻³)</td>
<td>2.093 and -1.291</td>
<td>0.769 and -0.577</td>
<td></td>
</tr>
</tbody>
</table>

* Details in common: Siemens P4 diffractometer, λ(Mo-Kα) = 0.7107 Å, ω scan type.