N.M.R. STUDIES OF SOME NOVEL FLUORO-IRIDIUM COMPLEXES

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Declaration

Except where specific reference is made to other sources, the work presented in this thesis is the original work of the author. It has not been submitted, in whole or in part, for any other degree. Certain of the results have already been published.
To my mother, brother, Gwenda and the memory of my father.
Acknowledgements

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Contents

Abstract

Page

XX

Chapter 1

1.1 An Introduction to Oxidative Addition

1

1.2 Oxidative Addition and Stereochemistry

4

1.3 Kinetics and Thermodynamics in Oxidative Addition Reactions

8

1.4 Oxidative Addition and Free Radicals

9

1.5 Oxidative Addition at Electronically Unsaturated Metal Centres

10

1.6 Ligand Influences favouring 5 co-ordinate versus 4 co-ordinate geometry

12

1.7 The Trans Effect and the Trans Influence

14

1.8 Oxidative Addition and Main Group Elements

19

1.9 Methods of Monitoring Oxidative Addition Reactions

20

1.10 Oxidative Addition and Reductive Elimination

24

1.11 Oxidative Addition in Catalysis

27

1.12 Pseudorotation Processes in Inorganic Chemistry

30
Chapter 2

2.0 An Introduction to the Formation of Ir-SF₃ complexes

2.1 The Background to the Oxidative Addition of t-IrClCO[P(CH₂CH₃)₃]₂ with SF₄.

2.2 The Reaction of t-IrCl(CO)[P(CH₂CH₃)₃]₂ (2.0.1) with SF₄

2.3 An Investigation into Exchange Processes Involving Complexes Containing the -SF₃ Ligand

2.4 Calculation of Activation Energy for Processes Relating to Fluorine exchange in (2.1.1).

2.5 Other Halo-Complexes containing an -SF₃ Ligand

2.6 Conclusions on the Data for (2.1.1), (2.3.1) and (2.3.2)

2.7 The Reaction of t-Ir(NCO)(CO)[P(CH₂CH₃)₃]₂ (2.4.0) with SF₄
2. 8 An Investigation into the susceptibility of (2.4.1) to Fluorine Exchange.

2. 9 The Reaction of $t$-Ir(NCS)(CO)[P(CH$_2$CH$_3$)$_3$]$_2$ with SF$_4$

2.10 Conclusions on the Reactions of $t$-IrX(CO)[P(CH$_2$CH$_3$)$_3$]$_2$ (X= Cl, Br, I, NCO, NCS) with SF$_4$

Chapter 3

3. 0 Introduction

3. 1 The Reaction of the Ir-SF$_3$ Complex (2.1.1) with BF$_3$

3. 2 Discussion of Fluorine exchange in relation to the Ir-SF$_2^+$ Complex (3.1.1).

3. 3 The Reaction of (3.1.1) with excess BF$_3$

3. 4 The Reaction of (3.1.1) with 50% deficiency of BF$_3$

3. 5 The Reaction of (3.1.1) with N(CH$_3$)$_3$

3. 6 The Reaction of (3.1.1) with NH(CH$_3$)$_2$

3. 7 The Reaction of (3.1.1) with P(CH$_3$)$_3$

3. 8 The Reaction of (3.1.1) with Cl$^-$

3. 9 The Reaction of (3.1.1) with CH$_3$OH

3.10 The Reaction of (3.1.1) with H$_3$COSi(CH$_3$)$_3$
3.11 Discussion of alternative structures to (3.8.1)

3.12 The Reactions of (3.1.1) with CH₃CH₂OH and some other alcohols

3.13 The Reaction of (3.1.1) with 100% excess of CH₃OH

3.14 The Reaction of (3.1.1) with (H₃C)₂NSi(CH₃)₃

3.15 Conclusions on the Formation and Reactivity of the Ir-SF₂⁺ Complex (3.1.1)

Chapter 4

4. 0 The Reaction of t-IrCl(CO)[P(CH₃)₃]₂ (4.0.1) with SF₄

4. 1 Discussion of the Exchange Processes Relating to (4.1.1)

4. 2 The Reaction of (4.0.1) with SF₄ and BF₃

4. 3 The Reaction of (4.0.1) with SF₄

4. 4 The Reaction of t-IrF(CO)[P(C₆H₅)₃]₂ (4.0.2) with SF₄

4. 5 The Reaction of (4.0.2) with SF₄ and BF₃
4. 6 The Reaction of $t$-Ir$X$(CO)[P(C$_6$H$_5$)$_3$]$_2$ (1.3.1) ($X$= Br, NCO, NCS) with SF$_4$

4. 7 The Reaction of $t$-IrCl(CO)[P(C$_6$H$_{11}$)$_3$]$_2$ (4.0.3) with SF$_4$

4. 8 The Reaction of $t$-IrCl(CO)[P(CH$_2$CH$_3$)$_2$(C$_6$H$_5$)]$_2$
(4.6.0) with SF$_4$

4. 9 The Reaction of $t$-IrCl(CO)[P(CH$_2$CH$_3$)(C$_6$H$_5$)$_2$]$_2$
(4.7.0) with SF$_4$

4.10 The Reaction of $t$-Ir(NCO)(CO)[P(CH$_2$CH$_3$)(C$_6$H$_5$)$_2$]$_2$
(4.8.0) with SF$_4$

4.11 The Reaction of $t$-Ir(NCS)(CO)[P(CH$_2$CH$_3$)(C$_6$H$_5$)$_2$]$_2$
(4.9.0) with SF$_4$

4.12 Conclusions on the Reactivity of SF$_4$ towards the Ir$^1$ complexes $t$-Ir$X$(CO)[P]$_2$ as a Function of P

Chapter 5

5. 0 Introduction to Adducts of SF$_4$

5. 1 Adducts of Lewis Acids with SF$_4$

5. 2 Adducts of Lewis Bases with SF$_4$
| 5.3 | The Adduct formed between N(CH₃)₃ and SF₄ | 192 |
| 5.4 | Discussion of Exchange involved in SF₄·N(CH₃)₃ | 196 |
| 5.5 | The Effect of [NH(CH₃)₃]+F⁻ on SF₄ | 201 |
| 5.6 | The Reaction of NH(CH₃)₂ with SF₄ | 202 |
| 5.7 | The Interaction of N(CH₂CH₃)₃ with SF₄ | 203 |
| 5.8 | The Interaction of N(C₅H₅) with SF₄ | 204 |
| 5.9 | The Reaction of P(CH₃)₃ with SF₄ | 205 |
| 5.10 | The Interaction of t.h.f. with SF₄ | 206 |
| 5.11 | Conclusions | 207 |
|      | Experimental | 209 |
|      | References | 224 |
### List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>An Illustration of how the Modification of a Phenylphosphine Ligand can affect the Electron Density on an Iridium to which it is bound</td>
<td>4</td>
</tr>
<tr>
<td>1.2</td>
<td>The Product of Reaction of $t$-IrX(CO)[P(C_6H_5)_3]_2 and H_2</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>An Illustration of the Trans Effect on the Orbitals Between the Metal and Ligands</td>
<td>15</td>
</tr>
<tr>
<td>1.4</td>
<td>The Structure of SF_4</td>
<td>33</td>
</tr>
<tr>
<td>1.5</td>
<td>Possible Structures of a Dimeric Form of SF_4 in Solution</td>
<td>44</td>
</tr>
<tr>
<td>2.1</td>
<td>A Diagrammatic Representation of the Chemical Inequivalence of F_A and F_A' in (2.1.1)</td>
<td>54</td>
</tr>
<tr>
<td>2.2</td>
<td>A Diagrammatic Representation of the Orientation of the -PF_4 Group in (2.1.3)</td>
<td>55</td>
</tr>
<tr>
<td>2.3</td>
<td>The Proposed Structure of (2.9.1)</td>
<td>89</td>
</tr>
<tr>
<td>2.4</td>
<td>The Proposed Structure of (2.9.2)</td>
<td>91</td>
</tr>
<tr>
<td>2.5</td>
<td>The Proposed Structure of (2.9.3)</td>
<td>93</td>
</tr>
<tr>
<td>2.6</td>
<td>The Proposed Structure of (2.9.4)</td>
<td>94</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3.1a</td>
<td>Diagrammatic representations of views along the Ir-S bond which show why the phosphines are non-equivalent in (3.8.1)</td>
<td>125</td>
</tr>
<tr>
<td>3.2</td>
<td>Alternative structures to (3.8.1)</td>
<td>130</td>
</tr>
<tr>
<td>3.3&amp;</td>
<td></td>
<td>131</td>
</tr>
<tr>
<td>3.4</td>
<td></td>
<td>132</td>
</tr>
<tr>
<td>4.1</td>
<td>Some iridium complexes containing fluoride ligands</td>
<td>153</td>
</tr>
<tr>
<td>5.1</td>
<td>The Structure of SF₄.BF₃ involving Donation of the Sulphur lone pair to the Boron</td>
<td>188</td>
</tr>
<tr>
<td>5.2</td>
<td>Possible Structures of SF₄.BF₃ with Bridging Fluorines</td>
<td>189</td>
</tr>
<tr>
<td>5.3</td>
<td>A Proposed Structure of the Adduct Formed between SF₄ and diethylether</td>
<td>191</td>
</tr>
<tr>
<td>5.4</td>
<td>A Proposed Structure of the Adduct Formed between SF₄ and N(CH₃)₃</td>
<td>192</td>
</tr>
<tr>
<td>5.5</td>
<td>The Structure of SF₄.N(CH₃)₃</td>
<td>193</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.1</td>
<td>$^{19}$F n.m.r. data of (2.1.1), (2.3.1), and (2.3.2).</td>
<td>74</td>
</tr>
<tr>
<td>2.2</td>
<td>Coalescence and $\Delta G_C^\dagger$ data for (2.1.1), (2.3.1), and (2.3.2).</td>
<td>74</td>
</tr>
<tr>
<td>2.3</td>
<td>$^{19}$F n.m.r. data of (2.4.1).</td>
<td>78</td>
</tr>
<tr>
<td>2.4</td>
<td>$^{19}$F n.m.r. data of (2.4.2).</td>
<td>78</td>
</tr>
<tr>
<td>2.5</td>
<td>$^{19}$F n.m.r. data of (2.9.1).</td>
<td>90</td>
</tr>
<tr>
<td>2.6</td>
<td>$^{19}$F n.m.r. data of (2.9.2).</td>
<td>92</td>
</tr>
<tr>
<td>2.7</td>
<td>$^{19}$F n.m.r. data of (2.9.3).</td>
<td>93</td>
</tr>
<tr>
<td>3.1</td>
<td>$^{19}$F and $^{31}$P(1H) n.m.r. data of (3.1.1)</td>
<td>102</td>
</tr>
<tr>
<td>3.2</td>
<td>$^{19}$F n.m.r. data of (3.2.1)</td>
<td>106</td>
</tr>
<tr>
<td>3.2a</td>
<td>$^{19}$F n.m.r. data of (3.2.2)</td>
<td>106</td>
</tr>
<tr>
<td>3.3</td>
<td>N.m.r. data of (3.3.1)</td>
<td>110</td>
</tr>
<tr>
<td>3.4</td>
<td>N.m.r. data of (3.4.1)</td>
<td>112</td>
</tr>
<tr>
<td>3.5</td>
<td>$^{19}$F n.m.r. data of (3.9.1)</td>
<td>135</td>
</tr>
<tr>
<td>3.6</td>
<td>$^{19}$F n.m.r. data of (3.9.2)</td>
<td>138</td>
</tr>
<tr>
<td>3.7</td>
<td>$^{19}$F n.m.r. data of (3.9.3)</td>
<td>138</td>
</tr>
<tr>
<td>3.8</td>
<td>$^{19}$F n.m.r data for the products of reaction of (3.1.1) with alcohols</td>
<td>139</td>
</tr>
<tr>
<td>3.9</td>
<td>$^{19}$F n.m.r. data of (3.11.1)</td>
<td>144</td>
</tr>
<tr>
<td>4.1</td>
<td>$^{19}$F and $^{31}$P(1H) n.m.r. data of (4.1.1)</td>
<td>152</td>
</tr>
<tr>
<td>4.2</td>
<td>$^{19}$F n.m.r. data of the complexes in fig. 4.1</td>
<td>154</td>
</tr>
<tr>
<td>4.3</td>
<td>$^{19}$F(1H) n.m.r. data of (4.2.1) and (4.2.2)</td>
<td>158</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>4.3a</td>
<td>$^{19}$F($^1$H) n.m.r. data for $F_A$ and $F_C$ of (3.3.1) and (3.4.1)</td>
<td>159</td>
</tr>
<tr>
<td>4.4</td>
<td>$^{19}$F($^1$H) n.m.r. data of (4.3.1)</td>
<td>163</td>
</tr>
<tr>
<td>4.5</td>
<td>$^{19}$F($^1$H) n.m.r. data of (4.4.1)</td>
<td>166</td>
</tr>
<tr>
<td>4.6</td>
<td>$^{19}$F($^1$H) n.m.r. data of (4.5.1)</td>
<td>170</td>
</tr>
<tr>
<td>4.7</td>
<td>$^{19}$F($^1$H) n.m.r. data of (4.6.1)</td>
<td>176</td>
</tr>
<tr>
<td>4.7a</td>
<td>$^{19}$F($^1$H) n.m.r. data of (4.6.2)</td>
<td>176</td>
</tr>
<tr>
<td>4.8</td>
<td>$^{19}$F($^1$H) n.m.r. data of (4.7.1)</td>
<td>179</td>
</tr>
<tr>
<td>4.9</td>
<td>$^{19}$F($^1$H) n.m.r. data of (4.8.1)</td>
<td>181</td>
</tr>
<tr>
<td>4.9a</td>
<td>$^{19}$F($^1$H) n.m.r. data of (4.8.2)</td>
<td>181</td>
</tr>
<tr>
<td>5.1</td>
<td>$^{19}$F n.m.r. data of SF$_4$.N(CH$_3$)$_3$</td>
<td>194</td>
</tr>
<tr>
<td>5.2</td>
<td>$^{19}$F n.m.r. data of SF$_4$.N(CH$_3$)$_3$</td>
<td>198</td>
</tr>
</tbody>
</table>
### List of Diagrams

<table>
<thead>
<tr>
<th>Diagram</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>$^{19}$F($^1$H) n.m.r. spectrum of (2.1.1) at 178K</td>
<td>52(a)</td>
</tr>
<tr>
<td>2.1a</td>
<td>Expansion of $F_A$ in (2.1.1)</td>
<td>52(b)</td>
</tr>
<tr>
<td>2.1b</td>
<td>Expansion of $F_A'$ in (2.1.1)</td>
<td>52(c)</td>
</tr>
<tr>
<td>2.1c</td>
<td>Expansion of $F_E$ in (2.1.1)</td>
<td>52(d)</td>
</tr>
<tr>
<td>2.1d</td>
<td>Expansion of $F_C$ in (2.1.1)</td>
<td>52(e)</td>
</tr>
<tr>
<td>2.1e</td>
<td>Expansion of $F_C$ in (2.1.1) with $^{13}$C at CO</td>
<td>57(a)</td>
</tr>
<tr>
<td>2.2</td>
<td>$^{31}$P($^1$H) n.m.r. spectrum of (2.1.1) at 178K</td>
<td>57(b)</td>
</tr>
<tr>
<td>2.3</td>
<td>$^{19}$F n.m.r. spectrum of (2.1.1) with HF present at 178K</td>
<td>58(a)</td>
</tr>
<tr>
<td>2.3a</td>
<td>$^{19}$F n.m.r. spectrum of (2.1.1) with HF present at 220K</td>
<td>58(b)</td>
</tr>
<tr>
<td>2.3b</td>
<td>$^{19}$F n.m.r. of (2.1.1) with HF present at 298K</td>
<td>58(c)</td>
</tr>
<tr>
<td>2.4</td>
<td>$^{19}$F n.m.r. spectrum of (2.1.1) at 220K with HF absent</td>
<td>60(a)</td>
</tr>
<tr>
<td>2.4a</td>
<td>Expansion of $F_C$ in (2.1.1) at 270K</td>
<td>60(b)</td>
</tr>
<tr>
<td>2.4b</td>
<td>$^{19}$F n.m.r. spectrum of (2.1.1) at 306K with HF absent</td>
<td>60(c)</td>
</tr>
<tr>
<td>2.4c</td>
<td>$^{19}$F n.m.r. spectrum of (2.1.1) at 341K with HF absent</td>
<td>60(d)</td>
</tr>
<tr>
<td>2.2a</td>
<td>$^{31}$P($^1$H) n.m.r. spectrum of (2.1.1) at 306K with HF absent</td>
<td>61(a)</td>
</tr>
</tbody>
</table>
2.5  $^{19}$F n.m.r. spectrum of the products of reaction of (2.4.0) and SF$_4$ at 178K

2.5  Expansion of high frequency region

exp1

2.5  Expansion of mid frequency region

exp2

2.5  Expansion of low frequency region

exp3

2.5a  Expansion of FC in each of (2.4.1) and (2.4.2) with $^{13}$C at CO

2.5b  $^{19}$F n.m.r. spectrum of (2.4.1) at 190K

2.5c  $^{19}$F n.m.r. spectrum of (2.4.1) at 230K

2.5d  $^{19}$F n.m.r. spectrum of (2.4.1) at 300K

2.6  $^{31}$P($^{1}$H) n.m.r. spectrum of (2.4.1) at 248K

2.7  $^{19}$F n.m.r. spectrum of the reaction between (2.9.0) and SF$_4$ at 150K

2.7a  Expansion of high frequency region at 150K

2.7b  Expansion of mid frequency region at 150K

2.7c  Stick diagram of mid frequency region

85(a)
2.7d Expansion of low frequency region at 150K

2.7 Expansion of $F_A$ and $F_A'$ in (2.9.1) at 220K

exp1

2.7 Expansion of $F_E$ in (2.9.1) at 220K

exp2

2.7 Expansion of $F_E$ in (2.9.2) at 220K

exp3

2.7 Expansion of $F_C$ and $F_C'$ in (2.9.2) at 220K

exp4

2.7 Expansion of $F_A$ and $F_A'$ in (2.9.3) at 220K

exp5

2.7 Expansion of $F_E$ in (2.9.3) at 220K

exp6

2.7 Expansion of $F_C$ in each of (2.9.3) and (2.9.4) at 220K and also of $F_C$ in (2.9.4) at 300K

exp7

3.1 $^{19}F$ n.m.r. spectrum of (3.1.1) at 178K

exp

3.1 Expansion of $F_A$ and $F_C$ in (3.1.1)

exp

3.2 $^{31}P(^{1}H)$ n.m.r. spectrum of (3.1.1) at 178K

3.1a $^{19}F$ of $F_C$ in (3.1.1) at 178K with $^{13}C$

3.3 $^{19}F$ n.m.r. spectrum of (3.1.1) with 100% excess BF$_3$ at 178K
3.3a  $^{19}$F n.m.r. spectrum of (3.3.1) at 220K

3.3b  $^{19}$F n.m.r. spectrum of (3.3.1) and (3.4.1) at 178K

3.3c  Expansion of $F_C$ in (3.3.1) and (3.4.1)

3.4  $^{31}$P($^1$H) n.m.r. spectrum of (3.3.1) and (3.4.1) at 178K

3.5  $^{19}$F n.m.r. spectrum of the reaction of (2.1.1) with a 50% deficiency of BF$_3$

3.6  $^{19}$F n.m.r. spectrum of F$_3$B:NM$_3$ at 178K

3.7  $^{19}$F n.m.r. spectrum of (3.8.1) at 178K

3.7a  $^{19}$F n.m.r. spectrum of (3.8.1) at 240K

3.7b  Expansion of $F_A$ in (3.8.1) with the retention of $^1$H coupling

3.8  $^{31}$P($^1$H) n.m.r. spectrum of (3.8.1) at 178K

3.9  $^{19}$F n.m.r. spectrum of (3.10.1) at 178K with expansion of $F_C$ at 306K
3.10  $^{19}$F n.m.r spectrum of (3.11.1) at 178K

4.1  $^{19}$F n.m.r. spectrum of (4.1.1) at 178K

4.1  Expansion of $F_A$, $F_E$ and $F_C$ in exp (4.1.1)

4.1a  Coalescence of peaks of $F_A$ and $F_E$ in (4.1.1)

4.2  $^{31}$P($^1$H) n.m.r. spectrum of (4.1.1) at 178K

4.3  $^{19}$F n.m.r spectrum of (4.4.1) at 178K

4.4  $^{19}$F n.m.r. spectrum of (4.6.1) and (4.6.2) at 178K

5.1  $^{19}$F n.m.r. spectrum of SF$_4$.NMe$_3$ at 123K

5.1a  $^{19}$F n.m.r spectrum of SF$_4$.15NMe$_3$ at 123K

5.2  $^{19}$F n.m.r spectrum of 4SF$_4$.1NMe$_3$ at 123K

5.2a  $^{19}$F n.m.r spectrum of 4SF$_4$.1NMe$_3$ at 168K

5.2b  $^{19}$F n.m.r. spectrum of 4SF$_4$.1NMe$_3$ at 177K

5.2b  $^{19}$F n.m.r. spectrum of 4SF$_4$.1NMe$_3$ at 187K
5.3 $^{19}$F n.m.r spectrum of SF$_4$ and 100% excess NMe$_3$ at 123K

5.3a $^{19}$F n.m.r spectrum of SF$_4$ and 100% excess NMe$_3$ at 200K

5.3b $^{19}$F n.m.r spectrum of SF$_4$ and 100% excess NMe$_3$ at 230K

5.4 $^{19}$F n.m.r. spectrum of reaction of SF$_4$ with NHMe$_2$

5.5 $^{19}$F n.m.r spectrum of NC$_5$H$_5$ and 100% excess of SF$_4$ at 150K with a reference spectrum of SF$_4$ at this temperature
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Et</td>
<td>ethyl</td>
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<tr>
<td>Ph</td>
<td>phenyl</td>
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<tr>
<td>Me</td>
<td>methyl</td>
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<tr>
<td>PEt₃</td>
<td>triethylphosphine</td>
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<tr>
<td>PMe₃</td>
<td>trimethylphosphine</td>
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<tr>
<td>PEtPh₂</td>
<td>diphenylethylphosphine</td>
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<tr>
<td>PEt₂Ph</td>
<td>diethylphenylphosphine</td>
</tr>
<tr>
<td>PPh₃</td>
<td>triphenylphosphine</td>
</tr>
<tr>
<td>PCy₃</td>
<td>tricyclohexylphosphine</td>
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<tr>
<td>I.R.</td>
<td>infrared</td>
</tr>
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<td>n.m.r.</td>
<td>nuclear magnetic resonance</td>
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<tr>
<td>p.p.m.</td>
<td>parts per million</td>
</tr>
<tr>
<td>t</td>
<td>trans</td>
</tr>
<tr>
<td>fig.</td>
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</tr>
<tr>
<td>eqn.</td>
<td>equation</td>
</tr>
</tbody>
</table>
Abstract

This thesis describes the formation of some iridium complexes which contain an -SF₃ group. Although monosubstituted derivatives of SF₄ have been reported in organic chemistry, the -SF₃ ligand was previously unknown in transition metal complex chemistry.

The first iridium complex containing an -SF₃ ligand was the product of reaction between t-IrCl(CO)[P(CH₂CH₃)₃]₂ and SF₄, the reaction being carried out in a d₂-dichloromethane solution. As a result of variable temperature ¹⁹F(¹H) and ³¹P(¹H) n.m.r. studies, this complex was found to possess fluxionality at the -SF₃ site and also to undergo fluorine exchange by an intermolecular mechanism. These processes were found to be influenced by the presence of HF.

Further information about factors influencing this exchange was obtained from other halo- and pseudohalo-complexes containing the -SF₃ group. Complexes with different phosphines (both alkyl and aryl) were also synthesized and investigated.

Additional experiments showed that BF₃ removes a fluoride from sulphur to generate a novel -SF₂⁺ ligand, which is isoelectronic with -PF₂. The -SF₂⁺ group can undergo nucleophilic substitution reactions with specific reagents, for example methanol, ethanol, CH₃OSi(CH₃)₃ and (H₃C)₂NSi(CH₃)₃.
The structure of the adduct formed between SF₄ and trimethylamine [N(CH₃)₃] has been determined from solution ¹⁹F{¹H} n.m.r. studies. This has effectively resolved the problem of previous conflicting reports on the structure and doubts as to the existence of this species.

Finally, the crystal structures of two complexes produced during the course of this work are reported. The compounds concerned are:
- a new form of t-IrCl(CO)[P(C₆H₅)₃]₂ into which two d₂-dichloromethane molecules have been incorporated in the crystal lattice.
- a sulphur dioxide, SO₂, adduct of this complex unsolvated. The crystal structure of this compound has been previously reported[¹], but was found to have different unit cell parameters( awaiting publication).
Chapter 1

1.1 An Introduction To Oxidative Addition

In the 1950's when there was a rapid development of transition metal organometallic chemistry, vast numbers of previously unknown compounds were discovered. This led to some interesting new concepts and theories. One specific observation was that certain transition metal complexes could adsorb covalent molecules to form new species in which the co-ordination number and oxidation state of the metal were both formally increased by two. This concept became known as OXIDATIVE ADDITION[2]. One of the first reported examples was the reaction between H₂ and t-IrCl(CO)[P(C₆H₅)₃]₂. This is illustrated in equation 1.1 below:

Eqn. 1.1[3]

\[
\begin{align*}
\text{PPh}_3 & \quad \text{PPh}_3 \\
\mid & \quad \mid \\
\text{OC} - \text{Ir} - \text{Cl} + \text{H}_2 & \quad \text{Cl} - \text{Ir} - \text{H}_2 \\
\mid & \quad \mid \\
\text{PPh}_3 & \quad \text{PPh}_3 \\
\end{align*}
\]

(1.0.1) (1.1.1)

Several similar reactions involving the incorporation of a variety of smaller molecules[2] into a wide range of transition metal complexes have been subsequently reported.

For a complex to undertake an oxidative addition, it must be co-ordinatively and electronically unsaturated at
the metal centre. The reaction can either proceed directly, as in the example at eqn. 1.1, or by the initial expulsion of a ligand from the central atom of the complex. This latter case generally applies to transition metal species with 5 co-ordinated ligands and trigonal bipyramid geometry at the metal and specific examples are discussed later in this chapter.

The most commonly studied oxidative additions involve transition metal complexes with the d$^8$ electron configuration and square planar geometry at the metal centre. The main factors determining the ease with which these 16-electron complexes undergo this type of reaction are now discussed:

1. The central metal atom:

The trend favouring addition increases on descending the triad of group (VIII) elements and from right to left across the row. Thus, complexes of Pt$^{II}$ are more susceptible to addition than those of Pd$^{II}$. Similarly, Os$^0$ species are more reactive than Ir$I$ and Pt$^{II}$ complexes. These trends are in agreement with higher oxidation states of the metal being stabilized going down the triad.

2. The ligands at the metal centre:

a) ligands which tend to increase the electron density at the metal favour oxidative addition at this site$^4$. An example illustrating this is the addition of O$_2$ to the
series of complexes $t$-IrX(CO)[P(CH₂CH₃)₃]₂ (X= Cl, Br, I).

The equation (1.2) is given below:

Eqn. 1.2

The rate of uptake of O₂ by the iridium is enhanced as the electron donating properties of the halide ligands increases. This is aptly illustrated by the conditions required for handling of the Irᴵ complexes. In the case of X= Cl, the reagent can be manipulated in air in the solid phase for a few minutes with no significant degree of oxidation. However, $t$-IrI(CO)[P(CH₂CH₃)₃]₂ must be kept under vacuum or an inert atmosphere.

b) the substitution of a proton by an o-methoxy group on a phenylphosphine ligand increases the electron density at the metal (iridium in the figure), by donation of an oxygen lone pair to the metal centre with respect to the phenylphosphine analogue (see fig. 1.1). This is another way of activating a metal centre to oxidative addition.
Fig. 1.1[5]

Diagram Illustrating how the Modification of a Phenylphosphine Ligand can affect the Electron Density on an Iridium to which it is bound.

3. The steric properties of the ligands:

Species which contain bulky phosphine ligands such as P(CH₂CH₃)₂[C(CH₃)₃] are sterically crowded at the metal centre. This can hinder attack by approaching molecules and lower the susceptibility of these complexes to oxidative addition. In certain cases, involving phosphines with very large cone angles[6] [e.g. P(C₆H₁₁)₃], the addition can be sterically blocked, even though the phosphines increase the electron density at the metal by donation.

1.2 Oxidative Addition and Stereochemistry

Oxidative addition can lead to the formation of a number of products, each of which has a unique stereochemical configuration. This may be dependent on the mechanism and/or the nature of the species involved. The general cases of symmetric (scheme 1.1) and asymmetric
(scheme 1.2) addenda are illustrated.

Scheme 1.1

There are two theoretical products, allowing for the restriction that ligands P, which are mutually trans in the starting complex, remain trans in the products. (1.1.2) is formed by a trans addition of A-A, and (1.1.3) results from a cis addition.

Scheme. 1.2

When the addendum is asymmetric there are three theoretical products, allowing for the same restriction imposed on P as above. (1.2.1) is formed by simple trans addition whereas (1.2.2) and (1.2.3) are the two possible products of cis addition. These are chemically distinct, because A is trans to X in (1.2.2) and trans to Y in (1.2.3).

The mechanisms of cis[7][8] and trans[9] addition are different. However, kinetic studies have shown that both
types of reaction obey a second-order rate law. Each is discussed with reference to a specific example.

An example of Oxidative Addition via a cis Mechanism

The addition of $H_2$ to the complexes $t$-IrX(CO)[P(C_6H_5)₃]₂, (1.3.1), (X= Cl, Br, I) follows a cis mechanism. (the specific case with X= Cl is illustrated at eqn. 1.1). The product in each case contain two hydride ligands which are located cis to each other. This is illustrated in fig. 1.2 below:

Fig. 1.2
The general product of reaction of (1.3.1) with $H_2$.

\[ \begin{align*}
    & \text{PPh}_3 \\
    & \quad \mid \quad H \\
    \text{X} & \quad \text{Ir} \quad \text{H} \\
    & \quad \mid \\
    & \text{OC} \quad \text{PPh}_3
\end{align*} \]

The rate of addition increases in accordance with the effective electron donating properties of X (see earlier). When the reaction is studied using $D_2$ instead of $H_2$, the observed kinetic isotope effect[10] ($k_H/k_D = 1.22$) is small. This suggests that cleavage of the H-H (D-D) bond is not involved in the rate determining step. These observations are consistent with a mechanism which involves a concerted insertion[2] of the iridium into the H-H (D-D) bond, in a similar manner to SN2-type substitution reactions[11] of alkyl halides in organic chemistry.
An example of an Oxidative Addition via a trans Mechanism

The reaction of bromomethane with each complex in the series t-IrX(CO)[PCH₃(C₆H₅)₂]₂ (X= Cl, Br, I) follows a trans mechanism and this is illustrated at eqn. 1.3:

\[
\text{Eqn. 1.3}^{[9]}
\]

\[
\begin{array}{c}
\text{PMePh}_2 \\
\text{OC} \quad \text{Ir} \quad X \quad \text{OC} \\
\text{PMePh}_2 \\
\end{array}
\xrightarrow{+ \text{MeBr}}
\begin{array}{c}
\text{PMePh}_2 \\
\text{OC} \quad \text{Ir} \quad \text{Me} \\
\text{PMePh}_2 \\
\end{array}
\]

In the above reaction the rate of addition of CH₃Br at iridium decreases as X varies from chloride to iodide. This trend is the reverse of that described previously for addition by a cis mechanism.

Another significant difference between the two series of reactions is the effect on the rate by the nature of the solvent medium. A trans mechanism proceeds more readily in polar solvents such as dimethylformamide than in non-polar benzene. No such solvent dependence is observed in the cis additions (see eqn. 1.1). It is therefore concluded that the reaction in eqn. 1.3, above, is a binuclear displacement at the methyl carbon of CH₃Br with the iridium acting as a nucleophile.
1.3 Kinetics and Thermodynamics in Oxidative Addition Reactions

Kinetic and thermodynamic factors must be considered in any discussion relating to the stereochemistry of a reaction. This is because it does not necessarily follow that a reaction following a trans mechanism will produce a complex in which the fragments of the addendum remain in a trans configuration. A specific case is illustrated by the addition of CH$_3$Cl to the complex t-IrBr(CO)[PCH$_3$(C$_6$H$_5$)$_2$]$_2$ in accordance with eqn. 1.4 below:

Eqn. 1.4

\[
\begin{array}{c}
\text{PMePh}_2 \\
\text{OC} - \text{Ir} - \text{Br} \\
\text{PMePh}_2
\end{array}
\quad +
\begin{array}{c}
\text{PMePh}_2 \\
\text{MeCl}
\end{array}
\quad \rightarrow
\begin{array}{c}
\text{PMePh}_2 \\
\text{OC} - \\
\text{PMePh}_2
\end{array}
\quad \text{Cl} - \text{Ir} - \text{Me} \\
\quad \rightarrow
\begin{array}{c}
\text{PMePh}_2 \\
\text{OC} - \\
\text{PMePh}_2
\end{array}
\quad \text{Br} - \text{Ir} - \text{Me}
\]

(1.4.1)

Initially CH$_3$Cl adds to give the kinetically favoured trans product, (1.4.1). However, in a benzene/methanol mixture, a rearrangement involving an interchange of the chloride and bromide ligands takes place. This gives the thermodynamically favoured product i.e. the cis product.
1.4 Oxidative Addition and Free Radicals

Certain oxidative addition reactions are believed to proceed by a mechanism which involves free radicals\(^{[12]}\). One such example is the addition of PhCHFCH\(_2\)Br to t-IrCl(CO)[P(CH\(_3\))]\(_2\). This is thought to involve several stages and these are illustrated in mech. 1.1 below:

Mech. 1.1 \(^{[13]}\)

\[
\begin{align*}
\text{Ir}^I & + \text{Q} & \rightarrow & \text{Ir}^{II} \text{Q} \\
\text{Ir}^{II} - \text{Q} & + \text{R-Br} & \rightarrow & \text{Br-Ir}^{III} \text{Q} + \text{R} \\
\text{Ir}^I & + \text{R} & \rightarrow & \text{Ir}^{II} \text{R} \\
\text{Ir}^{II} - \text{R} & + \text{R-Br} & \rightarrow & \text{Br-Ir}^{III} \text{R} + \text{R}
\end{align*}
\]

(Q\(^*\) = radical initiator)

(Ir\(^X\), \(X = \) the formal oxidation state of the iridium)

(R = C\(_6\)H\(_5\)CHFCH\(_2\))

There are a number of points in support of a free radical mechanism in the above reaction. These are listed below:

1. The rate of addition is greatly enhanced by the presence of dioxygen or other radical initiator.

2. The reaction is inhibited by the presence of free radical scavengers such as hydroquinone.
3. The alkyl halide involved in the above reaction is stereospecific at the chiral carbon. This stereospecificity is lost after the addition reaction, an observation which is consistent with a planar configuration being adopted at this carbon at some stage during the course of reaction. The racemization in the products is possible with a radical mechanism.

1.5 Oxidative Addition at Electronically Saturated Metal Centres

So far, only oxidative addition reactions occurring at unsaturated 16e\(^-\) transition metal centres have been discussed. Similar additions can also take place at metal centres which are electronically saturated. These complexes are usually 5 co-ordinate species with trigonal bipyramidal geometry at the metal centre. The addition must involve the expulsion of a ligand and this can happen at two different stages during the course of reaction. Each case is now discussed in relation to a specific example.

Example 1.

The addition of \( \text{H}_2 \) to the complex \( \text{Os(CO)}_5 \) involves the expulsion of a molecule of carbon monoxide before the addition takes place. This is illustrated in eqn. 1.5:
The intermediate in eqn. 1.5 has only a transient existence and rapidly adsorbs \( \text{H}_2 \) to give the product. Prior dissociation is suggested by the observation that the related complex \( t-\text{Os(}\text{CO})_3[\text{P(}\text{C}_6\text{H}_5)_3]_2 \) does not uptake \( \text{H}_2 \) under similar reaction conditions\(^{15}\). This complex would be expected to enhance the addition. However, the phosphine ligands stabilize the Os-CO bonds by electron donation, making the complex less susceptible to loss of carbon monoxide.

Example 2.

In example 1, above, expulsion of a ligand took place before the addition. However, in certain cases, namely the addition of \( \text{Br}_2 \) to the osmium-phosphine complex, mentioned above, the loss of carbon monoxide occurs in the final stage of the reaction. This is illustrated in equation 1.6.
Eqn. 1.6[16]

\[
PPh_3 \quad \text{OC} \quad \text{Os} \quad \text{Br}_2 \quad \text{OC} \quad \text{Os} \quad \text{Br}^{-} \quad \text{OC} \quad \text{Os} \quad \text{Br}^{-}
\]

Note: the intermediate in eqn. 1.6 can be isolated and characterized.

In the final stage of the reaction, the bromide counter ion may displace either the carbonyl trans to the bromide or one of the mutually trans carbonyl ligands. It is one of these latter carbonyls which is displaced as these are mutually labilized by the trans effect (see section 1.7).

1.6 Ligand Influences Favouring 5-Coordinate Versus 4-Coordinate Geometry

Section 1.5 has discussed how certain 5 co-ordinate transition metal complexes can expel a ligand, to form highly reactive intermediates. There are also a few examples in which both 4 co-ordinate species and their 5 co-ordinate derivatives, have more than a transient existence. An example of such a system is the series of complexes \( t-\text{IrX(CO)}[\text{P(C}_6\text{H}_5)_3]_2 \) \( (X=\text{Cl, I, H}) \) in the presence of carbon monoxide and this is illustrated in eqn. 1.7:
The stability of (1.7.1), relative to (1.3.1), depends on the nature of (X). When \( X = \text{Cl} \), (1.3.1) is favoured, although (1.7.1) may be obtained by placing (1.3.1) under positive carbon monoxide pressure.

When \( X = \text{I} \), (1.7.1) is isolable and stable up to room temperature. Heating is required to remove the second carbonyl and regenerate (1.3.1).

When \( X = \text{H} \), it is the (1.7.1) complex which is stable, relative to (1.3.1).

These observations are consistent with the 5 co-ordinate complexes being stabilized by "soft" ligands, and this is the basis of the strong trans effect of hydride and other similar ligands in nucleophilic substitution reactions involving square planar PtII complexes (see next section).
1.7 The Trans Effect and Trans Influence

The ligand arrangement around the metal centre can have an influence on the progress of a reaction at the metal and may determine the stereochemical arrangement of the ligands in the product. This is particularly applicable for complexes which undergo nucleophilic substitution reactions. These complexes may have either square-planar or octahedral geometry at the metal centre.

Example 1
An example showing how the trans effect[19] can induce stereospecificity into ligand substitution reactions is the treatment of a square planar PtII complex, PtCl4^{2-} with NH3 (see eqn. 1.8):

Eqn. 1.8[20]

\[
\begin{align*}
\text{Cl} \ &\ 2^- \ &\ \text{Cl} \ &\ 2^- \\
| \ &\ \ | \ &\ \ | \\
\text{Cl} \ &\ \text{Pt} \ &\ \text{Cl} \ &\ \rightarrow \ &\ \text{Cl} \ &\ \text{Pt} \ &\ \text{Cl} \\
| \ &\ \ | \\
| \ &\ \ | \\
\text{Cl} \ &\ \text{NH}_3 \ &\ \ \ &\ \text{Cl}
\end{align*}
\]

The first stage of the reaction involves displacement of one of the four equivalent chloride ligands by an ammonia (NH₃) molecule, as shown. Further displacement of chloride by an excess of NH₃, could theoretically result in the formation of two neutral platinum complexes. In
the above example, only the cis isomer (1.8.1) is formed. However, the trans complex may be formed via a different synthetic route (see later).

This is a kinetic parameter and is a measure of the rate of substitution at the co-ordination site opposite a specific ligand or group. In general, ligands with a strong affinity to $r$-bond to the metal are the most effective trans directors. It is therefore suggested that the trans effect of these species arises from weakening of the $r$-interaction of the metal to the trans ligand as illustrated at fig. 1.3:

Fig. 1.3
An Illustration of the Trans Effect on the Orbitals Between the Metal and Ligands

\[
\text{M= metal} \\
\text{P= trans-directing group} \\
\text{L= ligand}
\]

Note: In the above figure, the size of the lobes is proportional to the degree of interaction between the orbitals of the metal and ligands P and L.

However, figure 1.3 does not explain the labilizing of an NH$_3$ molecule by a strong $r$-bonding ligand such as a
cyanide ion (CN\(^{-}\)). NH\(_3\) ligands are not stabilized by \(\pi\)-interactions, with or without the presence of a good trans-directing ligand. Furthermore, ligands such as hydride and alkyl groups\([21]\) are very efficient trans directors and these species do not have the capacity for \(\pi\)-bonding.

Langford and Gray\([22]\) suggested that ligands which are mutually trans effectively compete for the p-orbital of the metal, which lies along the axis through both ligands and the metal centre. The ligand which competes more effectively for this orbital, will experience a stronger interaction with the metal, to the detriment of the bonding with the trans ligand. Hence, the trans ligand is more easily displaced.

The Trans Influence

Another term often confused with the trans effect is the TRANS INFLUENCE\([23]\). This is defined as the extent by which the interaction between a ligand and the metal is weakened due to the trans directing group. Unlike the trans effect, the trans influence is a thermodynamic parameter and does not involve ligand displacement.
Example 2

t-PtCl\(_2\)(NH\(_3\))\(_2\) is formed when Pt(NH\(_3\))\(_4\)\(^{2+}\) is treated with a 100% excess of chloride ions. This is thought to be the result of both the trans influence and the trans effect and is illustrated at eqn. 1.9:

\[ \text{Eqn. 1.9[20]} \]

\[ \begin{align*}
\text{NH}_3 & \quad \quad \quad \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \quad \quad \quad \text{Cl} \\
\text{NH}_3 & \quad \quad \quad \quad \text{Cl} \\
\text{NH}_3 & \quad \quad \quad \quad \text{NH}_3
\end{align*} \]

(1.9.1) (1.9.2)

The first step in the above equation involves displacement of one of the four equivalent NH\(_3\) ligands by chloride, to give the monocationic complex Pt(NH\(_3\))\(_3\)Cl\(^+\) (1.9.1). Chloride has a greater trans influence than NH\(_3\) and this results in displacement of the NH\(_3\) ligand which is trans to chloride, in the second stage. This results in the formation of the neutral complex t-Pt(NH\(_3\))\(_2\)Cl\(_2\) (1.9.2). In the previous example, at eqn. 1.8, the superior trans influence of chloride leads to the formation of the cis isomer only, which according to the trans effect is the kinetically stable product.

From these definitions of the trans effect and trans influence it is implied that the weakening of a trans bond leads to more facile substitution. This suggests that the mechanism involves a dissociative component. The
Experimental data from certain substitution reactions in platinum complexes of the form \([\text{PtX}]_4^2-\) [19], are second order and therefore depend on the concentrations of the complex and incoming ligand. This implies that the mechanism contains an associative component and that a 5 co-ordinate activated complex with trigonal bipyramidal or square pyramidal geometry may be present. The trans effect is still relevant for a trigonal bipyramidal activated complex, as the following general scheme 1.3 illustrates:

Scheme 1.3[15]

\[ \begin{array}{c}
  \text{P} \\
  \text{N} \\
  \text{L} \\
  \text{E} \\
  \text{N} \\
  \text{P} \\
\end{array} \quad \begin{array}{c}
  \text{E} \\
  \text{L} \\
  \text{P} \\
  \text{N} \\
  \text{N} \\
  \text{E} \\
\end{array} \]

P = trans directing group of low electronegativity
N = non-directing group of high electronegativity
E = entering ligand
L = leaving ligand

In the activated complex, the ligands N, which are of highest electronegativity, will tend to occupy the axial co-ordination sites of a trigonal bipyramid, in accordance with Bent's Rule[24]. This states that an atom tends to direct its s-character in orbitals pointing towards electropositive groups. In a regular trigonal bipyramid, the hybridized \(sp^3d\) orbitals on the central atom may be
considered to be a combination of $p_zd_z^2$ and $sp_3d_y$ hybrids. The former accounts for the two linear hybrid orbitals bonding axially and the latter forms the three trigonal, equatorial bonds. Hence, substituents $N$ in the general example above, occupy the axial co-ordination sites and do not act as trans directors.

The loss of the leaving group, $L$, results in the product of substitution at the site trans to $P$.

Bent's Rule is seen to apply to a whole range of organic and inorganic compounds. Although there are a few exceptions\[^{25}\], these will not be discussed at this point.

1.8 Oxidative Addition and Main Group Elements

Oxidative addition reactions are not confined to transition metal species. Main group elements which have several common oxidation states and co-ordination numbers, such as sulphur and phosphorus, can also participate in this type of reaction. One specific example in relation to fluorine chemistry, is the addition of $F_2$ to $PF_3$ and this is shown in eqn. 1.10:

Eqn. 1.10\[^{2}\]

$$\text{PF}_3 + F_2 \rightarrow \text{PF}_5$$

This example may be thought of as an oxidative addition at the phosphorus centre, because the
co-ordination number and formal oxidation state (III-V) at this site are both increased by two.

There are other similar examples in the chemistry of tin and other main group elements.

1.9 Methods of Monitoring Oxidative Addition Reactions

Oxidative addition reactions can be effectively monitored by I.R. and multinuclear solution n.m.r. spectroscopic measurements. These techniques may be used in conjunction in certain cases.

Example. 1

The oxidative addition of \( \text{H}_2 \) to \( \text{t-IrCl(CO)(P(C}_6\text{H}_5)_3)_2} \) (1.0.1) (see eqn. 1.1).

The I.R. spectrum of (1.0.1)\(^{26}\) contains a sharp absorption at 1950\(\text{cm}^{-1}\) which is assigned to the carbon-oxygen stretch of the carbonyl ligand. This band is shifted to 1970\(\text{cm}^{-1}\)\(^{3}\) in the product (1.1.1), reflecting the reduction in electron density at iridium and strengthening of this bond. This is due to less electron donation by the metal into an anti-bonding \(\pi\)-orbital of the carbonyl ligand.

Two additional sharp bands\(^{3}\) in the I.R. spectrum of (1.1.1), at 2222\(\text{cm}^{-1}\) and 2098\(\text{cm}^{-1}\), are assigned to Ir-H stretches. The wavenumbers of these bands reflect the donor-acceptor properties of the ligand trans to hydride.
One hydride, $H_A$, is trans to a $\pi$-donating chloride ligand, which strengthens the Ir-$H_A$ bond by electron donation. The other one, $H_B$, is trans to a $\pi$-accepting carbonyl ligand, which weakens the Ir-$H_B$ bond by accepting electron density from the orbitals involved in bonding between the iridium and $H_B$. As a result, the Ir-$H_B$ bond is weak with respect to the Ir-$H_A$ bond. Accordingly, the band at $2222\text{cm}^{-1}$ is assigned to the Ir-$H_A$ stretch and the band at $2098\text{cm}^{-1}$ is assigned to the Ir-$H_B$ stretch.

The $^1H$ n.m.r. spectrum of (1.0.1) contains peaks in the region $\delta (+6$ to $+8)$ p.p.m. These are due to the protons on the aromatic rings of the phosphine ligands. The $^1H$ n.m.r. spectrum of (1.1.1) contains similar peaks and, in addition, there are two others to low frequency, at $\delta -7.3$ p.p.m. and $\delta -18.4$ p.p.m. These are in the region associated with hydrides which are bound directly to a transition metal, which in this case is iridium. Each resonance is a doublet of triplets. The doublets are due to mutual coupling between $H_A$ and $H_B$. These are chemically distinct, because $H_B$ is trans to the carbonyl ligand and $H_A$ is trans to the chloride. The triplet splittings arise from coupling between each hydride and the pair of chemically equivalent phosphorus nuclei. The resonance to lowest frequency, at $\delta -18.4$ p.p.m., is assigned to $H_A$ and the other one, at $\delta -7.3$ p.p.m., is assigned to $H_B$. These assignments are based on shielding properties of the ligand trans to the hydride. Chloride
has a more efficient shielding effect than carbonyl, because it is a \( \tau \)-donor ligand.

Example. 2

An example\(^{[27]}\) relating to fluorine chemistry, in which multinuclear n.m.r. spectroscopy is the only practical technique for monitoring the reaction, involves the reaction of \( \text{XeF}_2 \) with \( t\text{-IrCl(CO)}[P(\text{CH}_2\text{CH}_3)_3]_2 \) in \( d_2\)-dichloromethane. Several species are formed, as illustrated at eqn. 1.12, and these are identified by their \( ^{31}\text{P}(^{1}\text{H}) \) and \( ^{19}\text{F} \) n.m.r. spectra.

Eqn. 1.11\(^{[27]}\)

\[
\begin{align*}
\text{PEt}_3 & \quad \text{PEt}_3 \\
\text{OC} & \quad \text{Ir} \quad \text{Cl} \quad \text{XeF}_2 \\
& \quad \text{Cl} \quad \text{Ir} \quad \text{F} \\
& \quad \text{F} \\
\text{PEt}_3 & \\
(1.11.1) & \quad (1.11.2)
\end{align*}
\]

\[
\begin{align*}
\text{PEt}_3 & \quad \text{PEt}_3 \\
\text{OC} & \quad \text{Ir} \quad \text{Cl} \\
& \quad \text{Cl} \quad \text{Ir} \quad \text{F} \\
& \quad \text{F} \\
\text{PEt}_3 & \\
(1.11.3) & \quad (1.11.4) & \quad (1.11.5)
\end{align*}
\]

The identity of each product can be established by a combination of the splitting patterns, intensities and coupling constants in the n.m.r. spectra. Each fluorine resonance is split into a triplet, due to coupling to the
pair of chemically equivalent phosphorus nuclei. The fluorine spectra of the products are now discussed omitting this observation for clarity.

The $^{19}\text{F}$ n.m.r. spectrum of (1.11.1) comprises two peaks, each of which is split into a doublet, due to mutual coupling between each fluorine. These are chemically non-equivalent, because one of them is trans to chloride and the other is trans to carbonyl.

The $^{19}\text{F}$ n.m.r. spectrum of (1.11.2) also comprises two signals. One of these is a triplet. This is assigned to the fluoride which is trans to carbonyl with splitting due to coupling to the pair of chemically equivalent trans fluorides. The signal which denotes these latter fluorides, is a doublet from coupling to the cis fluoride.

The $^{19}\text{F}$ n.m.r. spectra of (1.11.3), (1.11.4), and (1.11.5) each comprise one resonance only, indicating that each complex has only one type of fluorine environment. It is therefore necessary to refer to the $^{31}\text{P}(^{1}\text{H})$ n.m.r. spectra of these complexes to distinguish between them.

The $^{31}\text{P}(^{1}\text{H})$ n.m.r spectrum of (1.11.4) is a triplet from coupling between the phosphorus nuclei and the pair of chemically equivalent fluoride ligands. The corresponding spectra of (1.11.3) and (1.11.5) are doublets because there is coupling to one fluoride only.

It is apparent that the splitting patterns in both the $^{19}\text{F}$ and $^{31}\text{P}(^{1}\text{H})$ n.m.r. spectra of (1.11.3) and (1.11.5) are comparable. However, the relative chemical
shifts of Ir-F's in related complexes (see table 2.2, chapter 2) are affected by the trans ligand. In (1.11.3) the fluoride (which is trans to chloride) would be expected to be deshielded with respect to that of (1.11.5) (F trans to carbonyl) on the basis of the donor-acceptor properties of these trans ligands. Hence, the structures illustrated above were assigned on this basis.

The $^{31}$P($^1$H) n.m.r. spectra of (1.11.1) and (1.11.2) are definitive for these reaction products. The spectrum of (1.11.1) is a doublet of doublets due to unequal coupling between the phosphorus nuclei and each fluoride. The corresponding splitting pattern in (1.11.2) is a triplet, because both fluorines are chemically equivalent.

The range of chemical shifts in the $^{31}$P($^1$H) n.m.r. spectrum is smaller than those in the fluorine spectra of the above complexes. This is because the phosphine ligands are chemically equivalent and there is no variation in the ligand to which they are trans.

1.10 Oxidative Addition and Reductive Elimination

Oxidative addition reactions can often be reversible. This is usually the case for transition metal complexes with metals which prefer to exist in a lower oxidation state and with smaller co-ordination number i.e. metals of the first and second rows and towards the right hand end of each row. More specifically, complexes of Rh$^{III}$ or
Pt\textsuperscript{IV} are more susceptible to reversible reactions of this type than Ir\textsuperscript{III} or Os\textsuperscript{II}. The addition of molecular oxygen to the complex \( t-\text{RhCl(CO)[P(C}_6\text{H}_5)_3]_2 \) is one such example, as illustrated at equation 1.12:

\begin{equation}
\text{Eqn. 1.12}[27]
\begin{array}{c}
  \text{OC} \quad \text{Rh} \quad \text{Cl} \\
  \downarrow \\
  \text{PPh}_3
\end{array}
\xrightarrow{+\text{O}_2}
\begin{array}{c}
  \text{OC} \quad \text{Rh} \quad \text{O} \\
  \downarrow \\
  \text{PPh}_3
\end{array}
\begin{array}{c}
  \text{Cl} \\
  \downarrow \\
  \text{PPh}_3
\end{array}
\xleftarrow{-\text{O}_2}
\begin{array}{c}
  \text{OC} \\
  \downarrow \\
  \text{PPh}_3
\end{array}
\end{equation}

The forward reaction is a straightforward oxidative addition of dioxygen to the Rh-centre with \textit{cis} co-ordination of the O-atoms. These remain singly bonded. The reverse reaction, involving loss of molecular oxygen from the metal centre, is an example of a REDUCTIVE ELIMINATION\[28\]. In such a case, the formal oxidation state and co-ordination number at the metal decrease by two. The resulting complex is both co-ordinatively and electronically unsaturated.

However, not all reductive elimination reactions involve expulsion of the molecule which undertakes the initial oxidative addition. This is illustrated generally at scheme 1.4:
Reductive elimination has been invaluable in the synthesis of new species from transition metal complexes which do not undergo direct ligand substitution. This is clearly illustrated in eqn. 1.13 in which a square planar PtII complex containing a hydride and a triphenylgermane ligand is formed.

Eqn. 1.13[30]

\[
\begin{align*}
\text{PEt}_3 & \quad \text{Ph}_3\text{Ge} \quad \text{Pt} \quad \text{GePh}_3 \quad + \text{H}_2 \\
\text{PEt}_3 & \quad \text{H} \quad \text{Pt} \quad \text{GePh}_3 \quad \text{HGePh}_3 \quad \text{H} \quad \text{Pt} \quad \text{GePh}_3 \\
\text{PEt}_3 & \quad \text{PEt}_3 \\
(1.13.1) & \quad (1.13.2)
\end{align*}
\]

The initial product (1.13.1), in the above equation results from oxidative addition of \( \text{H}_2 \) at the square planar PtII centre. This then expels a molecule of triphenylgermane, HGePh\(_3\), via a reductive elimination to generate the new square planar PtII product (1.13.2).

A similar, but slightly more complex situation, occurs in iridium chemistry[31]. This involves the formation of a square planar IrI species containing a co-ordinated dinitrogen molecule. The general reaction
involving Vaska's compound and organic azides is illustrated in eqn. 1.14.

Eqn. 1.14[31]

\[
\begin{array}{ccc}
\text{PPh}_3 & \text{PPh}_3 & \text{PPh}_3 \\
\text{OC} & \text{Ir} & \text{Cl} \\
\text{Cl} & \text{Ir} & \text{N} \\
\text{OC} & \text{RN}_3 \quad \text{Cl} & \text{Ir} \\
\text{Cl} & \text{Ir} & \text{N} \\
\end{array}
\]

Note: species (1.14.1) has not been isolated.

1.11 Oxidative Addition in Catalysis

The previous section has illustrated a limited usage of the combination of oxidative addition followed by reductive elimination. This is widely utilized in industrial catalysis. One example in rhodium chemistry[32] is the role of ClRh[P(C_6H_5)_3]_3 in the homogeneous hydrogenation of ethene. The catalytic activity of the complex, in a benzene solution, involves oxidative addition of molecular hydrogen followed by reductive elimination of ethane, as illustrated in eqn. 1.15:
The first step in the above equation, 1.15, is the addition of $H_2$ to the square planar Rh$^I$ complex, (1.15.1), which is accompanied by displacement of a phosphine ligand by a solvent, Sol., molecule. This produces complex (1.15.2). An approaching ethene molecule then binds to the cis hydride ligands, as well as forming a $\pi$-interaction with the metal. This results in displacement of the co-ordinated solvent, to give (1.15.3). The final stage of the process is the reductive elimination of an ethane molecule. A molecule of solvent takes the place of the co-ordinated ethane to leave the rhodium with four co-ordinated ligands (1.15.4). This species is highly reactive and can absorb a further molecule of hydrogen to continue the catalytic cycle.
Points to Note In Connection with Equation 1.15

1. When the catalyst, (1.15.1), is exposed to a mixture of hydrogen and deuterium, followed by ethene, only $\text{C}_2\text{H}_6$ and $\text{C}_2\text{H}_4\text{D}_2$ are formed. There is no evidence for the production of $\text{C}_2\text{H}_5\text{D}$. This is consistent with concerted elimination, as proposed, with no scope for the formation of the mixed alkane from $\text{H}_2$ and $\text{D}_2$ starting materials.

2. Instead of absorbing $\text{H}_2$, (1.15.4) can absorb a molecule of ethene, giving a species with molecular formula $\text{ClRh[P(C}_6\text{H}_5\text{)]}_2(\text{C}_2\text{H}_4)$. This complex does not possess catalytic activity in this hydrogenation cycle.

3. The analogous complex to (1.15.1), $\text{ClIr[P(C}_6\text{H}_5\text{)]}_3$, is also known, but is of little value as a catalyst in this process. This is because the iridium$^{\text{III}}$ centre is stable to reductive elimination.

There are very many other examples of transition metal complexes as catalysts reported in the literature [33].
1.12 Pseudorotation Processes in Inorganic Chemistry

1. The Berry-pseudorotation[34]

There are a number of small 5 co-ordinate inorganic molecules, which are capable of adopting more than one geometrical configuration. In certain instances, for example, in the case of PF$_5$, the energy barrier to interconversion between the trigonal bipyramidal and square-based pyramidal forms is sufficiently low to enable this change to occur below room temperature. $^{19}$F n.m.r. studies of PF$_5$ at temperatures down to 173K implied that all five fluorines in the molecule were chemically equivalent. The spectrum at 173K is a doublet, arising from the fluorines coupling to the central phosphorus atom. Those observations can be explained by a mechanism like the one proposed by Berry, mech. 1.2, in 1960, which accounts for a rapid interconversion, on the n.m.r. timescale, of axial and equatorial sites:

Mech. 1.2[35]

\[
\begin{array}{c}
\begin{array}{c}
1 \\
2 \\
3 \\
4 \\
5 \\
\end{array}
\end{array}
\Rightarrow
\begin{array}{c}
\begin{array}{c}
3 \\
5 \\
1 \\
2 \\
4 \\
\end{array}
\end{array}
\Rightarrow
\begin{array}{c}
\begin{array}{c}
3 \\
5 \\
2 \\
1 \\
4 \\
\end{array}
\end{array}
\]

In the above mechanism, site 4 acts as a pivot for the interconversion of positions (1,5 and 2,3).

PF$_5$ was the first molecule in which this effect was observed. It is conceivable that it may, in part, be
responsible for fluorine exchange in SF₄.

2. The Turnstile-pseudorotation[36]

Another similar mechanism of exchange is the Turnstile-pseudorotation. This is where two sites of the trigonal bipyramid remain fixed and the three others become interchangeable by rotation, like a turnstile, as illustrated in mech. 1.3 below:

Mech. 1.3 [36]

In the above scheme, sites 1, 2 and 3 interchange by rotation, while 4 and 5 remain fixed. This mechanism may also be occurring in SF₄.

Both of these exchange mechanisms are first-order processes and entirely intramolecular.
1.13 An Introduction to Sulphur Tetrafluoride (SF₄)

SF₄ is one of several fluoro-sulphur compounds. Its existence was in doubt up to 1950 at which time Silvey and Cady[37] isolated it as a decomposition product of CF₃SF₅ in an electrical discharge[38]. Since then it has been the subject of intense interest. Several investigators have discovered that it possesses a combination of unusual physical, chemical and structural characteristics. A number of these are reviewed here.

The ability of SF₄ to act as a Lewis acid or base in relation to a adduct formation is discussed in chapter 5.

Synthesis

SF₄ can be prepared relatively easily by treating a metal fluoride with SC₁₂ in a medium of high dielectric constant[39]. Sodium fluoride was used in this work (see chapter 6).

This method of preparation was finally developed after several others[40][41][42] had proved to be awkward and inefficient.

Purification

The main impurities in SF₄ from the preparation described above[39] are Cl₂ and the products of partial hydrolysis by moisture, SOF₂ and HF. These are removed
under vacuum, once SF$_4$ has been converted to an SF$_4$.BF$_3$ adduct (see chapter 6).

Structure

The structure of SF$_4$ is essentially a trigonal bipyramid with two fluorines and a lone pair occupying equatorial positions, the other fluorines in axial sites and sulphur at the centre (see fig. 1.4):

Fig. 1.4

The Structure of SF$_4$

\[
\begin{array}{c}
\text{F} \\
\text{S} \\
\text{X} \\
\text{F} \\
\text{Y} \\
\text{F} \\
\end{array}
\]

X = 164.6 p.m.  
Y = 154.5 p.m.  
\(\alpha = 186.56^\circ\)  
\(\beta = 101.33^\circ\)

The above geometry was established from n.m.r. experiments\[43\][44] while the bond lengths and angles were derived from microwave studies\[45\].

Bonding

Initially the bonding in SF$_4$ was thought to be sp$^3$d hybridized\[46\], like that in PF$_5$. However, the presence of a lone pair at sulphur was subsequently thought to invoke large energy differences between the s, p and d orbitals of sulphur, causing a significant alteration to the hybridisation ratios. On this basis it was proposed that the three equatorial bonds are based on sp$^2$ hybrids whereas the two axial ones consist of p and d orbitals.
Physical Properties

SF₄ is a colourless gas under standard conditions (1 atm., 298K) with a boiling point of 235K and a melting point of 156K[47]. It has a vapour pressure of approximately 10 atm. at 298K[47] and a dipole moment of 0.632 ± 0.003 Debye.

The average S-F bond energy is approximately 326 kJmol⁻¹[48].

Chemical Properties

SF₄ is hydrolyzed instantly by moisture to SOF₂ and HF. SOF₂ is further converted to SO₂ and HF. This is illustrated in the equation below:

Eqn. 1.16

\[
\begin{align*}
SF_4 + H_2O & \rightarrow SOF_2 + 2HF \\
SOF_2 + H_2O & \rightarrow SO_2 + 2HF
\end{align*}
\]

The effects of moisture and HF (see later) on SF₄ make the reagent tricky to manipulate, although with proper precautions it may be handled in standard pyrex glass, under vacuum. The following reactions illustrate some of the synthetic uses of SF₄.
Organic Carbonyls

SF$_4$ can selectively replace oxygen with fluorine in a range of organic carbonyl compounds[49]. This is illustrated generally in scheme 1.5:

Scheme 1.5

\[
\text{C}=\text{O} + \text{SF}_4 \rightarrow \text{CF}_2 + \text{SOF}_2
\]

A typical reaction of this type is between SF$_4$ and benzal fluoride and this is shown below:

Eqn. 1.17

\[
\text{C}_6\text{H}_5\text{CHO} + \text{SF}_4 \rightarrow \text{C}_6\text{H}_5\text{CHF}_2 + \text{SOF}_2
\]

In general, the reactivity of SF$_4$ with aldehydes and ketones is similar. However, when there is as an $\alpha$-hydrogen, in relation to the carbonyl group, the yield of the difluoride product is significantly reduced. This is presumably due to the highly favoured elimination of HF.

SF$_4$ can also convert acyl fluorides to trifluoromethyl groups. These reactions are usually two step processes. The first of these is the conversion of the acyl group to an acyl fluoride. This is then converted to an $-\text{CF}_3$ group.
Alcohols

$\text{SF}_4$ can convert organic hydroxyl groups into fluorides. The yield of the product is approximately correlated with the acidity of the hydroxyl group. Typically, $\text{SF}_4$ reacts with polyfluorinated alcohols to form the corresponding polyfluoroalkanes. A specific case is illustrated below:

Eqn. 1.18

$$\text{H(CF}_2\text{)}_3\text{CH}_2\text{OH} + \text{SF}_4 \rightarrow \text{H(CF}_2\text{)}_3\text{CH}_2\text{F} + \text{SOF}_2$$

Less acidic alcohols, such as methanol and ethanol, also give the corresponding alkylfluoride with $\text{SF}_4$, although a major by-product is the alkyl ether.

Catalysis and the Role of Inorganic Fluorides In Fluorination Reactions of $\text{SF}_4$

The reactions of $\text{SF}_4$ with carbonyl and hydroxyl groups are known to be catalyzed by inorganic fluorides such as HF, $\text{BF}_3$ and others. A possible mechanism, in relation to fluorination of carbonyls, is given at mech. 1.4:
$XF_n$ is one of the catalysts, HF or BF$_3$ etc.

$n$ is the number of fluorines in $XF_n$

Initially the catalyst is believed to bind to the oxygen of the carbonyl, (1.4.2). The complex then reacts with SF$_4$ as illustrated (1.4.3) to form a thioether, (1.4.4). A further molecule of the catalyst attacks this ether, (1.4.5), to generate the product, (1.4.6), as illustrated.

SF$_4$ is thought to react with alcohols by elimination of HF to give an intermediate of the form (1.4.4), and then as indicated in mech. 1.4.
Points to note in Connection with Mech. 1.4

1. The stronger the Lewis acid, the greater effectiveness is its role as a catalyst.

2. SF₄ can also act as a Lewis acid and this may account for its ability to react with the carbonyls in the absence of catalysts. However, much milder reaction conditions are required when stronger Lewis acids are present.

3. The reaction is inhibited when the carbonyl is bonded to two strongly electron-withdrawing groups. It is thought that the lowering of the Lewis base character of the carbonyl group weakens the bonding of the Lewis acid at this site, hence reducing its catalytic ability.

Reactions with Olefins

SF₄ is highly specific in relation to the olefinic linkages which it will fluorinate. These are fluoro-olefins. An example is illustrated in eqn. 1.19:

Eqn. 1.19[50]

\[ \text{CH}_3\text{OOF} \text{CF}_2 + \text{SF}_4 \rightarrow \text{CH}_3\text{OFCF}_2\text{CF}_2\text{SF}_3 \]
Reaction with Compounds Containing Carbon-Nitrogen Multiple Bonds

Other multiple bonds which are fluorinated by SF₄ are C=N and C≡N[51]. A mechanism has been proposed and this is illustrated for a C=N bond in scheme 1.6:

Scheme 1.6

\[ \text{RN} = \text{C} = \text{O} + \text{SF}_4 \rightarrow \text{RN} = \text{SF}_2 + \text{COF}_2 \]

Mech. 1.5

\[
\begin{align*}
\text{R} - \text{N} &= \text{C} = \text{O} \\
\text{R} - \text{N} &= \text{C} - \text{F} \\
\text{F}_2\text{S} &\rightarrow \text{F}
\end{align*}
\]

It is thought that the mechanism initially involves addition of SF₄ across the C=N bond, followed by an intramolecular rearrangement and elimination of carbonyl fluoride.

The reactivity of SF₄ towards C≡N bonds is similar. The products in these cases are of the form RCF₂N=SF₂.

Oxidation of SF₄

SF₄ can be oxidized to SOF₄ only in the presence of a vigorous oxidizing agent[52]. Typical reaction conditions involve treating SF₄ with O₂ at 473K in the presence of NO₂ as a catalyst. This is illustrated in eqn. 1.20:
Eqn. 1.20

$$\text{SF}_4 + \text{O}_2 \rightarrow \text{SOF}_4 + \frac{1}{2}\text{O}_2$$

Other Reactions of SF$_4$

SF$_4$ can react with metal oxides, sulphides and carbonyls to form a range of new inorganic fluorides\[53\][54]. One specific case is the fluorination of tungsten oxide in the presence of NaF at 523K, as illustrated in eqn. 1.21 below:

Eqn. 1.21

$$2\text{NaF} + \text{WO}_3 \rightarrow \text{Na}_2\text{WF}_8$$

SF$_4$ and Fluorine Exchange

It soon became apparent from variable temperature $^{19}\text{F}$ n.m.r. studies\[43\][44], that SF$_4$ does not possess a static structure at room temperature, but is subject to exchange. It had already been established that the PF$_5$ molecule was fluxional\[55\]. Perhaps this also applies to SF$_4$ although this is much less easy to illustrate. Exchange in PF$_5$ can be monitored in terms of $^1J$(PF). However, sulphur does not have a suitable spinning nucleus for such a study.

Several mechanisms have been postulated and many have been investigated and discounted. Others cannot be excluded as possible exchange mechanisms. Details of this work are now outlined.
Possible Exchange Processes Relating to SF₄

1. A radical mechanism[56]

The reversible dissociation of SF₄ into SF₃• and F• radicals is one possible route to fluorine exchange. Free radicals are highly reactive and it is likely that the presence of either SF₃• or F• would result in fluorination of the organic solvent. Fluorinated solvents ought to be detected by ¹⁹F n.m.r. studies.

2. An intramolecular pseudorotation process

An intramolecular pseudorotation, like the one postulated by Berry[34] (see earlier), could render the fluorines of SF₄ equivalent. This would obey a first-order rate law and a series of concentration studies should help to establish if this is the case.

3. An intermolecular exchange process via a fluorine-bridged dimer[56]

Fluorine exchange could be instigated by two molecules becoming associated via fluorine bridging. A possible mechanism is shown below:

Mech. 1.6[56]

The ringed fluorines are from one starting monomer.
4. An intramolecular fluorine exchange via a fluorine-bridged dimer[57]

Fluorine exchange via a dimeric species, as above, may also be intramolecular. This depends on the ability of SF₄ to exist as a stable dimer in solution. A dimer which is consistent with the available n.m.r. data can be postulated. However, the gas phase structure of SF₄ is monomeric.

5. Ionization to SF₃⁺ and F⁻[56]

A reversible dissociation of SF₄ into SF₃⁺ and F⁻ in solution is another possible source of exchange. SF₃⁺ would not necessarily react with the solvent, thus making its detection more difficult.

6. A wall reaction[56]

Fluorine exchange in SF₄ could be induced by a wall reaction. This process can easily be detected by varying significantly the surface area of the vessel containing the sample of SF₄.

Initial experiments by Muetterties and Phillips[56] established that the two fluorine chemical environments of SF₄ became one at 226K, on the n.m.r. timescale. They reported that the exchange was second order or higher and that the coalescence temperature of various
concentrations of SF₄ in a range of solvents was dependent on the solvent medium. However, they could not relate the coalescence temperature to the dielectric constant of the solvent. Also, they reported no evidence for fluorination of the n.m.r. solvent.

In an additional experiment, they noted that there was no significant change in the coalescence temperature of the n.m.r. signals, when a large number of glass beads was added to a sample of neat SF₄. This effectively increased the surface area of the vessel by a factor of approximately 100.

Redington and Berney[57] reported that SF₄ associates to form a dimer, or polymer, when isolated in an argon matrix. From I.R. studies they concluded that the association involved the equatorial fluorines, but not the axial ones. Possible structures of this dimer are given in fig. 1.5:
These workers also claim that there is an association between SF₄ and SOF₂ under these conditions.

Later work by Ibbott and Janzen[58] established that fluorine exchange in SF₃N(CH₃)₂ is catalyzed by the addition of H₂O. This was confirmed when (H₃C)₃SiN(CH₃)₂ was added to remove H₂O and HF. The ¹⁹F(¹H) and ¹H n.m.r. spectra of SF₃N(CH₃)₂ after the removal of these impurities was found to be identical to those for the pure reagent in an anhydrous environment. These workers also
reported a revised coalescence temperature[59] for free SF₄ of 288K. This was also under anhydrous conditions and concurs with the value obtained during this work when CsF was present. It is assumed that HF catalyzes the exchange in free SF₄, as CsF is known to absorb HF to form CsHF₂.

Conclusions

It is clear from the above accounts that fluorine exchange in SF₄ does not proceed via a free radical mechanism or by a wall reaction. Also, a pseudorotation mechanism alone could not account for exchange, although one may be occurring simultaneously with other processes. Ionization cannot be discounted. Neither can intermolecular exchange involving bridging fluorines, as illustrated at mech. 1.4.

Redington and Berney conclude that fluorine exchange in SF₄ is not intermolecular, as claimed by Muetterties and Phillips. They claim that if this is the case it may also reasonably be expected to involve SOF₂.

The problem with this type of analysis is that the behaviour of SF₄ in a matrix may differ considerably from that in solution. The arguments for and against these models are well documented[60][61].

Muetterties and Phillips reported that they used NaF to absorb HF. However, NaF does not effectively remove HF from solutions in dichloromethane or toluene, as was
established during the work described in this thesis (see next chapter).

Further evidence that SF$_4$ and HF undergo intermolecular exchange was obtained from conductivity experiments. The conductivity of solutions of SF$_4$ ionized in HF was that expected for a 1:1 electrolyte and the following equilibrium (eqn. 1.22) was proposed:

Eqn. 1.22

$$\text{SF}_4 + \text{HF} \rightarrow \text{SF}_3^+ + \text{HF}_2^-$$

In spite of all previous efforts, the exact nature of fluorine-exchange in SF$_4$ remains a mystery. It appears that the experiments of Muetterties and Phillips may be affected by HF, in spite of their efforts to remove it. They have established that other Lewis acids affect fluorine exchange in SF$_4$.

Similarly, Redington and Berney made no mention of whether HF had been eliminated in their experiments or what effect its presence may have on their results and conclusions.
1.14 Other Fluorides of Sulphur

Although the work described in this thesis is based on SF₄ and its derivatives, several other fluorides of sulphur are known. This section describes the more common ones, in relation to their synthesis, structure and some physical and chemical properties.

\( S_2F_2 \)

This compound is synthesized[63] by heating a mixture of sulphur and silver fluoride (AgF) to 398K under anhydrous conditions. It is a gas under standard conditions (B.Pt. = 288K, M.Pt. = 140K) and is most easily handled at low pressures in the gas phase. There are two sulphur sites, each of which exhibits a co-ordination number of two. The structure is analogous to \( H_2O_2 \), with an S-S bond length of 189 p.m. Each S-F bond length is 163.5 p.m. The F₆S angle is 108.3° and the angle between the fluorines and the S-S bond is 87.9°.

\( S_2F_2 \) hydrolyses rapidly, in the presence of moisture, to \( S_8 \), HF and a mixture of polythionic acids.

\( SSF_2 \)

This reagent is formed by the isomerization of \( S_2F_2 \)[64] in the presence of alkali metal fluorides. It contains both 1- and 3 co-ordinate sulphur sites, with the sulphur centres formally joined by a double bond. The
length of this bond is 186 p.m.\cite{65}, which is very similar to the single S-S bond length in \( S_2F_2 \). The two S-F bonds are each 160 p.m. long and the SSF and FSF angles are 107.5° and 92.5° respectively.

\( SSF_2 \) is also a gas under standard conditions (B.Pt. = 262K, M.Pt. = 108K) and is thermally stable up to 523K. However, in the presence of acid catalysts such as BF\(_3\) or HF, it rapidly disproportionates to SF\(_4\) and sulphur.

\( SSF_2 \), like \( S_2F_2 \), is readily hydrolysed by moisture and gives the same products.

An alternative synthesis of \( SSF_2 \) is the fluorination of \( S_2Cl_2 \) by KF in an SO\(_2\) solution.

\( SF_2 \)

\( SF_2 \) is generated\cite{66} from fluorination of \( SCl_2 \) by KF in an SO\(_2\) solution. This species is highly reactive and has only a transient existence\cite{67}. The geometry at sulphur is bent with an F\( \equiv \)SF angle of 98.3°. The two S-F bond lengths are each 159 p.m.

\( SF_3SF \)

The main reason for the transient existence of \( SF_2 \), is the rapid dimerization, by an unusual insertion of one \( SF_2 \) molecule into the S-F bond of another. This generates a novel species with molecular formula \( SF_3SF \)\cite{68} which contains both 4 and 2 co-ordinate sulphur sites. The sulphur with greater co-ordination number lies
essentially at the centre of a trigonal bipyramid, with two fluorines occupying the axial sites. A further fluorine, a lone pair and an S-F group are located in the equatorial positions. The angle between the fluorine of the S-F group and the S-S bond is less than 180°, and motion around this bond is slow on the n.m.r. timescale, at 173K, as suggested by the presence of four distinct resonances in the 19F n.m.r. spectrum at that temperature.

SF₆

The geometry[69] at sulphur in this compound is a regular octahedron, as all angles between adjacent sites are 90°. Each S-F bond distance is 156.4 p.m. The structure is confirmed by the 19F n.m.r. spectrum of the species, which is a singlet.

SF₆ is a colourless gas under standard conditions and is prepared by the combustion of sulphur in an atmosphere of fluorine. It is unreactive, non-toxic, non-flammable and insoluble in water.

S₂F₁₀

The structure of S₂F₁₀[69] is related to SF₆. It is essentially two -SF₅ units joined together by a long, weak S-S bond (221 p.m.). The S-F bond lengths are all 156.0 p.m. and all the angles between adjacent fluorines and sulphur are 90°. The reagent is a colourless liquid (B.Pt.= 303K, M.Pt.= 221K) under standard conditions.
$S_2F_{10}$ is synthesized by photolysis of $SF_5Cl$ and $H_2$. Its reactivity is intermediate between $SF_4$ and $SF_6$. It is not hydrolyzed by water or dilute acids, but is extremely toxic. It disproportionates at 423K to $SF_4$ and $SF_6$, probably by a mechanism which involves the $SF_5^-$ radical.
Chapter 2

2.0 An Introduction to the Reaction Between the Series of Complexes \( t-\text{IrX(CO)}[\text{P(CH}_2\text{CH}_3)_3]\_2 \) (\( X = \text{Cl, Br, I, NCO, NCS} \)) and SF\(_4\).

This chapter discusses the oxidative addition reaction of SF\(_4\) with the complexes \( t-\text{IrX(CO)}[\text{P(CH}_2\text{CH}_3)_3]\_2 \) (\( X \) as above). The products are the first transition metal complexes known which contain an -SF\(_3\) ligand. This work was first reported in a provisional study[70]. These complexes possess fluxionality at sulphur and are also subject to intermolecular fluorine exchange. All of the exchange processes are influenced by HF.

2.1 The Background to the Oxidative Addition of SF\(_4\) to \( t-\text{IrCl(CO)}[\text{P(CH}_2\text{CH}_3)_3]\_2 \)

Preliminary \( ^{19}\text{F n.m.r.} \) studies on the reaction between the iridium complex and SF\(_5\)Cl[71] indicated that an oxidative addition had occurred. The spectrum of a \( \text{d}_2\)-dichloromethane solution at 180K contained a set of four resonances each of comparable intensity. Three of these, at \( \delta+74.7\text{p.p.m.}, \delta+45.9\text{p.p.m. and } \delta-66.5\text{p.p.m.} \) are in the region associated with fluorine bonded to a main group element, which is sulphur in this complex. This suggested that an -SF\(_3\) ligand had been formed. The fourth
resonance at δ-336.9 p.p.m. is in the region associated with a fluorine bonded directly to a transition metal\cite{72} i.e. iridium. The low frequency of this resonance has been attributed to effective shielding of the fluorine by the iridium d-orbitals. There was also evidence for the presence of other fluorine-containing products.

2.2 The Reaction of $t$-IrCl(CO)[P(CH$_2$CH$_3$)$_3$)$_2$ (2.0.1) with SF$_4$

A sample of pure SF$_4$ was prepared and reacted with an equimolar amount of (2.0.1) in d$_2$-dichloromethane. The yellow solution turned colourless at 178K suggesting that a reaction had taken place. From previous experiments\cite{73} octahedral iridium$^{III}$ compounds were found to be colourless or very pale in colour.

Results and Conclusions

The $^{19}$F n.m.r. spectrum of this solution at 178K contains the same set of resonances as before (see diagram 2.1). It is therefore concluded that this product is a novel species containing an –SF$_3$ ligand bonded directly to the metal. The rate of addition at 178K is too rapid to enable the determination of a reaction mechanism.

The geometry at sulphur is believed to be based on a trigonal bipyramid with two fluorines occupying axial co-ordination sites while the equatorial positions are
Diagram 2.1

$^{19}F(\text{H})$ n.m.r. spectrum of (2.1.1) at 178K.

N.B. ALL $^{19}F$ n.m.r. SPECTRA ARE AT 75.39 MHz.
Diagram 2.1(a)

Expansion of $F_A$ in (2.1.1).

$\delta$/p.p.m.
Diagram 2.1(b)

Expansion of $F_A$ in (2.1.1).
Diagram 2.1(c)

Expansion of $F_E$ in (2.1.1).
Diagram 2.1(d)

Expansion of $F_C$ in (2.1.1).
filled by the third fluorine, the sulphur lone pair and the iridium fragment of the complex.

The number of different substituents at iridium gives rise to the possibility of isomer formation. Assuming that the product is one of straight addition with a cis arrangement of the fluoride and -SF₃ ligands, the pair of isomeric complexes in the following equation must be considered as potential reaction products:

Eqn. 2.1

\[
\begin{align*}
\text{PEt}_3 & \quad \text{PEt}_3 & \quad \text{PEt}_3 \\
\text{OC} \quad \text{Ir} \quad \text{Cl} + \text{SF}_4 & \quad \text{Cl} \quad \text{Ir} \quad \text{S}^\ominus \quad \text{F}_C \quad \text{F}_A & \quad \text{Cl} \quad \text{Ir} \quad \text{S}^\ominus \quad \text{F}_C \quad \text{F}_A \\
\text{PEt}_3 & \quad \text{OC} \quad \text{F}_A \quad \text{F}_E & \quad \text{PEt}_3 \quad \text{F}_A \quad \text{F}_E \\
\text{(2.0.1)} & \quad \text{(2.1.1)} & \quad \text{(2.1.2)}
\end{align*}
\]

Note: In all Ir-SF₃ complexes in this thesis, F₈ will denote a fluorine bound to iridium unless the complex has two Ir-F bonds. In such cases (where these are chemically distinct), one shall be labelled F₈ and the other F₈'. The fluorines bound axially to sulphur shall be labelled F₈ (or one F₈ and the other F₈', if they are chemically distinct) and the one bound equatorially to sulphur shall be denoted by F₈.

In order to establish the ligand arrangement at iridium some crystals[70] of the complex were grown and a low temperature X-ray crystallographic study confirmed that the product is that of simple addition and has the
structure proposed at (2.1.1) i.e. $F_C$ is \textit{trans} to carbonyl and the $-SF_3$ group is \textit{trans} to chloride.

It is easy to see why there should be three fluorine environments in this Ir-$SF_3$ complex. Clearly, $F_C$ is different from $F_A$, $F_A'$, and $F_E$. Also, $F_E$ is distinct from $F_A$ and $F_A'$ as axial and equatorial bonds in a trigonal bipyramid are different, owing to differing degrees of hybridization.

However, it is perhaps less obvious why $F_A$ and $F_A'$ (both axial and mutually \textit{trans}) are chemically distinct. This is explained by the asymmetry of the ligands at iridium. $F_A$ is distinct from $F_A'$ because it is thought to be \textit{cis} to $F_C$ whereas $F_A'$ would be \textit{cis} to the carbonyl ligand. This is illustrated in fig. 2.1:

![Fig. 2.1](image)

A Diagrammatic Representation of the Chemical Inequivalence of $F_A$ and $F_A'$:

$$
\begin{array}{ccc}
F_C & F_A & \text{Ir} \\
\mid & \| & \mid \\
& S & \mid \\
& & CO \\
& & F_A'
\end{array}
$$

Note: The labels of $F_A$ and $F_A'$ in the above figure (and in all subsequent figures of Ir-$SF_3$ complexes in which $F_A$ and $F_A'$ are chemically distinct) are interchangeable, because these fluorines cannot be chemically distinguished.
Unfortunately, the X-ray crystallographic study failed to establish the orientation of the -SF$_3$ ligand owing to a high degree of disorder in the crystal. In fig. 2.1 the plane containing the Ir-P bonds is illustrated bisecting the FA$\tilde{\text{S}}$FA' angle. It is possible that the actual orientation of the -SF$_3$ group is rotated up to 90° from fig. 2.1. Even if the FA$\tilde{\text{S}}$FA' angle bisects the plane containing the Ir-F$_C$ and Ir-C bonds, FA and FA' remain distinct. In such a case FA and FA' are cis to a phosphine. However, these latter ligands are non-equivalent because FE lies in closer proximity to one than to the other.

A Comparison with the Orientation of a -PF$_4$ Group bonded to Iridium

The orientation of the -PF$_4$ group in the iridium fluoro-phosphine complex (2.1.3)[74], in solution, (see fig. 2.2) is postulated such that the axially bound fluorines, FA and FA', are in the plane containing the Ir-Cl$_C$ and Ir-C bonds.

Fig. 2.2

A Diagrammatic Representation of the Orientation of the -PF$_4$ group in (2.1.3)
The $^{19}\text{F}$ n.m.r. spectrum of (2.1.3) at 123K in a 1:2 d$_2$-dichloromethane/diethylether mixture\textsuperscript{74} suggests that there are three resonances assigned to the fluorines of the -PF$_4$ group. This would confirm that one pair are equivalent under these conditions. The signal with the largest value of $^1J(\text{FP}')$ is assigned to this pair. This suggests that these fluorines are bound equatorially to P' as $^1J(\text{FeqP}')$'s are larger than the corresponding axial couplings in a trigonal bipyramid. This is a consequence of the hybridization ratio giving the equatorial bonds a greater degree of s-character.

If the group had been rotated through 90° the axial fluorines would then be equivalent and the equatorial ones distinct.

In an intermediate orientation, all four fluorines are non-equivalent. This cannot be discounted, because the two equatorial fluorines would be very similar and small differences in their chemical shifts may be hard to detect due to the inherent broadness of the lines.

However, it is clear that the axial P-F bonds lie out of the plane which incorporates the Ir-P bonds and P'.

It is reasonable to assume that the -SF$_3$ ligand, which is of comparable steric bulk and geometry to -PF$_4$, will adopt a similar orientation to the phosphorus group. This is as illustrated in fig. 2.1.
Additional Structural Information on (2.1.1)

Further information about (2.1.1) was obtained from a sample containing 99% $^{13}$C-enrichment at carbonyl. The value of $^{2}J_{(CC)}$ is strongly influenced by the structural arrangement at the metal centre (a typical value for trans $^{2}J_{(CC)}$ is 70Hz whereas the corresponding cis coupling may range from 2-15Hz[72]). In (2.1.1) the signal denoting F contains an additional doublet splitting of 77Hz when the sample is 99% $^{13}$C-enriched (see diagram 2.1(e)). This is in accordance with the X-ray structure in which the carbonyl ligand is trans to F. The other signals are not affected by the presence of $^{13}$C.

The $^{31}$P($^{1}$H) n.m.r. spectrum of (2.1.1) at 178K in d$_{2}$-dichloromethane is an AB pattern and some first order couplings to the fluorines are resolved (see diagram 2.2) (when HF is excluded). This confirms that the phosphines are chemically distinct at this temperature.

2.3 An Investigation into Exchange Processes Involving Complexes Containing the -SF$_{3}$ Ligand

The temperature dependence of the $^{19}$F n.m.r. spectrum of SF$_{4}$ and possible explanations have been discussed in detail in chapter 1. There are a number of transition metal complexes which also have temperature sensitive $^{19}$F n.m.r. spectra. One of these is the Ir-PF$_{4}$ complex (2.1.3). Variable temperature $^{19}$F n.m.r. studies[74]
Diagram 2.1(e)

Expansion of $F_C$ in (2.1.1) with $^{13}$C at CO.
Diagram 2. 2

$^{31}\text{P}^{(1\text{H})}$ n.m.r. spectrum of (2.1.1)

at 178K
showed that the complex possesses fluxionality at P' and
the fluorines remain bound to phosphorus up to 300K. The
-SF₃ ligand is of similar steric bulk and geometry to
-PF₄. The main difference is that one fluorine in the
-PF₄ ligand is replaced by a lone pair in the -SF₃ group.
The fluorines at sulphur may reasonably be expected to
undergo exchange by a mechanism similar to those at P' in
(2.1.3).

A Discussion of Fluorine Exchange of (2.1.1) with HF Present

In order to investigate the susceptibility of (2.1.1)
to fluorine exchange, a sample of the complex in
d₂-dichloromethane was warmed to 295K. The ¹⁹F(¹H) n.m.r.
spectrum of this solution which contains HF, an impurity
in the SF₄, shows marked changes with temperature.

As the solution is warmed above 178K the signals
assigned to FA, FA', and FE broaden and no couplings are
resolved by 230K. The peaks coalesce at 273K (see diagram
2.3).

The resonance denoting FC in the spectrum is broad
and featureless at 178K, but it sharpens to a triplet by
273K.

The ³¹P(¹H) n.m.r. spectrum of (2.1.1) is second
order and very broad at 178K. It sharpens to a doublet at
273K. The magnitude of this coupling (31Hz) is equal to
that in the triplet of FC.
Diagram 2. 3

$^{19}$F n.m.r. spectrum of (2.1.1) with

HF present at 178K
Diagram 2.3a

$^{19}$F n.m.r. spectrum of (2.1.1) with

HF present at 220K
Diagram 2.3b

$^{19}$F n.m.r. of (2.1.1) with HF

present at 298K
These spectroscopic changes are reversible when the solution is cooled to 178K.

Conclusions

The n.m.r. data on (2.1.1) over the temperature range 178-295K confirm that the complex is susceptible to fluorine exchange, although the nature of this exchange is not fully understood.

The loss of all $^3J(FF)'s$ and $^3J(FP)'s$ at 273K has established that there is an intermolecular component which is significant on the n.m.r. timescale, at this temperature. This implies that $F_A$, $F_A'$, and $F_E$ are involved. However, $F_C$ does not participate in the exchange to any great extent because $^2J(F_CP)$ is retained up to 295K.

In subsequent solutions with variable concentrations of HF the coalescence temperature of the $-S-F$ peaks was not reproducible. This suggests that the rate of exchange is influenced by the concentration of the acid. An equation depicting a possible mechanism for this exchange process is given below:

Eqn. 2.2

$$\text{Ir-SF}_3 + \text{HF} \rightleftharpoons \text{Ir-SF}_2^+ + \text{HF}_2^-$$

Clearly, altering the concentration of HF in the above equation is going to affect the equilibrium
constant.

Perhaps the stability of FC to exchange with HF, by
the mechanism at eqn. 2.2, is due to the required
formation of a 5-coordinate iridium complex, which is
disfavoured.

An Investigation into Fluorine Exchange of (2.1.1) in the
Absence of HF

HF can be removed from the system by N(CH₃)₃ or CsF.
The latter is chemically safer, but more expensive and
generally less soluble in organic solvents. NaF is much
cheaper than CsF and can also absorb HF. However, it has
been found to be ineffective at removing the acid from
d₂-dichloromethane solutions.

In order to establish the susceptibility of (2.1.1)
to fluorine exchange in the absence of the acid the
complex has been prepared in a d₂-dichloromethane solution
containing an excess of CsF. Variable temperature n.m.r.
studies on this solution reveal some interesting
observations which are not seen in samples with HF
present.

Results

The four ¹⁹F n.m.r. resonances of the complex are
resolved multiplets at 178K. As the solution is warmed
(see diagram 2.4) the two high frequency signals (those
assigned to Fₐ and Fₐ') broaden but retain fine structure
Diagram 2. 4

$^{19}\text{F n.m.r. spectrum of (2.1.1) at 220K with HF absent}$
Diagram 2.4a
Expansion of Fc in (2.1.1) at 270K
Diagram 2.4b

$^{19}$F n.m.r. spectrum of (2.1.1) at 306K with HF absent
Diagram 2.4c

19F n.m.r. spectrum of (2.1.1) at 341K with HF absent
up to 270K. The resonance which denotes $F_E$ sharpens to a triplet at 232K and at 270K it remains sharp. An extra doublet splitting arising from coupling to $F_C$ is resolved at this temperature. The Ir-$F$ resonance sharpens to a triplet of near quartets at 270K. The $^{31}P(^1H)$ n.m.r. spectrum at this temperature is broad and contains no fine structure.

As the sample is warmed above 270K the three $-S-F$ resonances broaden and at 293K those of $F_A$ and $F_A'$ coalesce. The other one loses its structure and the peak of $F_C$ is a well-resolved triplet of pseudo-quartets at this temperature.

At 306K the peaks assigned to the $-S-F$'s are broad, whereas that of $F_C$ remains sharp and all couplings are retained. The $^{31}P(^1H)$ n.m.r. spectrum has become a first order doublet of pseudo-quartets at 306K (see diagram 2.2(a)).

All of these observations have been reproducible in subsequent samples of (2.1.1) in the presence of CsF or $N(CH_3)_3$ and the coalescence temperature of the peaks assigned to $F_A$ and $F_A'$ remains constant to within 2K. All exchange processes have been found to be reversible as the samples are cooled to 178K.

Additional samples of (2.1.1) have been prepared in $d$-trichloromethane and $d_3$-cyanomethane to enable a study of the exchange processes involving the complex at higher temperature. The spectra recorded up to 306K show no
Diagram 2.2a

$^{31}$P($^1$H) n.m.r. spectrum of (2.1.1)

at 306K with HF absent
significant change from those of (2.1.1) in d$_2$-dichloromethane at the corresponding temperature. On further warming the -S-F resonances continue to broaden until they coalesce at 341±2K. This coalescence temperature is also reproducible and the processes are reversible as the sample is cooled to 306K.

At 341K the signal of FC is a sharp triplet with no other couplings retained. The $^{31}$P($^1$H) n.m.r. is a doublet with coupling equal to the observed triplet in the Ir-F resonance. All other couplings to fluorines are no longer resolved at this temperature.

Discussion of Fluorine Exchange Relating to (2.1.1) in the Absence of HF.

It is clear from the reproducibility of the data on (2.1.1) in the absence of unbound HF that the acid is responsible for some of the exchange processes discussed earlier. It may be catalyzing fluorine exchange or undergoing exchange with the complex directly.

An interesting observation from the $^{19}$F n.m.r. spectrum of (2.1.1), unlike that of SF$_4$, is that the complex has no significant interaction with the base (see later).

The first evidence that (2.1.1) possesses fluxionality is the broadening of the two high frequency -S-F resonances (those of FA and FA') and sharpening of the low frequency -S-F resonance (that of FE) to a
triplet. The broadening may result from either a rocking motion or rotation about the Ir-S bond. In either case this motion must not take these fluorines through a plane of symmetry of the complex, at a significant rate on the n.m.r. timescale. Otherwise F_A and F_A', would become chemically equivalent. These fluorines remain chemically distinct up to 293K, as they retain separate chemical shifts.

The triplet structure in the low frequency -S-F resonance arises from equal coupling between the fluorine, F_E, bound equatorially to sulphur and the axially bound -S-F's. The retention of these couplings implies that the -SF_3 group remains intact. Also, as J(F_EF_C) is resolved at 270K, the entire framework of the complex remains intact at that temperature with no significant intermolecular fluorine exchange on the n.m.r. timescale.

At 293K, the exchange process which causes F_A and F_A' to become chemically equivalent is occurring at a significant rate on the n.m.r. timescale. However, the loss of resolution of J(F_EF_A) and J(F_EF_A') would not result from either a rocking motion or rotation about the Ir-S bond, irrespective of the rate of that process. This requires an additional mechanism.

One possible way of exchanging equatorial and axial sites in a trigonal bipyramid is via the Berry-pseudorotation[34] (see chapter 1). The initiation of such a mechanism would have the effect of broadening
the resonance of \( F_E \).

Another possibility is the introduction of significant intermolecular fluorine exchange, involving any of the fluorines bound to sulphur in (2.1.1). However, at 306K, couplings between \( F_C \) and the phosphorus nuclei to \( F_A, F_A', \) and \( F_E \) are retained. This effectively precludes such a mechanism occurring at 293K.

One further aspect of this combination of exchange processes, is that the phosphines become chemically equivalent. The first-order nature of the \( ^{31}P(^1H) \) n.m.r. spectrum at 306K, a resolved doublet of pseudo-quartets, confirms that no significant intermolecular exchange mechanism is occurring. The rate of the pseudo-rotation process must necessarily be slow, because \( F_A \) and \( F_A' \) remain chemically distinct from \( F_E \).

At 341K, all \(^3J(FP's)\) and \(^3J(FF's)\) are lost. This indicates that intermolecular fluorine exchange involving \( F_A, F_A', \) and \( F_E \) has become increasingly important as the solution is warmed. The retention of \(^2J(F_CP)\) at 341K implies that none of these exchange mechanisms significantly involves \( F_C \).

Conclusions on Fluorine Exchange Relating to (2.1.1)

1. The iridium complex (2.1.1) is fluxional at sulphur with both intra- and intermolecular fluorine exchange processes taking place. The process which is most energetically favoured is believed to be a rocking motion
or rotation about the Ir-S bond. This has the effect of rendering $F_A$ and $F_A'$ chemically equivalent and is illustrated in the spectra by broadening of the resonances of these fluorines. As the rate of this motion increases, they coalesce at 293K. This process also has the effect of equalizing the values of $^2J(F_AF_E)$ and $^2J(F_A'F_E)$ and this is illustrated by the signal of $F_E$ becoming a triplet. However, below the coalescence temperature this triplet begins to broaden. This is thought to result from the initiation of a Berry-pseudorotation at sulphur. Such a mechanism would render all three S-F’s equivalent.

By the coalescence temperature of all three fluorines on sulphur, 341K, intermolecular exchange has become important as the $^3JFF$’s are no longer resolved.

2. The susceptibility of (2.1.1) to fluorine exchange is influenced by HF. It is possible that the effect of HF on both SF$_4$ and (2.1.1) is similar. It is clear that the presence of HF increases the tendency of the -S-F’s of (2.1.1) to undergo intermolecular fluorine exchange. However, the experiments involving SF$_4$ have only shown that coalescence of the peaks of the axially and equatorially bound fluorines occurs at lower temperature when HF is present.

The rate of exchange may be fast, but the equilibrium constant, $K_E$, of the above process must be small. There
is no $-S-F$ resonance in the $^{19}\text{F}$ n.m.r. spectrum to indicate the presence of an Ir-$\text{SF}_2^+$ species (see later).

3. Another aspect of the interaction between HF and (2.1.1), not previously discussed, is the apparent lowering of the energy barrier to rotation of the $-\text{SF}_3$ group. The coalescence temperature of $F_A$ and $F_{A'}$ is reduced in solutions containing HF. Perhaps the proposed exchange mechanism between HF and the fluorines bound to sulphur in (2.1.1) reduces the steric interaction between $F_A$, $F_{A'}$ and the neighbouring phosphine ligands, as the geometry at sulphur varies between a pseudo-trigonal bipyramid and a distorted pyramid.

4. The Ir-F in (2.1.1) is not subject to fluorine exchange up to 341K, either in the presence or absence of HF. This is in spite of the labilizing effect of the trans carbonyl ligand. The most likely explanation is that formation of a 5-coordinate iridium complex, which would result from dissociation of this fluorine (assuming the mechanism to be dissociative) is too energetically unfavourable.

5. The fluorine exchange relating to (2.1.1) is not affected by the nature of the solvent. The coalescence temperature of $F_A$ and $F_{A'}$ is the same in $d_2$-dichloromethane and $d$-trichloromethane. Similarly, the coalescence temperature of $F(A,A')$ and $F_E$ is the same in $d$-trichloromethane and $d_3$-cyanomethane. This contrasts
with literature reports[56] which claim that there is a solvent dependence on the exchange processes involving SF₄. However, subsequent papers[57][58] contradict some of the details of these reports and the conclusions about solvent dependence may be mistaken.

6. The exchange mechanisms described above do not appear to be affected by the presence of SF₄ or SOF₂. In the case of SOF₂, this is not unexpected because this species does not undergo exchange with SF₄ in solution up to 341K. For SF₄ the position is not so straightforward. This species would not be expected to affect rotation about the Ir-S bond or a pseudo-rotation mechanism at sulphur in the complex. However, the nature of the species involved in an intermolecular exchange mechanism are more difficult to determine. At 341K the sole peak denoting the fluorines of unreacted SF₄ is broad. The resonance of the -S-F's of the complex is also broad and in the same region of the spectrum. It is possible that, with both present together, one peak could be lost underneath the other even although there is no significant interaction between the two species. On the other hand SF₄ may exchange fluorines with the complex by a mechanism which does not affect the coalescence temperature of the -S-F's of the complex.
2.4 Calculation of the Activation Energy for the Processes Relating to Fluorine Exchange in (2.1.1)

The activation energy parameters, $\Delta G_{C1}^\dagger$ and $\Delta G_{C2}^\dagger$, have been calculated for the processes involving coalescence of:

1. the axial $\text{-S-F's (} \Delta G_{C1}^\dagger \text{)}$
2. the equatorial and axial $\text{ -S-F's (} \Delta G_{C2}^\dagger \text{)}$

$\Delta G_{C}^\dagger$ is the kinetic activation energy and is defined for this specific complex as the minimum energy the species must possess in order to overcome the thermal energy barrier to the process(es) equilibrating the magnetic moments of the fluorine atoms. An equation[75] defining the activation energy using the data from solution n.m.r. experiments is known and is of the form:

Eqn. 2.3

$$\Delta G_{C}^\dagger = A \times T_C [B + \log_{10}(\frac{T_C}{\Delta \nu})]$$

$A$, $B$ are constant ($A = 1.914 \times 10^{-2}$ when $\Delta G$ is in kJmol$^{-1}$)

$B = 9.972$

$T_C$ is the coalescence temperature (in K) as obtained directly from the n.m.r. experiments

$\Delta \nu$ is the difference (in Hz) between the peaks when the coalescence process of interest is not occurring to any significant degree.
1. Equation 2.3 was used to calculate the activation energy parameter, $\Delta G^\dagger_{C1}$, for the process rendering the two axial -S-F's equivalent. This is believed to involve simple rotation or a rocking motion about the Ir-S bond. The coalescence temperature was found to be 293K.

$$
\Delta G^\dagger_{C1} = 1.914 \times 10^{-2} \times 293 \left[ 9.972 + \log_{10}(293/2131) \right] \\
= 5.61 \times [9.11] \\
= 51.0 \pm 0.5 \text{kJmol}^{-1}
$$

2. Similarly, the activation energy parameter, $\Delta G^\dagger_{C2}$, has been evaluated for the processes rendering the equatorial and axial -S-F's equivalent. These are believed to be a combination of a Berry-pseudorotation and fluorine exchange via an intermolecular mechanism, the exact nature of which has not been fully established. The coalescence temperature, $T_C$, is 341K.

$$
\Delta G^\dagger_{C2} = 1.914 \times 10^{-2} \times 341 \left[ 9.972 + \log_{10}(341/9572) \right] \\
= 6.53 \times [8.52] \\
= 55.5 \pm 0.5 \text{kJmol}^{-1}
$$
The values of $\Delta G_{C1}^\dagger$ and $\Delta G_{C2}^\dagger$ do not mean very much on their own in the absence of any comparable data from related species. In order to make some sense out of them the analogous bromo- and iodo- complexes to (2.1.1) were prepared and studied in a similar manner.

2.5 Other Halo-Complexes Containing an $\text{-SF}_3$ ligand

In order to understand some of the factors which influence the fluxional behaviour of the $\text{-SF}_3$ group, there have been attempts to prepare other complexes containing this ligand. Complexes in which the phosphines have been changed are discussed in chapter 4.

This section discusses the species in which the chloride (in 2.1.1) is replaced by another halide (Br or I) or a pseudohalide (NCO or NCS). The case of the bromo-complex will now be considered. The formation of the desired product was attempted by reacting SF₄ with an equimolar amount of $t$-IrBr(CO)[P(CH₂CH₃)₃]₂ (2.3.0) in $d_{2}$-dichloromethane. The yellow solution turned colourless suggesting that a reaction had taken place.

Results

The $^{19}\text{F}$(¹H) n.m.r. spectrum of the solution at 178K contains a set of four resonances, similar to those of (2.1.1). However, there is a slight shift to low frequency in the chemical shift of the Ir-F [$\delta$F= -344.2
p.p.m., cf -336.5 p.p.m. in (2.1.1)].

The chemical shifts of the -S-F's are virtually the same in both of these halide complexes. A smaller shift in these peaks, relative to the Ir-F, would be expected because these fluorines are one bond further away from the halide and so are less sensitive to change of halogen.

Conclusions

When (2.3.0) is treated with SF$_4$ a reaction analogous to the one between the sulphur reagent and (2.0.1) takes place. This is illustrated in eqn. 2.4:

Eqn. 2.4

\[
\begin{align*}
\text{PEt}_3 & \quad \text{PEt}_3 \\
\text{OC} & \quad \text{Ir} \quad \text{Br} \\
\text{Br} & \quad \text{Ir} \quad \text{S} \\
\text{OC} & \quad \text{F}_\text{C} \quad \text{F}_\text{A}
\end{align*}
\]

In the absence of isomers, the structure of (2.3.1) is assumed to be similar to that of (2.1.1), but with the bromide trans to the -SF$_3$ group, as illustrated in (2.3.1). The shift to low frequency in the $\delta$-value of F$_C$ may arise from more effective shielding of the fluoride by the iridium, which should have a greater electron density in the bromo-complex, relative to (2.1.1), due to the reduced electronegativity of the bromide.

The fluxionality of this complex has been studied in the presence of CsF. The spectra change in a similar
manner to those of (2.1.1). However, averaging of $^{2}J(FAFE)$ does not occur until 247 K. This indicates that motion about the Ir-S bond requires more energy than for the same process in (2.1.1). This is borne out by the coalescence temperature of the axial -S-F resonances, which is 307±2 K.

The activation energy of this process has been calculated. Using the coalescence temperature obtained from the n.m.r. data:

$$\Delta G_C^\dagger = 1.914 \times 10^{-2} \times 307 \left[9.972 + \log_{10}(307/2220)\right]$$

$$= 5.88 \times 9.11$$

$$= 53.6 \pm 0.5 \text{ kJmol}^{-1}$$

This is 2.5 kJmol$^{-1}$ higher than for the same process in (2.1.1). This slight increase in energy barrier is thought to arise from the greater $\pi$-donating ability of bromide, relative to chloride, into an Ir-S $\pi$-bonding orbital, thus making rotation less facile. However, the greater steric bulk of bromide, with respect to chloride may also be significant. The halide is thought to be trans to the -SF$_3$ group in both cases and direct steric interaction with the -SF$_3$ ligand is not deemed likely. However, the bulkier bromide may cause distortion of the other ligands at iridium, particularly the phosphines,
which may have a direct bearing on the fluxionality of the -SF₃ group.

The Formation of the Iodo-complex Analogous to (2.1.1) and (2.3.1)

This complex (2.3.2) has been prepared from t-IrI(CO)[P(CH₂CH₃)₃]₂ and SF₄ in d₂-dichloromethane. The ¹⁹F(¹H) n.m.r. spectrum of the complex at 180K again consists of four resonances. The three peaks in the spectrum denoting the -S-F's are marginally shifted to lower frequency in relation to the other complexes (2.1.1) and (2.3.1), already discussed. The Ir-F resonance is also shifted to low frequency [δF = -356.5 p.p.m., cf -336.5 p.p.m. in (2.1.1) and -344.2 p.p.m. in (2.3.1)]. This is in keeping with the iodide ligand being less electronegative than either chloride or bromide. The averaging of ²J(FₐFₑ) occurs at 252±2K and coalescence of the peaks denoting the axial -S-F's is seen at 317 ± 2K.

The activation energy of this process has been calculated as before. It is found to be 55.2 ± 0.5 kJmol⁻¹. This is 1.7 kJmol⁻¹ higher than for the corresponding process in (2.3.1). Once again, this is believed to result from greater π-donation from the halide into an Ir-S π-bonding orbital.

In conclusion, the data for the three analogous complexes (2.1.1), (2.3.1) and (2.3.2) are listed in tables 2.1 and 2.3.
Table 2.1

\(^{19}\)F n.m.r. data of (2.1.1), (2.3.1) and (2.3.2) in d\(_2\)-dichloromethane at 178K.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\delta)-S-F's/p.p.m.</th>
<th>(\delta)Ir-F/p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.1.1)</td>
<td>+74.7 +45.9 -66.5</td>
<td>-336.4</td>
</tr>
<tr>
<td>(2.3.1)</td>
<td>+74.0 +44.6 -66.2</td>
<td>-344.2</td>
</tr>
<tr>
<td>(2.3.2)</td>
<td>+72.1 +41.2 -67.7</td>
<td>-356.5</td>
</tr>
</tbody>
</table>

Table 2.2

Coalescence and \(\Delta G^\ddagger\) Data for (2.1.1), (2.3.1) and (2.3.2).

<table>
<thead>
<tr>
<th>Complex</th>
<th>(2J(F_{A,A'}= F_E)/K)</th>
<th>(\delta F_{A''} = \delta F/\varepsilon K)</th>
<th>(\Delta G^\ddagger/kJmol^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.1.1)</td>
<td>232</td>
<td>293</td>
<td>51.1</td>
</tr>
<tr>
<td>(2.3.1)</td>
<td>247</td>
<td>307</td>
<td>53.6</td>
</tr>
<tr>
<td>(2.3.2)</td>
<td>252</td>
<td>317</td>
<td>55.2</td>
</tr>
</tbody>
</table>

Note: \(F_{A''}\) denotes the coalesced form of \(F_A\) and \(F_{A'}\).

2.6 Conclusions on the data for (2.1.1), (2.3.1) and (2.3.2).

The data in tables 2.1 and 2.2 illustrate that the fluxionality at the \(-SF_3\) group, in the above series of
complexes, is affected by the ligand trans to sulphur. There is a correlation between \( \tau \)-donating properties of the halogen and the coalescence temperature of the axial \(-S-F\) peaks.

The activation energy, \( \Delta G_C^\ddagger \), of the process giving rise to this \( T_C \), increases with greater \( \tau \)-donating ability of the halide. This is consistent with the halide donating \( \tau \)-electron density into an \( \text{Ir-S} \) \( \tau \)-bonding orbital, with motion becoming less facile as the electron density in this orbital increases. However, it is likely that this is an oversimplification and is only one factor in explaining the above trend. As the steric bulk of the halogen increases from chloride to iodide, crowding at the iridium centre also increases. This could imply that steric factors are also become more important with increasing size of halogen. Chloride is known to be trans to the \(-SF_3\) group, and the n.m.r. data are consistent with bromide and iodide also being trans to sulphur (isomers in which carbonyl is trans to the \(-SF_3\) group are discussed in the next section). On this basis a direct steric involvement between halogen and the \( SF_3 \) group is not likely. However, larger halogens may affect the alignment of the phosphine ligands in such a way as to increase the steric interaction between these ligands and the \(-SF_3\) group.

The contribution of \( \sigma \)-electrons to motion around the \( \text{Ir-S} \) bond is not known.
The shift of the Ir-F resonance to low frequency with decreasing electronegativity of the cis halide is almost certainly not due to this factor alone. This is borne out by the chemical shift of F_C (δ = -337.2 p.p.m.) in the analogous complex with -NCO cis to fluoride (see next section).

There is insufficient knowledge of the bonding in this type of complex to determine all the relevant factors which establish the chemical shift of F_C.

The differences in the ^19F(^1H) n.m.r. spectra of (2.1.1), (2.3.1) and (2.3.2) at a common temperature can be profound, but the change in energy covering the calculated values of ΔG_C†, in relation to the exchange processes, is very small.

The analogous fluoro-analogue of (2.1.1) can not be prepared by the same route, because the starting complex t-IrF(CO)[P(CH₂CH₃)₃]₂ is unobtainable. However, the desired product is formed as one of several Ir-SF₃ complexes produced by the reaction of SF₄ and t-Ir(NCS)(CO)[P(CH₂CH₃)₃]₂. This is discussed in a later section.

2.7 Reaction of t-Ir(NCO)(CO)[P(CH₂CH₃)₃]₂ with SF₄

The Ir-SF₃ complexes studied so far all contain τ-donor halide ligands trans to the -SF₃ group. A study of the fluxional behaviour of a related species with a
τ-acceptor ligand trans to the -SF₃ group would provide a useful comparison.

In an attempt to synthesize one such complex, t-Ir(NCO)(CO)[P(CH₂CH₃)₃]₂ (2.4.0) has been prepared and treated with SF₄ in d₂-dichloromethane. The yellow solution turned colourless by 178K, suggesting that a reaction had taken place.

Results

In order to discount the possibility that chloride is present in either (2.4.1) or (2.4.2) a sample of the IrI-NCO complex was submitted for chlorine analysis and a value of 0% Cl was obtained. In addition, a sample of this chlorine-free complex was reacted with SF₄ in d₈-toluene. The ¹⁹F n.m.r. parameters of the isomeric products at 178K are similar to those in d₂-dichloromethane. This implies that chloride is not present in either species.

The ¹⁹F(¹H) n.m.r. spectrum of the solution at 178K (see diagram 2.5) comprises two sets of resonances, each of which consists of four multiplets and is similar in appearance to those of other Ir-SF₃ complexes. One set is approximately ten times as intense as the other. The chemical shifts of the peaks of the major (2.4.1) and minor (2.4.2) products are listed in tables 2.3 and 2.4.
Diagram 2.5

$^{19}$F n.m.r. spectrum of the products of reaction of (2,4,0) and SF$_4$ at 178K.
Diagram 2.5 exp1

Expansion of high frequency region

at 150K
Diagram 2.5 exp2

Expansion of mid frequency region

δ/p.p.m.
Diagram 2. 5 exp3
Expansion of low frequency region

$F_c$

$(2\cdot4\cdot2)$
Table 2.3

19F n.m.r. data of (2.4.1) in d₂-dichloromethane at 178K

<table>
<thead>
<tr>
<th>Fₓ</th>
<th>δ/p.p.m.</th>
<th>Couplings/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fₐ</td>
<td>+ 78.4</td>
<td>²J(Fₐ') = 181 ²J(Fₑ) = 66</td>
</tr>
<tr>
<td>Fₐ'</td>
<td>+ 57.2</td>
<td>²J(Fₐ) = 181 ²J(Fₑ) = 66</td>
</tr>
<tr>
<td>Fₑ</td>
<td>- 63.2</td>
<td>²J(Fₐ) = 66 ²J(Fₐ') = 66</td>
</tr>
<tr>
<td>Fₖ</td>
<td>-385.4</td>
<td>²J(P,P') = 25</td>
</tr>
</tbody>
</table>

Table 2.4

19F n.m.r. data of (2.4.2) in d₂-dichloromethane at 178K

<table>
<thead>
<tr>
<th>Fₓ</th>
<th>δ/p.p.m.</th>
<th>Couplings/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fₐ</td>
<td>+ 69.7</td>
<td>²J(Fₐ') = 170 ²J(Fₑ) = 66</td>
</tr>
<tr>
<td>Fₐ'</td>
<td>+ 43.0</td>
<td>²J(Fₐ) = 170 ²J(Fₑ) = 90</td>
</tr>
<tr>
<td>Fₑ</td>
<td>- 72.7</td>
<td>²J(Fₐ') = 90 ²J(Fₐ) = 66</td>
</tr>
<tr>
<td>Fₖ</td>
<td>-337.2</td>
<td>²J(P,P') = 29</td>
</tr>
</tbody>
</table>

Note: In the resonance denoting Fₑ in (2.4.2) there are resolved couplings between this fluorine and the two phosphines [³J(Fₚ,p')= 4Hz]. Also, in the signals denoting Fₐ' and Fₖ there is a mutual coupling of 10Hz.
Conclusions

On the basis of the n.m.r. data it is concluded that the Ir\(^{1}\)-NCO complex reacts with SF\(_4\) to produce a pair of isomers. The major product is believed to have the carbonyl trans to the \(-\text{SF}_3\) group and in the minor isomer (thought to be the other product of cis addition) \(-\text{NCO}\) is assigned trans to the \(-\text{SF}_3\) ligand. The equation for the reaction and proposed structures of the isomeric products are shown below:

Eqn. 2.5

\[
\begin{align*}
\text{PEt}_3 & \quad \text{PEt}_3 \quad \text{PEt}_3 \\
\uparrow & \quad \uparrow & \quad \uparrow \\
\text{OC} \quad \text{Ir} \quad \text{NCO} & + \text{SF}_4 & \quad \text{OC} \quad \text{Ir} \quad \text{S}^\text{\textdagger} & + \text{OCN} \quad \text{Ir} \quad \text{S}^\text{\textdagger} \\
\downarrow & \quad \downarrow & \quad \downarrow \\
\text{PEt}_3 & \quad \text{PEt}_3 \quad \text{PEt}_3 \\
\end{align*}
\]

Further Structural Information on (2.4.1) and (2.4.2)

In order to obtain further structural information on (2.4.1) and (2.4.2) the experiment was repeated using SF\(_4\) and \(t\)-Ir(NCO)(\(^{13}\text{CO})[\text{P(\text{CH}_2\text{CH}_3)}_3]\) in \(\text{d}_2\)-dichloromethane.

The signals in the \(^{19}\text{F}(\text{H})\) n.m.r. spectrum assigned to the fluorines of the \(-\text{SF}_3\) groups remain unchanged at 178K. However, there is an extra doublet splitting in each of the Ir-F peaks (see diagram 2.5(a)), due to coupling to the \(^{13}\text{C}\) of the carbonyl ligand. In the major isomer \(2J(\text{FC})= 6\text{Hz}\). The corresponding value of \(2J(\text{FC})\) in the minor isomer is 76Hz. From the magnitudes of these couplings it is deduced that the carbonyl ligand is trans
Diagram 2.5a
Expansion of $F_C$ in each of (2.4.1) and (2.4.2) with $^{13}C$ at C0
to the -SF\textsubscript{3} ligand in the major isomer and \textit{trans} to the fluoride in the minor one (as illustrated at (2.4.1) and (2.4.2)).

2.8 An Investigation into the Susceptibility of (2.4.1) to Fluorine Exchange

The reaction between the \textit{Ir}-NCO complex and SF\textsubscript{4} was repeated in the presence of CsF to enable a study of the fluxional behaviour of (2.4.1) and (2.4.2) in the absence of unbound HF. A mixed solvent system comprising 1:1 \textit{d}_2-dichloromethane/diethylether (by volume) was used to enable a study below 178K.

In this mixed solvent medium the ratio of major:minor isomer increases to around 100:1. This effectively precludes a study of the fluorine exchange processes occurring in the minor isomer.

In the major isomer at 150K the two high frequency signals which denote \textit{F}_\text{A} and \textit{F}_\text{A}', at \delta+78.4 \text{ p.p.m.} and \delta+57.2 \text{ p.p.m.} are broad doublets of doublets. The resolved couplings are $2J(F_A F_E)$, $2J(F_A' F_E)$ and $2J(F_A F_A')$.

The signal which denotes \textit{F}_E is a broad triplet at this temperature, due to couplings to \textit{F}_\text{A} and \textit{F}_\text{A}', which are equal to within ca. 2Hz. The resonance assigned to \textit{F}_C is broad and without fine structure.

As the sample is warmed (see diagrams 2.5(b to e)) the two high frequency resonances broaden and the couplings are no longer resolved by 178K. The low
Diagram 2.5b

$^{19}F$ n.m.r. spectrum of (2.4.1) at

190K
Diagram 2.5c

$^{19}F$ n.m.r. spectrum of (2.4.1) at 230 K
Diagram 2.5d

$^{19}$F n.m.r. spectrum of (2.4.1) at 300K
frequency -S-F resonance retains its couplings at this temperature. The resonance which denotes FC contains a triplet for $^2J(FCP)$ at 178K.

Further warming of the solution results in coalescence of the peaks denoting $F_A$ and $F_A'$ at 190±2K. At this temperature the equatorial -S-F resonance is a sharp triplet, $[^2J(F_{EF_A,A'})= 68\text{Hz}]$, of narrower doublets, $[^3J(F_{EF_C})= 8\text{Hz}]$, as coupling to the Ir-F is resolved.

The resonance of FC is a triplet, $[^2J(FCP)= 29\text{Hz}]$, of near quartets, $[^3J(FC_{FA,A',E})= 8\text{Hz}]$. Coupling between this fluorine and the phosphines is retained. In addition, couplings to all three fluorines of the -SF$_3$ group are resolved. These are equal to within ca. 1Hz.

Further warming of the system results in sharpening of the coalesced -S-F resonance up to 223K, although no fine structure is resolved. Above this temperature both -S-F peaks broaden and the one to low frequency loses its structure. The $^3J(FF)$'s in the signal denoting FC decrease and at 280K they are no longer resolved. Only the triplet coupling to the phosphorus nuclei is retained. The -S-F resonances continue to broaden and coalesce at 301±2K.

The $^{31}\text{P}(^1\text{H})$ n.m.r. spectrum of the complex is a poorly resolved AB pattern at 150K which broadens to a single structureless peak at 178K. At 248±2K the pattern becomes first-order and is a resolved doublet $[^2J(PFC)= 29\text{Hz}]$ of near-quartets $[^3J(P_{FA,A',E})= 11\text{Hz}]$ (see diagram
Diagram 2.6

$^{31}P(^1H)$ n.m.r. spectrum of (2.4.1)

at 248K
2.6). The doublet arises from coupling to $F_C$ and the quartet from couplings to $F_A$, $F_{A'}$, and $F_C$, which are equal to within ca. 1Hz. At 301K, the signal is a broad doublet which sharpens on further warming.

All of these spectroscopic changes are reproducible and there is no significant variation in the coalescence temperatures when a 1:1 mixture of diethylether/$d_8$-toluene is used. They are also reversible as the samples are recooled to 150K.

A Discussion of Fluorine Exchange in Relation to (2.4.1)

The mechanisms of fluorine exchange affecting (2.4.1) are believed to be the same as those involved in (2.1.1) and the other Ir-SF$_3$ complexes described in this chapter. However, in this case the various processes are better spread out and the process requiring the least energy may be discussed without the problem of any overlap with the others.

At 190K, the only significant exchange is the mechanism which renders $F_A$ and $F_{A'}$ equivalent. This process must be simple motion about the Ir-S bond. On the n.m.r. timescale this is slow at 159K and fast at 190K. The $-SF_3$ group is intact at this temperature, because $^2J(F_A,F_E)$ and $^2J(F_{A'},F_E)$ are retained. Also, the geometry at sulphur is not thought to be significantly distorted by this exchange, because the signal denoting $F_E$ is sharp at 190K.
At 248K, this signal is broad suggesting that FE has become involved in exchange. This must also be intramolecular because the $^{31}$P($^1$H) n.m.r. spectrum at this temperature shows that $^3J$(FE$^1$P) is retained. A likely mechanism is the Berry-pseudorotation discussed earlier.

At 280K, intermolecular exchange is important, because coupling between FC and the other fluorines is lost. Similarly coupling between the phosphines and fluorines bound to sulphur is lost. However $^2J$(FC$^1$P) is retained and this illustrates that FC is stable to the exchange processes at 280K.

Calculation of the Activation Energy Parameters, $\Delta G_C^{\dagger}$ for the Exchange Processes in (2.4.1)

The activation energy parameters, $\Delta G_{C_1}^{\dagger}$ and $\Delta G_{C_2}^{\dagger}$, relating to the coalescence temperatures of FA and FA', and FA'' and FE (where FA'' represents the coalesced form of FA and FA') in (2.4.1) have been calculated by the same method as before (see eqn. 2.3). $\Delta G_{C_1}^{\dagger}$ is evaluated for the process which renders FA and FA' chemically equivalent and $\Delta G_{C_2}^{\dagger}$ is calculated for the combined processes which render FA'' and FE equivalent.
\[ \Delta G_{C_1}^\dagger = 1.914 \times 10^{-2} \times 190 \left[ 9.972 + \log_{10}(190/1539) \right] \]

\[ = 3.6366 \times 9.064 \]

\[ = 33.0 \pm 0.5 \text{ kJmol}^{-1} \]

\[ \Delta G_{C_2}^\dagger = 1.914 \times 10^{-2} \times 301 \left[ 9.972 + \log_{10}(301/9904) \right] \]

\[ = 5.761 \times 8.46 \]

\[ = 48.7 \pm 0.5 \text{ kJmol}^{-1} \]

A direct comparison of these \( \Delta G_C^\dagger \) values with those evaluated earlier is meaningless, because the degree of overlap of the various mechanisms is different. However, it is interesting to note that the \( T_C1 \) is much lower when the \(-SF_3\) group is trans to the \( \pi\)-accepting carbonyl ligand as opposed to \( \pi\)-donating halides.
2.9 The Reaction Between $\text{SF}_4$ and $t$-$\text{Ir(NCS)(CO)[P(CH}_2\text{CH}_3)_3]\_2$

The electronic properties of the -NCS ligand are similar to those of -NCO. Hence, the reaction between $\text{SF}_4$ and $t$-$\text{Ir(NCS)(CO)[P(CH}_2\text{CH}_3)_3]\_2$ (2.9.0) has been investigated under the same experimental conditions as for the analogous IrI-NCO reaction.

Results

I.R. studies of the IrI-NCS starting complex indicate that the -NCS ligand is N-bonded to iridium[76], although it has the potential to S-bond to transition metals.

The $^{19}\text{F}^{(1}\text{H})$ n.m.r spectrum of the reaction mixture, at 150K (see diagram 2.7), in a 1:1 $d_2$-dichloromethane/diethylether mixture contains many resonances in each of the three regions appropriate to the fluorine environments of Ir-SF$_3$ complexes. Namely, these are:

1. The high frequency region ($\delta$+90 p.p.m. to $\delta$+30 p.p.m.). This contains the peaks of the fluorines (F$_A$ and F$_{A'}$) which are bound axially to sulphur in an -SF$_3$ group (see diagram 2.7(a)).

2. The mid frequency region ($\delta$-60 p.p.m. to $\delta$-80 p.p.m.). The signals assigned to the fluorines (F$_E$) bound...
Diagram 2. 7

$^{19}$F n.m.r. spectrum of the reaction between (2.9.0) and SF$_4$ at 150K
Diagram 2.7a
Expansion of high frequency region
at 150K
Diagram 2.7b

Expansion of mid frequency region
at 150K
Diagram 2.7c

Stick diagram of mid frequency region at 150K.

\[ \alpha, \beta \text{ are doublet of doublets} \]

\[ F_e (2.9.2 \text{ and } 2.9.4) \text{ are triplets} \]
Diagram 2.7d

Expansion of low frequency region

at 150K
equatorially to sulphur, in an -SF₃ group, are located in this part of the spectrum (see diagrams 2.7(b) and (c)).

3. The low frequency region (δ-290 p.p.m. to δ-400 p.p.m.). The resonances of any fluorines (F₀ or F₁) directly bound to iridium are in this region of the spectrum (see diagram 2.7(d)).

Before attempting assignment of the data to specific complexes, the possible presence of chloride (from either the solvent or an incomplete metathesis having taken place during the formation of the Ir¹⁻NCS complex) was investigated.

A sample of the Ir¹⁻NCS complex, when analyzed for chlorine, produced a value of 0% Cl. This chlorine-free complex was then treated with SF₄ in d₈-toluene. The ¹⁹F(¹H) n.m.r. parameters of the reaction solution, at 178K, are similar to those in the 1:1 d₂-dichloromethane/diethylether mixture at this temperature. This suggests that chloride ligands take no part in the reaction.

Interpretation of the Data

Clearly, the presence of many signals in the ¹⁹F(¹H) n.m.r. spectrum at 150K indicates that this reaction is less straightforward than the others discussed in this chapter. Consequently, assignment of the data to specific
complexes is more difficult. It is facilitated, however, by establishing the number of -SF$_3$ containing products by a close examination of the mid frequency region. This indicates that there are four such species present.

The n.m.r data of the solution at 220K are now discussed, because below this temperature the spectral lines are poorly resolved and less informative.

Of the four (F$_E$) resonances in the mid frequency region, one is broad and structureless at 220K. The chemical shift of this peak is $\delta$=64.8 p.p.m. at 150K. Another, at $\delta$=66.4 p.p.m., contains a large triplet due to equal couplings to F$_A$ and F$_{A'}$. Each component of the triplet is split into a 6-line pattern due to couplings to several other spin 1/2 nuclei.

The two other resonances in this region, at $\delta$=73.0 p.p.m. and $\delta$=74.8 p.p.m., are doublets of doublets, because $^2J(F_EF_A)$ and $^2J(F_EF_{A'})$ are not equal. Of these two signals, the one at higher frequency contains no smaller couplings, whereas each component of the other one is split into pseudotriplets by almost identical couplings to two spin 1/2 nuclei.

From this data, it is apparent that two complexes (those in which $^2J(F_EF_A)$ and $^2J(F_EF_{A'})$ are non-equivalent) have fluorines bound axially to sulphur which are chemically distinct. In the two others these fluorines may be equivalent. In all previous cases where the resonance of F$_E$ is sharp and a well-resolved triplet, or
broadened by a mechanism of exchange, \( \text{F}_A \) and \( \text{F}_{A'} \) cannot be distinguished.

The high frequency region consists of four complex multiplets, the chemical shifts of which are:

\[ \delta +80.7 \text{ p.p.m.}, \delta +73.2 \text{ p.p.m.}, \delta +52.8 \text{ p.p.m.} \text{ and } \delta +43.6 \text{ p.p.m.} \]

A singlet at \( \delta +66.2 \text{ p.p.m.} \) indicates the presence of \( \text{SOF}_2 \) and all other resonances in this region form part of a broad, structureless peak centered at \( \delta +50 \text{ p.p.m.} \).

On the basis of the coupling constants and intensities of the signals, those at +80.7, +52.8 and -73.0 represent the fluorines of one of the \( -\text{SF}_3 \) groups (\( \alpha \)). In this species \( 2J(F_A'F_E) = 68\text{Hz}, 2J(F_A,F_E) = 85\text{Hz} \) and \( 2J(F_A,F_{A'}) = 175\text{Hz} \). In addition to these couplings, both of the resonances at higher frequency contain smaller couplings to two other spin 1/2 nuclei.

Another \( -\text{SF}_3 \) group (\( \beta \)) comprises the fluorines which resonate at \( (+73.2, +43.6 \text{ and } -74.8)\text{p.p.m.} \). In this ligand \( 2J(F_A'F_E) = 70\text{Hz}, 2J(F_A,F_E) = 87\text{Hz} \) and \( 2J(F_A,F_{A'}) = 177\text{Hz} \). The resonance at highest frequency contains an additional splitting to one other spin 1/2 nucleus and the one with the middle frequency has couplings to three other spin 1/2 nuclei.

The low frequency region contains four multiplets. Two of these, at \( (-315.1 \text{ and } -364.4)\text{p.p.m.} \) are assigned to the same complex by a mutual coupling \( 2J(F_C'F_C) = 140\text{Hz} \) in each resonance. Each signal is further split into a triplet of quartets. These arise from equal coupling to
two spin 1/2 nuclei (for the triplet) and three others (for the quartet).

Of the two other signals in this region, the one at -360.4 p.p.m. contains a doublet (7Hz) in addition to couplings to the phosphorus nuclei. The other one, at -393.3 p.p.m., contains couplings to two phosphines, but the lines are broad.

Assignment of the data

Much information is derived from the data at 220K. It is clear that, of the four peaks in the low frequency region, two belong to one complex. Hence, one Ir-SF$_3$ product has no Ir-F bonds. The resonances assigned to the -SF$_3$ group of this complex (2.9.1) are probably from (α). The two high frequency signals show additional couplings to the phosphines, but not to any Ir-F. Also, as $2J(^3F_{EA}) \times 2J(^3F_{EA'})$ this suggests that the -SF$_3$ group is not trans to the carbonyl ligand. The structure is therefore tentatively assigned as shown in fig. 2.3 with both the -SF$_3$ group and the carbonyl trans to an -NCS.

Fig. 2.3
The Proposed Structure of (2.9.1)
Diagram 2.7 exp1

Expansion of $F_A$ and $F_A'$ in (2.9.1)
at 220K
Diagram 2. $7^\text{exp}2$

Expansion of $F_E$ in (2.9.1) at 220K
Table 2.5

The $^{19}$F n.m.r. data of (2.9.1) at 220K

<table>
<thead>
<tr>
<th></th>
<th>$\delta$/p.p.m</th>
<th>Couplings/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>+80.7</td>
<td>$2J(F_A')=175$ $2J(F_E)=68$</td>
</tr>
<tr>
<td>$F_A'$</td>
<td>+52.8</td>
<td>$2J(F_A)=175$ $2J(F_E)=85$</td>
</tr>
<tr>
<td>$F_E$</td>
<td>-73.0</td>
<td>$2J(F_A')=85$ $2J(F_A)=68$</td>
</tr>
</tbody>
</table>

Note 1: The resonance of $F_A$ has a coupling of 10Hz to one phosphorus nucleus and 4Hz to the other. The signal of $F_A'$ couples equally (15Hz) to both phosphorus nuclei.

Note 2: In (2.9.1), and the other products of this reaction, all -NCS ligands are assigned as N-bonded to iridium (as in the Ir$^{1+}$-NCS starting complex). On steric grounds this is favoured. Also, as the electron density at the metal decreases, co-ordination of ligands via atoms with greater electronegativity is preferred.

The next assignment is for the complex with two Ir-F's. These belong to another -SF$_3$ complex (2.9.2), as each Ir-F resonance contains a "pseudoquartet" splitting from couplings to $F_A$, $F_A'$, and $F_E$, equal to within ca. 1Hz.

There are not two resonances in the high frequency region which have resolved couplings to $F_C$ and $F_C'$. Hence, the peaks of $F_A$ and $F_A'$ are broad and may have coalesced. In this case, $F_A$ and $F_A'$ couple equally to $F_E$. 

Therefore the resonance assigned to this latter fluorine is the peculiar triplet of multiplets at $\delta$-66.4 p.p.m., in which each component is a 6-lined pattern. This arises from equal couplings to the two identical phosphines and one of $F_C$ and $F_{C'}$ with coupling 1/2 this magnitude to the other Ir-F.

In (2.9.2), $F_C$ and $F_{C'}$ must be mutually cis otherwise they would be chemically equivalent at 220K. Therefore one, $F_{C'}$, is assigned trans to the -SF$_3$ group and the other, $F_C$, trans to the carbonyl ligand. This is illustrated in fig. 2.4.

Fig. 2.4
The Proposed Structure of (2.9.2)
Diagram 2.7 \text{exp3}

Expansion of $F_E$ in (2.9.2) at 220K
Diagram 2.7 exp4

Expansion of $F_C$ and $F_C'$ in (2.9.2) at 220K
<table>
<thead>
<tr>
<th></th>
<th>δ/p.p.m.</th>
<th>Couplings/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>n.r.</td>
<td>2J(F_E) = 71  3J(F_C') = 8  3J(F_C) = 4</td>
</tr>
<tr>
<td>FA'</td>
<td>n.r.</td>
<td>2J(F_E) = 71  3J(F_C') = 8  3J(F_C) = 4</td>
</tr>
<tr>
<td>F_E</td>
<td>-66.4</td>
<td>2J(F_A,F_A') = 71  3J(P) = 28  3J(F_C') = 4</td>
</tr>
<tr>
<td>F_C</td>
<td>-315.1</td>
<td>2J(F_C') = 140  2J(P) = 32  3J(F_A,F_A',E) = 4</td>
</tr>
<tr>
<td>F_C'</td>
<td>-364.4</td>
<td>2J(F_C) = 140  2J(P) = 28  3J(F_A,F_A',E) = 8</td>
</tr>
</tbody>
</table>

(n.r.= not resolved)

Assignment of the Ir-F at -360.4 p.p.m. is now possible on the basis of a resolved 3J(FF)= 9Hz coupling. This doublet is matched in the signal at +43.6 p.p.m., which is one of the fluorines belonging to (β).

As 2J(F_EF_A) ≠ 2J(F_EF_A') in this product (2.9.3), it is assumed that the -SF_3 group is not trans to a carbonyl ligand. Hence, the data is tentatively assigned to a complex in which the Ir-F is trans to the carbonyl and -NCS trans to the -SF_3 group (see fig. 2.5):
Fig. 2.5

The Proposed Structure of (2.9.3)

\[
\begin{align*}
\text{PEt}_3 & \quad | \quad FC \quad FA \\
\text{SCN} & \quad \text{Ir} \quad - \quad S & \quad \text{Ir} \quad - \quad S \\
\text{OC} & \quad \text{FA}' \quad \text{FE} \\
\text{PEt}_3 & 
\end{align*}
\]

Table 2.7

\[19^F\] n.m.r. data of (2.9.3) at 220K

<table>
<thead>
<tr>
<th>(F_X)</th>
<th>(\nu/\text{p.p.m.})</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_A)</td>
<td>+ 73.2</td>
<td>(2J(F_A') = 177) (2J(F_E) = 70)</td>
</tr>
<tr>
<td>(F_A')</td>
<td>+ 43.6</td>
<td>(2J(F_A) = 177) (2J(F_E) = 87) (3J(F_C) = 9)</td>
</tr>
<tr>
<td>(F_E)</td>
<td>- 74.8</td>
<td>(2J(F_A') = 87) (2J(F_A) = 70)</td>
</tr>
<tr>
<td>(F_C)</td>
<td>-360.4</td>
<td>(2J(P,P') = 24) (3J(F_A') = 9)</td>
</tr>
</tbody>
</table>

Note: the smaller couplings between \(F_A, F_A', \) and the phosphines have been omitted for clarity.

At this stage, it was not possible to assign the remaining \(-SF_3\) group and Ir-F to a specific complex (or complexes). In the absence of any resolved \(3J(FF)\) it was not clear if they belonged to the same complex. The chemical shift of \(F_C, -393.9\) p.p.m., suggests that this fluoride is not \textit{trans} to a carbonyl ligand. Similarly, the lack of structure on all of the \(-S-F\) resonances at 220K, suggests that motion about the Ir-S bond is facilitated relative to the other complexes. Hence, the
Diagram 2.7 exp5

Expansion of $F_A$ and $F_A'$ in (2.9.3)
at 220K
Diagram 27exp6

Expansion of $F_E$ in (2.9.3) at 220K
-SF$_3$ group may be trans to the $\pi$-accepting carbonyl ligand.

By 300K, the signal of F$_C$ has undertaken a remarkable transformation. Whereas at 220K it was a broad triplet, at 300K it has become a nicely resolved triplet of quartets. The magnitude of this quartet splitting, 11Hz, is similar to the other 3$\ J$(FF's) in this type of complex. Hence, the Ir-F and -SF$_3$ group are from the same species, with the fluorines at sulphur made equivalent by intramolecular exchange, which is fast on the n.m.r. timescale. It is not apparent why the 3$\ J$(FF's) are not resolved at 220K.

The proposed structure of this complex (2.9.4) is given in fig. 2.6.

Fig. 2.6

The Proposed Structure of (2.9.4)

```
PEt$_3$  
|   F$_C$  F$_A$
OC — Ir — S  /
SCN | F$_A'$ F$_E$
PEt$_3$
```

One remarkable, unexplained observation is that, whereas in (2.9.4) 3$\ J$(FF's) are retained at 300K, in the others, (2.9.1) and (2.9.3), these couplings are lost. In (2.9.4), however, the -S-F's become fluxional at the lowest temperature of all the products.
Diagram 2. 7 exp7

Expansion of $F_C$ in each of (2.9.3) and (2.9.4) at 220K and also of $F_C$ in (2.9.4) at 300K
The Reaction Between t-Ir(NCS)\(^{13}\text{CO})[\text{P(CH}_2\text{CH}_3)]_2\) and SF\(_4\)

In order to substantiate the proposed structures in the complexes (2.9.1), (2.9.2), (2.9.3) and (2.9.4), the reaction between t-Ir(NCS)\(^{13}\text{CO})[\text{P(CH}_2\text{CH}_3)]_2\) and an equimolar amount of SF\(_4\) was investigated in d\(_2\)-dichloromethane. This experiment should provide a value for \(^2J(F\text{C}C)\) in each of the complexes.

Results

From \(^{31}\text{P}(\text{H})\) n.m.r. data the degree of \(^{13}\text{C}\) enrichment in the Ir\(^I\)-starting complex is approximately 99%.

The \(^{19}\text{F}\) n.m.r. spectrum of the solution at 178K closely resembles that of the products of the analogous reaction in which the Ir\(^I\)-NCS complex is not \(^{13}\text{CO}\)-enriched. However, there are additional doublet splittings for \(^2J(F\text{C}C)\); these are 76Hz in the resonance of F\(_C\) in (2.9.2) and 74Hz in the corresponding signal of (2.9.3).

In the two other resonances assigned to Ir-F's (these correspond to F\(_C\) in (2.9.2) and F\(_C\) in (2.9.4)) there is slight broadening although no extra doublet splitting is resolved. Given the broadness of the spectral lines, this implies that \(^2J(F\text{C}C)\) in these cases is of the order of 2Hz. This data is consistent with complexes (2.9.1), (2.9.2), (2.9.3) and (2.9.4) having the structures proposed above. Indeed the additional splittings of \(^2J(F\text{C}C)\) confirm that each complex contains a carbonyl
Conclusions

$t$-Ir(NCS)(CO)[P(CH₂CH₃)₃]₂ reacts with SF₄ to produce four complexes which contain an -SF₃ ligand (2.9.1), (2.9.2), (2.9.3) and (2.9.4). The equation for this reaction is given below:

Eqn. 2.6

Note: Once all four products have formed, there is no interconversion between them as the solution is warmed to 300K, then recooled to 150K. This suggests that (2.9.1) and (2.9.2) are not formed from (2.9.3) and (2.9.4).

The reasons for the complex nature of this reaction are not fully understood. However, the initial interaction may be similar to the reaction of SF₄ with the Ir⁻⁻NCO complex. This would give complexes (2.9.3) and...
(2.9.4). The appearance of two products which are not isomers, (2.9.1) and (2.9.2), may be the result of attack by the sulphur end of -NCS of one complex at the metal centre of the Ir'-NCS starting complex via a concerted mechanism which also involves an -SF₄ molecule. The -SF₃ fragment binds to iridium with the fluoride replacing -NCS in the other complex. After this nucleophilic attack by sulphur there may be an intramolecular rearrangement to enable the thiocyanate ligand to N-bond to iridium.

2.10 Conclusions on the Reaction between t-IrX(CO)[P(CH₂CH₃)₃]₂ (X= Cl, Br, I) and SF₄.

The series of complexes t-IrX(CO)[P(CH₂CH₃)₃]₂ (X= Cl, Br, I, NCO, NCS) have been shown to react with SF₄ to give Ir-SF₃ products. In the cases of X= NCO and NCS there is more than one product. This may be due to the π-acceptor properties of these ligands or steric factors or a combination of each.

The ligand trans to the -SF₃ group affects motion about the Ir-S bond. This is made easier when π-acceptors occupy the trans position. This may result from a reduction in π-electron density at the Ir-S centre or in steric interaction between the axial fluorines of the -SF₃ group and the other ligands at iridium.

Although the appearance of the spectra as a function of the ligand trans to the sulphur group at a common
temperature may be profound, the actual difference in energy of the processes is only marginal.

The ligand trans to the Ir-F has a strong influence on the chemical shift of this fluoride. However, this is only a relative effect. The chemical shift of F\(_\text{C}\) in (2.1.1) is almost identical to the corresponding shift in (2.4.2). In both of these complexes, F\(_\text{C}\) is trans to a \(\pi\)-accepting carbonyl ligand. In the first it is cis to a \(\pi\)-donating chloride ligand whereas in the second it is cis to a \(\pi\)-accepting -NCO. However, in (2.3.1) and (2.9.2) it is cis to a bromide and fluoride respectively with all other factors the same and it shifts to lower frequency by 7 p.p.m. in (2.3.1) and by 22 p.p.m. to higher frequency in (2.9.2).
BF₃ reacts with SF₄ to give what is believed to be an infinite chain complex, consisting of boron and sulphur linked by fluorine bridges (see chapter 5). In view of this, it was thought likely that a similar reaction could be undertaken between BF₃ and an Ir-SF₃ complex.

To investigate this, a sample of the Ir-SF₃ complex (2.1.1) was treated with an equimolar amount of BF₃ in d₂-dichloromethane.

The results of the experiment form the basis of the work described in this chapter.

3.1 The Reaction of the Ir-SF₃ Complex (2.1.1) with BF₃

When a sample of (2.1.1) was allowed to react with an equimolar amount of BF₃ at 178K the colourless solution turned purple, indicating that a reaction had taken place. There was no sign of any solid material to suggest the formation of a polymeric product.

Results

In the ¹⁹F(¹H) n.m.r. spectrum of the solution at 178K (see diagram 3.1), the four resonances assigned to the fluorines of (2.1.1) are absent. This confirms that the complex has undergone a chemical transformation in the
Diagram 3.1

$^{19}$F n.m.r. spectrum of (3.1.1) at 178K

$F_A$

$F_B$

$F_C$
Expansions of $F_A$ and $F_C$ in (3.1.1).

Diagram 3. 1 exp

10 Hz
There are three new signals, the chemical shifts of which are: $\delta$-51.3 p.p.m., $\delta$-148.9 p.p.m. and $\delta$-361.9 p.p.m. In order of decreasing chemical shift the ratios of the intensities are 2:4:1. The signal to highest frequency, at $\delta$-51.3 p.p.m., is in the region of the spectrum associated with fluorine bound to a main group element, which, in this case is sulphur.

The peak at $\delta$-148.9 p.p.m. is broad. This $^{19}$F-chemical shift is associated with fluorines of a BF$_4$ group, as found in other complexes in which this anion is the only fluorine source, e.g. Ir(CO)$_3$[P(CH$_2$CH$_3$)$_3$]$^2^+[BF_4]^-[73]$.

The signal to lowest frequency, at $\delta$-361.9 p.p.m., is in the region associated with a fluoride which is bound to a transition metal i.e. iridium.

The $^{31}$P($^1$H) n.m.r. spectrum of the solution at 178K (see diagram 3.2) contains one first order resonance only. This confirms that the reaction product, in contrast to that of the Ir-SF$_3$ complex (2.1.1), contains only one phosphorus chemical environment, at this temperature.

Conclusions

When the Ir-SF$_3$ complex (2.1.1) is treated with an equimimolar amount of BF$_3$ in d$_2$-dichloromethane a reaction takes place at 178K. The $^{19}$F($^1$H) n.m.r. spectrum at this temperature reveals that the product of this reaction
Diagram 3.2

$^{31}P(1H)$ n.m.r. spectrum of (3.1.1) at 178K
contains only one type of -S-F environment. Also, there are twice as many fluorines bound to sulphur than are bound to iridium.

These observations, in conjunction with the presence of a peak to indicate the generation of [BF4]−, suggest that BF3 has removed a fluoride from the -SF3 group of (2.1.1) to produce a novel cationic iridium complex of the form Ir-SF2+[BF4]−. This is illustrated in eqn. 3.1 below:

Eqn. 3.1

\[
\begin{align*}
\text{PEt}_3 & \quad \text{PEt}_3 \\
\mid & \quad \mid \\
\text{Cl} & \quad \text{Ir} \quad -S^2 \quad \text{OC} \\
\mid & \quad \mid \\
\text{FA} & \quad \text{F} & \quad \text{FA'} \\
\text{PEt}_3 & \quad \text{PET}_3 \\
\end{align*}
\]

(2.1.1)  

\[
\begin{align*}
\text{PEt}_3 & \quad \text{PEt}_3 \\
\mid & \quad \mid \\
\text{Cl} & \quad \text{Ir} \quad -[S(F\text{A})_2]^+[B(F\text{B})_4]^− \\
\mid & \quad \mid \\
\text{OC} & \quad \text{PET}_3 \\
\end{align*}
\]

(3.1.1)

In (3.1.1): FA denotes the fluorines bound to sulphur

FB " " " " boron

FC " " fluorine " " iridium

Several coupling constants are resolved in both the 19F(1H) and 31P(1H) n.m.r. spectra of (3.1.1); thus confirming that FA, FC and the phosphines are from the same complex.

The fluorine signal at δ-51.3 p.p.m. is a resolved triplet \( ^2J(F\text{A}P)= 16\text{Hz} \), of doublets \( ^3J(F\text{A}P)= 13\text{Hz} \). It is assigned to two equivalent -S-F nuclei of an -SF2+
group in which the geometry at sulphur is based on a pyramid. These fluorines are equivalent. Hence, they lie equidistant from the plane incorporating the Ir-P and Ir-S bonds, or there is a facile rotation or a rocking motion about the Ir-S bond. The splittings arise from coupling to the equivalent pair of phosphorus nuclei, P, and to F_C.

The signal denoting F_C in the 19F(1H) n.m.r. spectrum is an overlapping triplet \([2J(F_CP)=31\text{Hz}],\) of triplets, \([3J(F_CFA)\text{ as above}].\) This results from coupling between F_C and the P's and F_A.

The 31P(1H) n.m.r. spectrum is an overlapping doublet of triplets which reflects \(2J(PFC)\) and \(2J(PFA),\) as illustrated above.

The n.m.r. data of (3.1.1) are listed in table 3.1.

Table 3.1

19F(1H) n.m.r. and 31P(1H) n.m.r. data of (3.1.1), at 178K

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>(\delta/\text{p.p.m.})</th>
<th>Couplings/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>F_A</td>
<td>-51.3</td>
<td>(3J_{FC}=13) (3J_{P}=16)</td>
</tr>
<tr>
<td>F_B</td>
<td>-148.9</td>
<td></td>
</tr>
<tr>
<td>F_C</td>
<td>-361.9</td>
<td>(3J_{FA}=13) (2J_{P}=31)</td>
</tr>
<tr>
<td>P</td>
<td>+9.9</td>
<td>(3J_{FA}=16) (2J_{FC}=31)</td>
</tr>
</tbody>
</table>
Confirmation of the Structure of (3.1.1)

The arrangement of the ligands at the iridium centre in (3.1.1) has been assumed to be the same as in (2.1.1), with simple transfer of fluoride from sulphur to boron. However, the labilizing effect of an $-\text{SF}_2^+$ group is not known and the possibility of rearrangement of the ligands could not be discounted.

In order to obtain further structural information about (3.1.1), a sample of (2.1.1) containing 99% $^{13}\text{C}$-enrichment at the carbonyl was treated with an equimolar amount of BF$_3$.

Results

The $^{19}\text{F}$(^1H) n.m.r. spectrum of the product with 99% $^{13}\text{C}$-enrichment at the carbonyl in d$_2$-dichloromethane at 178K (see diagram 3.1(a)) is similar to that of (3.1.1). However, there is an additional doublet splitting observed in the signal assigned to FC (the value of this is 69Hz).

Conclusions

The ligand arrangement at iridium in (2.1.1) is thought to be maintained, after the transfer of a fluoride from the $-\text{SF}_3$ group to boron (see eqn. 3.1). This is based on the magnitude of $^2J(\text{FC})$ in the resonance denoting FC in the complex with 99% $^{13}\text{C}$-enrichment at the carbonyl. The size of this coupling, 69Hz, compares with the corresponding value for $^2J(\text{FC})$ of 77Hz in (2.1.1), in
Diagram 3.1a

$^{19}\text{F}$ of $\text{F}_\text{C}$ in (3.1.1) at 178K with $^{13}\text{C}$ at CO

Δ/p.p.m.
which the fluoride is known to be *trans* to the carbonyl (see chapter 2). For complexes in which the fluoride is *cis* to the carbonyl, $^2J(FC)$ is in the order of 2-15Hz[].

3.2 A Discussion of Fluorine Exchange in Relation To The IR-SF$_2^+$ Complex (3.1.1)

In order to investigate the susceptibility of (3.1.1) to fluorine exchange, a solution of the complex was warmed to 306K.

At 306K, the signals denoting $F_A$ and $F_C$ in the $^{19}F(^{1}H)$ n.m.r. spectrum remain sharp and retain all couplings which were resolved at 178K. Hence, the complex is stable to significant intermolecular fluorine exchange on the n.m.r. timescale over the temperature range 178K-306K. This contrasts with the -S-F's of (2.1.1), which participate in exchange via an intermolecular mechanism at a significant rate at 306K (see chapter 2).

It is interesting to note that fluorine exchange in (3.1.1), unlike (2.1.1) is not enhanced by the presence of HF. This is consistent with (3.1.1) being stabilized to dissociation by expulsion of a fluorine attached to sulphur.

It is also likely that the positive charge in (3.1.1) precludes an exchange mechanism which involves association between the sulphur and $H^+$ and may stabilize the -S-F bonds with respect to intermolecular fluorine
The broadness of the peak which denotes the fluorines of the $[\text{BF}_4]^-$ anion may be explained by significant exchange on the n.m.r. timescale, between these fluorines and HF. This is illustrated in eqn. 3.2:

\[
\text{Eqn. 3.2}
\]

\[
[\text{BF}_4]^- + \text{HF} \rightarrow \text{BF}_3 + \text{HF}_2^-
\]

This mechanism of fluorine exchange is thought to be unlikely, however, because the boron is coordinatively saturated and a fluoride ion is removed from $[\text{BF}_4]^-$ with great difficulty. Additional data from subsequent experiments have enabled an alternative explanation to be proposed. This is discussed in a later section.

The Formation of some other Ir-SF$_2^+$ Complexes

The reactions between the Ir-SF$_3$ complexes (2.3.1) (see chapter 2) and t-IrCl(CO)[P(CH$_2$CH$_3$)(C$_6$H$_5$)$_2$]$_2$ (4.7.1) (see chapter 4) with BF$_3$ were attempted in d$_2$-dichloromethane to investigate how the more electron-releasing bromide (in the case of (2.3.1)) and the bulkier and less basic P(CH$_2$CH$_3$)[C$_6$H$_5$]$_2$ ligands (in the case of (4.7.1)) would affect the formation and chemical shifts of $F_A$ and $F_C$ in any products, relative to the reaction between BF$_3$ and (2.1.1).
Results

The $^{19}$F($^1$H) n.m.r. spectra of each solution at 178K establishes that a reaction has taken place. The $^{19}$F n.m.r. parameters of each reaction product is listed below:

Table 3.2
$^{19}$F($^1$H) n.m.r. data of the Ir-$\text{SF}_2^+$ complex (3.2.1) derived from (2.3.1) in d$_2$-dichloromethane at 178K

<table>
<thead>
<tr>
<th>$^3$F</th>
<th>$\delta$/p.p.m.</th>
<th>Couplings/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$FA</td>
<td>-52.0</td>
<td>$^3$J(P) = 22 $^3$J(F) = 15</td>
</tr>
<tr>
<td>$^3$FB</td>
<td>-149.8</td>
<td>$^2$J(P) = 31 $^3$J(FA) = 15</td>
</tr>
<tr>
<td>$^3$FC</td>
<td>-369.9</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2(a)
$^{19}$F($^1$H) n.m.r. data of the Ir-$\text{SF}_2^+$ complex (3.2.2) derived from (4.7.1) in d$_2$-dichloromethane at 260K

<table>
<thead>
<tr>
<th>$^3$F</th>
<th>$\delta$/p.p.m.</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$FA</td>
<td>-45.7</td>
<td>$^3$J(P) = 11 $^3$J(F) = 8</td>
</tr>
<tr>
<td>$^3$FB</td>
<td>-152.8</td>
<td>$^2$J(P) = 29 $^3$J(FA) = 8</td>
</tr>
<tr>
<td>$^3$FC</td>
<td>-356.4</td>
<td></td>
</tr>
</tbody>
</table>

Note: the n.m.r. data in table 3.2(a) were listed at 260K owing to the low solubility and poor resolution of the
peaks at lower temperature.

Conclusions

When the Ir-SF$_3$ complexes (2.3.1) and (4.7.1) are treated with an equimolar amount of BF$_3$, an Ir-SF$_2^+$ complex forms in each case.

It is apparent from table 3.2 that varying the ligand trans to the -SF$_2^+$ group from chloride to bromide does not significantly affect the chemical environment of F$_A$.

There is a larger difference in the chemical shift of F$_C$ in the bromo-complex relative to the chloro-analogue. However, this reflects the greater difference in the shift of F$_C$ in the parent Cl-Ir-SF$_3$ (2.1.1) and Br-Ir-SF$_3$ (2.3.1) complexes.

From the data in table 3.2(a), the Ir-SF$_2^+$ complex containing P(CH$_2$CH$_3$)[C$_6$H$_5$]$_2$ ligands does exhibit a larger variation in the chemical shift of F$_A$, relative to (3.1.1). However, this is still a relatively small difference. It suggests that this change in the phosphine ligands has only a minor effect on the chemical environment of F$_A$.

There is no dramatic change in the environment of F$_C$ in the Ir-SF$_2^+$ complex containing P(CH$_2$CH$_3$)[C$_6$H$_5$]$_2$ ligands relative to (3.1.1). This is based on a comparison of the values of F$_C$ in the respective Ir-SF$_3$ complexes.
3.3 The Reaction of the Ir-SF$_2^+$ Complex (3.1.1) with an Excess of BF$_3$

BF$_3$ has been shown to extract a fluorine from the -SF$_3$ group of (2.1.1). Thus, it was thought possible that this reagent may also remove a fluorine from the -SF$_2$ group of (3.1.1), to generate an iridium complex with an -SF group and a double positive charge. However, the stability of (3.1.1) to exchange with HF suggests that cleavage of an -S-F bond in the cation may be difficult.

In order to investigate this reaction, a sample of (3.1.1) was treated with an equimolar amount of BF$_3$ in d$_2$-dichloromethane.

Results

The $^{19}$F($^1$H) n.m.r. spectrum of the solution at 178K (see diagram 3.3) retains a signal in the -S-F region of the spectrum and also one for the [BF$_4$]$^-$ anion. However, there is no peak in the Ir-F region. Two new resonances are present. One of these, at $\delta$-145.8 p.p.m. has a large doublet coupling, which matches a quartet splitting in the other, at $\delta$-280.6 p.p.m. This latter signal is further split into a triplet. Its intensity is 0.5 times that of the peak in the -S-F region.

The $^{31}$P($^1$H) n.m.r. spectrum, at 178K, is similar to that of (3.1.1).
Diagram 3.3

$^{19}$F n.m.r. spectrum of (3.1.1) with

100% excess BF$_3$ at 178K
Diagram 3.3(a)

$^{19}\text{F}[^1\text{H}]$ n.m.r. spectrum of (3.3.1) at 230K.
Conclusions

The $^{31}\text{P}(^{1}\text{H})$ n.m.r. data suggest that an Ir-SF$_2^+$ species containing an Ir-F is present. However, this species must be chemically distinct from (3.1.1). The $^{19}\text{F}(^{1}\text{H})$ n.m.r. data are consistent with BF$_3$ forming an adduct with the Ir-F generating a BF$_4$ group co-ordinated via a fluorine bridge. This is illustrated in eqn. 3.3:

Eqn. 3.3

\[
\begin{align*}
\text{PEt}_3 & \quad + \quad \text{BF}_3 \\
\text{Cl} & \quad \text{Ir} & \quad [\text{S(F}_A^2]^+ [\text{BF}_4]^1 & \quad \text{Cl} & \quad \text{Ir} & \quad [\text{S(F}_A^2]^+ [\text{BF}_4]^1
\end{align*}
\]

In (3.3.1): $F_A$ represents the fluorines bound to sulphur

$F_B$ represents the fluorines of the [BF$_4]^-$ counter ion

$F_{B'}$ represents the non-bridging fluorines of the co-ordinated BF$_4$ group

$F_C$ represents the bridging fluorine of the co-ordinated BF$_4$ group

The large doublet in the resonance assigned to $F_{B'}$ is due to coupling to $F_C$. This is reflected by a quartet in the signal denoting $F_C$. The additional triplet results from coupling to the equivalent phosphorus nuclei. A narrower triplet from $^3J(F_CF_A)$ must be lost due to the
presence of the quadrupolar boron, because $^3J(F_AF_C)$ is resolved in the resonance assigned to $F_A$. This signal also contains a triplet from coupling to the phosphorus nuclei.

The $^{31}P(1\text{H})$ n.m.r. spectrum (see diagram 3.4) contains resolved couplings to $F_A$ and $F_C$ (see table 3.3). The n.m.r. data of this adduct (3.3.1.) are given in table 3.3 below:

Table 3.3
The n.m.r. Data of (3.3.1), at 178K

<table>
<thead>
<tr>
<th>NuX</th>
<th>$\delta$/p.p.m.</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>-52.5</td>
<td>$^3J(F_C) = 14$ $^3J(P) = 12$</td>
</tr>
<tr>
<td>$F_B$</td>
<td>-147.1</td>
<td>$^2J(F_C) = 92$</td>
</tr>
<tr>
<td>$F_B'$</td>
<td>-145.8</td>
<td>$^2J(F_B') = 92$ $^2J(P) = 19$</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-280.6</td>
<td>$^2J(F_C) = 19$ $^3J(F_A) = 12$</td>
</tr>
<tr>
<td>$P$</td>
<td>+16.8</td>
<td></td>
</tr>
</tbody>
</table>

As the solution is warmed, the coordinated $-F:BF_3$ adduct becomes labile. This is illustrated, in the $^{19}F$ spectra (see diagram 3.3(a)), by gradual broadening and eventual loss of structure in the signals which denote $F_A$ and $F_C$. The peaks of $F_B$ and $F_B'$ become indistinguishable, at 230K. When sufficient energy is supplied to the system, a rearrangement takes place and a new complex (3.4.1) is generated (see eqn. 3.4 below). The proposed
Diagram 3.3b

$^{19}\text{F n.m.r.}$ spectrum of (3.3.1) and (3.4.1) at 178K
Diagram 3.3c

Expansion of F_C in (3.3.1) and (3.4.1)

$\delta$/p.p.m.
Diagram 3.4

$^{31}\text{P}^{(1\text{H})}$ n.m.r. spectrum of (3.3.1) and (3.4.1) at 178K
ligand arrangement at iridium, in the rearranged product, has the chloride \textit{trans} to the carbonyl and the co-ordinated \([\text{BF}_4]^-\) group \textit{trans} to the \(-\text{SF}_2^+\) group.

Note: it is possible that the structure of (3.4.1) has the \(-\text{SF}_2^+\) group \textit{trans} to the carbonyl and chloride \textit{trans} to the \([\text{BF}_4]^-\) group. However, this is deemed less likely as this would involve interchange of the two bulkiest ligands (excluding the phosphines), whereas the structure at (3.4.1) requires swapping the site of the co-ordinated \([\text{BF}_4]^-\) group with the relatively small chloride.

Eqn. 3.4

\[
\begin{align*}
\text{PET}_3 & \quad \text{PET}_3 \\
\text{Cl} & \quad \text{Ir} & \quad [\text{SF}_2^-]^{\text{+}} \quad [\text{BF}_4]^- \\
\text{OC} & \quad \text{PET}_3 & \quad \text{PET}_3
\end{align*}
\]

The n.m.r. data of (3.4.1) are given in table 3.4.
Table 3.4
The n.m.r. Data of (3.4.1) in d₂-Dichloromethane, at 178K

<table>
<thead>
<tr>
<th>( \text{Nu}_X )</th>
<th>( \delta/\text{p.p.m.} )</th>
<th>Couplings/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_A )</td>
<td>-13.3</td>
<td>( 2J(P) = 19 )</td>
</tr>
<tr>
<td>( F_B )</td>
<td>-147.1</td>
<td></td>
</tr>
<tr>
<td>( F_B' )</td>
<td>-146.3</td>
<td>( 2J(F_C) = 86 )</td>
</tr>
<tr>
<td>( F_C )</td>
<td>-269.2</td>
<td>( 2J(F_B') = 86 ), ( 2J(P) = 19 )</td>
</tr>
<tr>
<td>( P )</td>
<td>+21.1</td>
<td>( 3J(F_A) = 19 ), ( 2J(F_C) = 19 )</td>
</tr>
</tbody>
</table>

These observations are consistent with work done by W. Beck[76], who recently studied metal complexes containing weakly coordinating anions. He described the \( ^{19}\text{F} \) n.m.r. spectra of complexes with a [BF₄]⁻ anion which is bound to the metal via a fluorine. The spectra are similar to those of \( F_B' \) and \( F_C \) in (3.3.1). These anions are reported as being weakly bound and very labile and may be displaced by coordinating solvents such as nitromethane. This is believed to be the reason for the proposed rearrangement.
3.4 The Reaction Between the Ir-SF$_3$ Complex (2.1.1) and a 50% Deficiency of BF$_3$

It has been shown that the Ir-SF$_2^+$ complex (3.1.1), in contrast to the Ir-SF$_3$ species (2.1.1) does not undergo significant intermolecular fluorine exchange, on the n.m.r. timescale, in d$_2$-dichloromethane, up to 306K. A 1:1 mixture of these two species was studied to observe the effect on the spectrum of (3.1.1) by the presence of (2.1.1) and vice versa. This mixture may be obtained by treating a solution of (2.1.1) with a 50% deficiency of BF$_3$.

Results

The $^{19}$F($^1$H) n.m.r. spectrum at 178K (see diagram 3.5) contains the resonances assigned to the fluorines of (2.1.1) and (3.1.1). All peaks are broad and contain no resolved structure.

As the solution is warmed (see diagram 3.5(a)) the resonances assigned to the Ir-F of each complex merge to give a structureless peak ($\delta$ = -354.1 p.p.m.) at 220K. At this temperature the signals which denote the -S-F's of both species have also averaged to give a new broad peak at $\delta$-30.2 p.p.m.

By 270K, the resonance at $\delta$-354.1 p.p.m. has sharpened to a triplet. The peak which denotes the fluorines of [BF$_4$]$^-$ is sharp and contains no splittings.
Diagram 3.5

$^{19}$F n.m.r. spectrum of the reaction of (2.1.1) with a 50% deficiency of BF$_3$
$^{19}$F n.m.r. spectrum of the reaction of (2.1.1) with a 50% deficiency of BF$_3$ at 220 K.
The signal at $\delta$-30.2 p.p.m. is still broad and without fine structure.

These spectroscopic changes are reversible as the solution is cooled to 178K.

Conclusions

When the Ir-SF$_3$ complex (2.1.1) is treated with a 50% deficiency of BF$_3$, a mixture of (2.1.1) and (3.1.1) is formed. These two complexes exist in dynamic equilibrium (see eqn. 3.5) below:

Eqn. 3.5

\[ \text{Ir-SF}_3 \rightleftharpoons \text{Ir-SF}_2^+ + \text{F}^- \]

At 178K, the rate of fluoride ion transfer between (2.1.1) and (3.1.1) is sufficiently slow, on the n.m.r. timescale, to enable the peaks of the $-S-F$'s and Ir-F of each species to be distinguished. As the solution is warmed the transfer rate increases and results in an averaging of the fluorine environments of both species. This is almost attained at 270K.

The $[\text{BF}_4]$ anion acts as a spectator ion in the equilibrium process.

This experiment has shown, once again, that Ir-F's are not susceptible to fluorine exchange. This is established, by the observed retention of coupling between the Ir-F and phosphorus nuclei, $[2J(\text{FP}) = 31\text{Hz}]$, at 270K.
3.5 The Reaction of the Ir-SF$_2^+$ Complex (3.1.1) with N(CH$_3$)$_3$

The ability of N(CH$_3$)$_3$ to act as a Lewis base, in conjunction with the coordinative unsaturation at sulphur in (3.1.1) and the nett positive charge in the complex, suggested that the amine may bind to the sulphur of (3.1.1). The product of such a reaction would contain an Ir-SF$_2$N(CH$_3$)$_3$ group.

To investigate this, a sample of (3.1.1) was treated with an equimolar amount of the amine in $d_2$-dichloromethane.

Results

The $^{19}$F($^1$H) n.m.r. spectrum of the solution at 178K contains the set of resonances which are assigned to the fluorines of the Ir-SF$_3$ complex (2.1.1) from which (3.1.1) derives. There is, in addition, a resonance containing four lines of equal intensity, at $\delta$-163.7 p.p.m (see diagram 3.6). However, the signals assigned to (3.1.1) are absent from the spectrum.

Conclusions

It is apparent from the n.m.r. data that treating the Ir-SF$_2^+$ complex (3.1.1) with N(CH$_3$)$_3$ results in the formation of the Ir-SF$_3$ complex (2.1.1). This could arise from the amine attacking the [BF$_4$]$^-$ counter ion to
Diagram 3.6

$^{19}$F n.m.r. spectrum of F$_3$B:NMMe$_3$ at 178K
generate an $\text{F}_3\text{B}:\text{N(CH}_3)_3$ adduct (3.6.1) (see eqn. 3.6) with release of a fluoride ion. The combination of this liberated ion with the $-\text{SF}_2$ group of (3.1.1), would result in the formation of (2.1.1). This is illustrated in eqn. 3.6:

Eqn. 3.6

\[
\begin{array}{c}
\text{PET}_3 \\
\text{Cl} - \text{N} - \text{OC} \\
\end{array} \xrightarrow{+\text{NMe}_3} \begin{array}{c}
\text{PET}_3 \\
\text{F} - \text{SF}_2^+\text{[BF}_4^-] \\
\end{array} \xrightarrow{\text{Me}_3\text{N:BF}_3} \begin{array}{c}
\text{PET}_3 \\
\text{Cl} - \text{N} - \text{OC} \\
\end{array}
\]

(3.6.1)

The resonance at $\delta-163.7$ p.p.m. is assigned to the fluorines on boron of (3.6.1). The splitting arises from coupling to the quadrupolar boron nucleus [$^{1}J(\text{FB}) = 16\text{Hz}$], as indicated. A similar coupling is not observed in $\text{[BF}_4^-]$, because the tetrahedral symmetry and lack of electric field gradient increases the rate of quadrupolar relaxation to the extent that $^{1}J(\text{FB})$ is lost.

There is no spectroscopic evidence to indicate that the amine has formed a stable adduct with (3.1.1) at sulphur. Although the formation of such a species may be possible, the equilibrium conditions dictate that the amine preferentially dislodges a fluoride ion from $\text{[BF}_4^-]$ rather than binding to sulphur.

A similar study of the analogous reaction between $\text{SF}_3^+\text{[BF}_4^-]$ and $\text{N(CH}_3)_3$ has not been possible, owing to the
insolubility of the adduct in all solvents apart from HF. However, weaker bases than N(CH₃)₃, such as diethylether, liberate SF₄ from SF₃⁺[BF₄]⁻ (see later). Diethylether, however, does not displace fluoride in the anion of (3.1.1), to form an ether:BF₃ adduct.

3.6 The Reaction of the Ir-SF₂⁺ Complex (3.1.1) with Dimethylamine (NH(CH₃)₂)

The reaction of the secondary amine NH(CH₃)₂ with (3.1.1) may differ from that between the complex and N(CH₃)₃. There is the possibility that NH(CH₃)₂ could react with the -SF₂ group of the complex via a mechanism involving the elimination of HF. This would generate an iridium complex which contains an -SFN(CH₃)₂⁺ group.

To investigate this, a further sample of (3.1.1) was treated with an equimolar amount of NH(CH₃)₂ in d₂-dichloromethane.

Results

As in the previous reaction (eqn. 3.6) the ¹⁹F(¹H) n.m.r. spectrum of the solution contains the resonances of (2.1.1), while those of (3.1.1) are absent.

Another signal, similar to that denoting the fluorines of (3.6.1), is at δ-159.5 p.p.m.
Conclusions

The n.m.r. data indicate that, although NH(CH₃)₂ has the potential to displace a fluorine attached to sulphur of (3.1.1) with an -N(CH₃)₂ group, the amine reacts with the complex in a manner analogous to N(CH₃)₃. The adduct which forms is F₃B:NH(CH₃)₂ and coupling between the fluorines and boron is 16Hz. This is the same as the ¹J(BF) in (3.6.1).

3.7 The Reaction of the Ir-SF₂⁺ Complex (3.1.1) with Trimethylphosphine (P(CH₃)₃)

Although tertiary amines, such as N(CH₃)₃, form adducts with SF₄ (see chapter 5), their phosphine equivalents are fluorinated by this reagent, to generate 5-coordinate phosphine compounds, which contain a pair of mutually trans fluorines.

In view of the ability of phosphorus to possess 5-coordination, it was thought possible that the -S-F's of (3.1.1) may fluorinate P(CH₃)₃ to generate t-PF₂(CH₃)₃.

This reaction was studied in d₂-dichloromethane by treating a sample of (3.1.1) with an equimolar amount of P(CH₃)₃.

Results

The ¹⁹F(¹H) n.m.r. spectrum of the solution, at 178K, contains the resonances of (2.1.1) and a four-lined
pattern, at δ-139.5 p.p.m., which is similar to that assigned to the fluorines of (3.6.1), but with an additional doublet splitting.

Conclusions

When (3.6.1) is treated with an equimolar amount of P(CH₃)₃, the Ir-SF₃ complex (2.1.1) is generated by a mechanism similar to those involved in the reactions of (3.1.1) with N(CH₃)₃ and NH(CH₃)₂. The spectrum of the adduct F₃B:P(CH₃)₃ (3.6.2) contains an additional doublet [2J(FP)= 225Hz] splitting, as a result of coupling between the fluorines and phosphorus atom. The value of 1J(BF) in (3.6.2) is 53Hz. This compares with 1J(FB)= 16Hz in (3.6.1) and reflects the weaker interaction in the case of the boron and phosphine. This results in greater s-character in the boron orbitals of (3.6.2) relative to (3.6.1).

There is no evidence to suggest that the phosphine has been fluorinated by the -S-F's of (3.1.1).

3.8 The Reaction of the Ir-SF₂⁺ Complex (3.1.1) with the Chloride Ion

It is clear from previous experiments involving the reactions of (3.1.1) with amines, that the -SF₂ group of the complex can uptake a fluoride ion, to generate an Ir-SF₃ species. This suggests that the complex may also
incorporate other anionic species at sulphur.

Tetrapropylammonium chloride (NPr$_4^+$Cl$^-$) is a common source of chloride ions in organic solvents.

To investigate if (3.1.1) would uptake a chloride ion and generate an iridium species containing an -SF$_2$Cl ligand, a sample of the complex was treated with an equimolar amount of NPr$_4^+$Cl$^-$, in d$_2$-dichloromethane.

Results

The $^{19}$F($^1$H) n.m.r. spectrum of the solution, at 178K, contains peaks at approximately the same chemical shifts as those assigned to (3.1.1). However, they are unusually broad compared with the spectrum of other authentic samples of the complex at this temperature. This implies that an exchange process involving the complex is taking place at a significant rate, on the n.m.r. timescale, at this temperature.

As the solution is warmed the resonance assigned to F$_C$ sharpens to a triplet by 230K. The peak associated with the fluorines bound to sulphur has broadened considerably and no fine structure is resolved. Further warming of the solution to 300K results in sharpening of the signal of F$_C$ while that of F$_A$ becomes so broad that it is indistinguishable from the baseline of the spectrum.

These spectroscopic changes are reversible as the solution is recooled to 178K.
Conclusions

It is clear from the $^{19}$F($^1$H) n.m.r. data that the presence of chloride ions influences exchange in (3.1.1). This exchange involves the fluorines bound to sulphur and contains a significant intermolecular component above 178K. A possible process is given in eqn. 3.7:

$$\text{Eqn. 3.7}$$

$$\text{Ir-SF}_2^+ + \text{Cl}^- \rightleftharpoons \text{Ir-SFCl}^+ + \text{F}^-$$

As the chemical shifts of the signals which denote $F_A$ and $F_C$ remain essentially unchanged from those in a pure sample of (3.1.1) this suggests the equilibrium constant ($K_E$), for the above process, is very small. The rate of exchange, however, is fast on the n.m.r timescale.

The absence of the peaks of the Ir-SF$_3$ complex (2.1.1) precludes this species from being involved in the above process.

The triplet in the signal denoting $F_C$ is due to coupling to the mutually trans phosphorus nuclei [$^2J(F_CP)=32\text{Hz}$]. Retention of this coupling up to 300K implies that $F_C$ is stable to significant intermolecular fluorine exchange, under these reaction conditions.

There is no spectroscopic evidence to indicate that a stable iridium complex containing an -SF$_2$Cl ligand has formed.
3.9 The Reaction of the Ir-SF$_2^+$ Complex (3.1.1) with Methanol (CH$_3$OH)

As a consequence of the amines and P(CH$_3$)$_3$ attacking the [BF$_4$]$^-$ ion to generate an adduct with BF$_3$ and releasing a fluoride ion, all attempts to date, at displacing a fluorine attached to sulphur in (3.1.1) have been unsuccessful. However, the outcome of these reactions is thought to be governed by the equilibrium constants of the various processes involved and does not preclude the formation of a complex containing an Ir-SF$_2$X (X= an anionic species other than fluoride) by an alternative route.

The affinity of BF$_3$ for alcohols is much lower than that for amines. This suggests that there may be a sufficient shift in the equilibrium position to enable the substitution of an -S-F of (3.1.1) by the alkoxy- group of an alcohol. The simple product of this substitution would contain an Ir-SFOR$^+$ group. This type of reaction would have the additional driving force of the highly favoured formation of HF as an elimination product.

With a view to substituting an -S-F in (3.1.1) by CH$_3$O-, a sample of the complex was treated with an equimolar amount of freshly distilled CH$_3$OH, in d$_2$-dichloromethane. The purple solution turned colourless, indicating that a reaction had taken place.
Results

The $^{19}\text{F}({}^{1}\text{H})$ n.m.r. spectrum of the solution, at 178K, (see diagram 3.7) shows that the resonances assigned to (3.1.1) are absent, although there remains a peak in the B-F region of the spectrum. The signals denoting the -S-F and Ir-F of (3.1.1) have been replaced by two signals of equal intensity, at $\delta$-79.1 and $\delta$-356.5 p.p.m. The one at higher frequency, is in the -S-F region of the spectrum and is a resolved doublet of triplets. The other is in the part of the spectrum associated with an Ir-F and is a resolved triplet of doublets.

The peak at $\delta$-151.1 p.p.m. is sharp. There is, in addition, a broad peak at $\delta$-182.2 p.p.m., which is in the H-F region of the spectrum.

Conclusions

It is clear from the $^{19}\text{F}({}^{1}\text{H})$ n.m.r. data, that (3.1.1) undergoes a chemical reaction in the presence of CH$_3$OH. The product contains only one type of -S-F and Ir-F and there are equal numbers of fluorines in each of these environments. The broad peak at $\delta$-182.2 p.p.m. suggests that HF is present and the resonance at $\delta$-151.1 p.p.m. indicates the presence of [BF$_4$]$^-$. The simplest structure consistent with this data is one in which the CH$_3$O- group of the alcohol has displaced a fluorine bound to sulphur in (3.1.1), as was intended. The structure of this complex (3.8.1) is illustrated in eqn. 3.8 below:
Diagram 3.7

$^{19}$F n.m.r. spectrum of (3.8.1) at 178K
Diagram 3.7a

$^{19}$F n.m.r. spectrum of (3.8.1) at

240 K
Diagram 3.7 exp1

Expansion of $F_A$ in (3.8.1)

Diagram 3.7b

Expansion of $F_A$ in (3.8.1) with the retention of $^1H$ coupling

Diagram 3.7 exp2

Expansion of $F_C$ in (3.8.1)

$\delta$/p.p.m.
Eqn. 3.8

\[
\begin{align*}
\text{Cl} & \quad \text{Ir} \\
& \quad [\text{SF}_2]^+ [\text{BF}_4]^- \\
\text{OC} & \quad \text{PET}_3 \\
& \quad \text{PET}_3 + \text{MeOH}
\end{align*}
\]

(3.8.1)

In (3.8.1):

- \(F_A\) denotes the -S-F
- \(F_B\) denotes the B-F's
- \(F_C\) denotes the Ir-F
- \(P,P'\) denote the phosphorus nuclei

The resonance in the spectrum denoting \(F_A\) is split into a doublet, \([J(F_A F_C) = 20\text{Hz}],\) of triplets, \([J(F_A P, P') = 15\text{Hz}],\) as a result of couplings to \(F_C, P\) and \(P'.\)

Similarly, the observed splittings in the signal assigned to \(F_C\) are due to equal couplings to \(P\) and \(P',\)
\([J(F_C P, P') = 33\text{Hz}]]\) and coupling to \(F_A,\) (as above).

The peak assigned to \(F_B\) is sharp, in contrast with the corresponding peak of (3.1.1). This suggests that the explanation for the broadness of this resonance in (3.1.1) is incorrect, because it is difficult to postulate a mechanism for exchange between the anion of (3.1.1) and HF, which does not also apply to (3.8.1).

An alternative explanation is that the \([\text{BF}_4]^-\) anion and \(\text{Ir- SF}_2^+\) species exist as an ion-pair. This destroys
the $T_d$ symmetry in the anion and causes broadening of the peak due to quadrupolar relaxation. In (3.8.1), however, the greater steric bulk of the CH$_3$O$^-$ group relative to the fluorine in (3.1.1) may prevent, or lessen the effect of, ion-pairing between the cation and anion. Also, CH$_3$O$^-$ is more electron-releasing than fluoride ion and as any ion-pair is likely to involve the positive sulphur and fluorines of the anion, electronic factors may inhibit this in (3.8.1).

It is believed to be coincidental that both the -S-F and Ir-F couple equally to each phosphorus nucleus in (3.8.1). There is no configuration of the -SFOCH$_3$ group, with pyramidal geometry at sulphur, which would render the phosphines equivalent. This is illustrated in figs. 3.1 and 3.1(a):

Figs. 3.1 and 3.1(a)
Diagramatic representations of the view along the Ir-S bond which show why the phosphines are non-equivalent in (3.8.1)

\[
\begin{align*}
\text{PEt}_3 & \quad \text{PEt}_3 \\
| & \quad | \\
\text{FA} & \quad \text{FA} \\
\text{FC} \quad \overset{\infty}{\longrightarrow} \quad \text{CO} & \quad \text{FC} \quad \overset{\infty}{\longrightarrow} \quad \text{CO} \\
| & \quad | \\
\text{OMe} & \quad \text{MeO} \\
\text{PEt}_3 & \quad \text{PEt}_3
\end{align*}
\]

$\infty$ - represents the view along the Ir-S bond
FC - fluorine bound to the metal
FA - fluorine bound to sulphur
The diagramatic representations in fig. 3.1, in which the $F_{A\text{g}O}$ angles bisect the plane perpendicular to the Ir-P bonds do not render the phosphines equivalent. One of the phosphines lies in closer proximity to $F_{A}$ than the other. In the case where the $-S-F$ bond lies in the plane of the OC-Ir-F$_C$ bonds (not illustrated), the phosphines are still distinct, because the CH$_3$O- group lies on the same side of this plane as one phosphine and the opposite to the other.

The $^{31}\text{P}^{(1)}\text{H}$ n.m.r. spectrum of (3.8.1) ought to be an ABXY pattern (for the reasons discussed above). However, this is not observed over the temperature range 178K to 306K. (see diagram 3.8). Although this is not consistent with the $^{19}\text{F}^{(1)}\text{H}$ n.m.r. spectra, the interpretation of these latter spectra virtually preclude the complex having any structure other than the one shown at (3.8.1) or the later alternatives. These are discussed in the next section. The reasons for this apparent anomaly are not understood.

3.10 The Reaction of the Ir-SF$_2$+ Complex (3.1.1) with Methoxytrimethylsilane [CH$_3$OSi(CH$_3$)$_3$]

An alternative source of CH$_3$O$^-$ is CH$_3$OSi(CH$_3$)$_3$. It has the advantage over CH$_3$OH that in the reaction with (3.1.1), the product of elimination would be (CH$_3$)$_3$SiF rather than HF. With this in mind CH$_3$OSi(CH$_3$)$_3$ was
Diagram 3. 8

$^{31}\text{P}({^1}\text{H})$ n.m.r. spectrum of (3.8.1) at 178K
reacted with an equimolar amount of (3.1.1) in d$_2$-dichloromethane. The purple solution turned colourless indicating that a reaction had taken place.

Results

The $^{19}$F($^1$H) n.m.r. spectrum of the transition metal product, at 178K, is identical to the one observed in the CH$_3$OH reaction.

There is also a sharp singlet at δ-157.7 p.p.m., with silicon satellites, [2J(FSi) = 135Hz]. Each of these peaks is split into decaplets on retention of $^1$H-coupling. The resonance is assigned to the fluorine of (CH$_3$)$_3$SiF.

Conclusions

This experiment illustrates that the Si-O bond of CH$_3$OSi(CH$_3$)$_3$ is broken in the presence of (3.1.1) to generate the same product as when (3.1.1) is reacted with CH$_3$OH.

Further Evidence in Support of the Proposed Structure of (3.8.1)

The product of reaction of (3.1.1) and CH$_3$OSi(CH$_3$)$_3$ has also been synthesized from a sample of (3.1.1) containing 99% $^{13}$C-enrichment at the carbonyl ligand, with a view to establishing the ligand arrangement at iridium. In the Ir-SF$_3$ (2.1.1) and Ir-SF$_2^+$ complexes from which (3.8.1) is derived, F$_C$ is located trans to the carbonyl.
This is based on the magnitude of $2J(F_C C)$ from other species in which an Ir-F is trans to the carbonyl and in the case of (2.1.1), has been backed up by a low temperature X-ray crystallographic study (see earlier). However, on the basis of the spectroscopic data obtained on (3.8.1) so far, the possibility of ligand rearrangement at the iridium centre could not be excluded.

Results

The $^{19}F(1H)$ n.m.r. spectrum of the solution, at 178K, confirms the presence of the three fluorine resonances of (3.8.1). The one to high frequency in the spectrum, at $\delta=79.1$ p.p.m., denoting the $-S-F$ of the complex, is essentially unaffected by the presence of the $^{13}C_0$-ligand, and the peak assigned to the fluorines of the anion remains sharp. The resonance to lowest frequency denoting the Ir-F, at $\delta=356.1$ p.p.m. (see diagram 3.7(a)), contains an extra doublet splitting [$^{2}J(F_C C)=71Hz$], which arises from coupling between this fluoride and the $^{13}C$ of the carbonyl ligand, as indicated. The magnitude of this coupling is comparable with the, [$^{2}J(F_C C)=69Hz$] observed in the Ir-$S F_2^+$ complex (3.1.1). On this basis the ligand arrangement at the iridium is thought to be the same as in (3.1.1).

The $^{19}F$ n.m.r. spectrum of an earlier sample of the complex (not containing $^{13}C$ enrichment at carbonyl) was recorded with retention of $1H$-coupling, once it had been
established that FC is trans to carbonyl. It had been hoped that the -S-F resonance would be split into a quartet due to coupling to the three protons of the CH₃O- group. In fact, this peak is broad (see diagram 3.7(b)) and without fine structure. This observation is consistent with coupling between the -S-F and these protons being too small to be resolved, but sufficiently large to remove the resolution of the other couplings to this fluoride. This broadening could also arise from coupling to the protons of the phosphine ligands. However, these are at least five bonds away and the corresponding -S-F resonance of (3.1.1) is not affected by retention of ¹H-coupling. The nearest protons in the phosphine ligands of that complex are also five bonds distant.

3.11 A Discussion of Alternative Structures to (3.8.1)

There are other plausible structures which are compatible with the ¹⁹F(¹H) n.m.r. spectra of (3.8.1). One of these is an isomer (3.8.2), in which the positions of chloride and CH₃O- are interchanged (see figure 3.2)
The structure of this complex places an extra bond between the \(-S-F\) and \(\text{CH}_3\text{O-}\) protons, with respect to (3.8.1). This suggests that the \(-S-F\) resonance, like that of (3.1.1), would not be affected by the retention of \(^1\text{H}\)-coupling. However, little is known about the relative difference in magnitude between such 4- and 5-bond couplings.

The formation of (3.8.2) is less likely than (3.8.1), however, because, unlike (3.8.1), it cannot be formed directly by simple nucleophilic substitution at sulphur. If the product of the treatment of (3.1.1) with \(\text{CH}_3\text{OH}\) is (3.8.2), there must be some sort of rearrangement occurring. This is possible, although the greater strength and stability of an \(-S-F\) bond relative to \(-S-\text{Cl}\), plus the labilization of the \(\text{Ir}-F\) by the strong trans influence of the carbonyl ligand, suggest that fluoride would participate in any rearrangement before chloride. In such a case, the structure of the product would be (3.8.3). This is illustrated in figure 3.3:
The spectrum of (3.8.3) would contain no resonance for an Ir-F and the -S-F signal would be either a triplet (if couplings to both phosphorus nuclei are the same) or a doublet of doublets (if they are different). The spectrum is not consistent with (3.8.3) being formed.

The possibility of the product of reaction of (3.1.1) with CH$_3$OH containing an Ir-H bond has not been previously discussed. Iridium complexes containing hydride ligands[73] are known to be formed by reaction of square planar Ir$^I$ complexes with reagents of the form H-X (X= Cl, Br, I, CH$_3$CO etc.). The possible dissociation of CH$_3$OH into CH$_3$O- and H- fragments during the course of reaction with (3.1.1) suggests a species containing an Ir-H bond may be formed. However, in this case, the $^1$H n.m.r. spectrum confirms that there is no hydride present in the product of the reaction. Ir-H ligands have chemical shifts to low frequency (-5 to -35 p.p.m.) of the protons of the phosphines.

Another possible product of the reaction between
(3.1.1) and CH$_3$OH is (3.8.4). This complex could form as a result of displacement of the CH$_3$O- group on sulphur by chloride from the solvent. It should be stressed, however, that there is no displacement of the fluorines bound to sulphur in (3.1.1) in d$_2$-dichloromethane. The structure of this possible chloro-substituted complex is illustrated in figure 3.4:

![Figure 3.4](image)

Another Alternative Structure to (3.8.1)

$\text{Cl} \quad \text{Ir} \quad \text{SF}_4\text{Cl}^+\text{[BF$_4$]}^-$

(3.8.4)

(3.8.4) like (3.1.1), contains no protons other than those in the alkyl groups of the phosphine ligands. This suggests that the $^{19}$F n.m.r. spectrum of both species may also be expected to be the same as the decoupled spectrum by analogy with the corresponding spectrum of (3.1.1). However, it is not known what effect the presence of a chloride instead of fluoride at sulphur would have on the value of $^5J(F_AH)$.

The low solubility of this species in non-chlorinated solvents means that further chemical reactions are necessary to establish if (3.8.4) is a reaction product.
3.12 The Reaction of the Ir-SF$_2^+$ Complex (3.1.1) with Ethanol (CH$_3$CH$_2$OH)

The comparable chemical properties of methoxy (CH$_3$O-) and ethoxy (CH$_3$CH$_2$O-) groups suggested that CH$_3$CH$_2$OH would react with (3.1.1) in a similar manner to CH$_3$OH. Given that the alkoxy- group forms part of an Ir-SFOR$^+$ complex in the product, the substitution of CH$_3$O- by CH$_3$CH$_2$O- should result in a slight change in chemical shifts of the Ir-F and -S-F resonances.

The reaction between (3.1.1) and an equimolar amount of freshly distilled CH$_3$CH$_2$OH was investigated in d$_2$-dichloromethane.

Results

The $^{19}$F($^1$H) n.m.r. spectrum of the solution, at 178K, indicates that there is one reaction product containing an -S-F bond. The signal assigned to this fluorine is at $\delta$-74.8 p.p.m. and is a doublet of triplets, just like the resonance denoting FA in (3.8.1). There is also a doublet of triplets at $\delta$-351.0 p.p.m. This signal has the same intensity as that assigned to FA, and the doublet coupling matches that in the resonance of FA.

The peak in the region of the spectrum denoting the [BF$_4$]$^-$ fluorines is sharp, as it is in (3.8.1).

There is also a broad peak, at $\delta$-182.0 p.p.m., which indicates the presence of HF.
As the solution is warmed to 306K, the spectrum shows no significant decomposition of the product. Also, the peaks of the complex remain sharp, with retention of all couplings.

Conclusions

A reaction takes place between CH₃CH₂OH and (3.1.1) in d₂-dichloromethane at 178K. The ¹⁹F(¹H) n.m.r. spectrum of the product (3.9.1) (see eqn. 3.9) is similar to that of (3.8.1). However, the slight shift to higher frequency, in the chemical shifts of FA and FC in (3.9.1) relative to (3.8.1), implies that the two species are not the same and suggests that the difference is due to the variation in the alkoxy-group of each species.

The formation of (3.9.1) is shown in eqn. 3.9.

Eqn. 3.9

\[
\text{PEt}_3 \quad \text{PEt}_3
\]

\[
\text{Cl} \quad \text{Ir} \quad [\text{SF}_2]^+ [\text{BF}_4]^- \quad + \text{EtOH} \quad \text{Cl} \quad \text{Ir} \quad [\text{S}([\text{FA}]\text{OEt})]^+ [\text{B}([\text{FB})_4]^- \\
\text{OC} \quad \text{PEt}_3 \quad \text{PEt}_3 \quad \text{OC} \quad \text{PEt}_3
\]
Table 3.5

$^{19}\text{F}(\text{H})$ n.m.r. Data of (3.9.1) at 178K

<table>
<thead>
<tr>
<th>$F_x$</th>
<th>$\delta$/p.p.m.</th>
<th>Couplings/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>-74.8</td>
<td>$2J(F_C) = 19$ $3J(P, P') = 14$</td>
</tr>
<tr>
<td>$F_B$</td>
<td>-149.7</td>
<td></td>
</tr>
<tr>
<td>$F_C$</td>
<td>-351.0</td>
<td>$2J(P, P') = 25$ $3J(F_A) = 19$</td>
</tr>
</tbody>
</table>

The n.m.r. data confirm that (3.9.1) is not susceptible to significant intermolecular fluorine exchange, up to 306K. This is in agreement with the stability of (3.1.1) to this type of exchange over the temperature range 178K-306K.

It is also apparent that (3.9.1), like (3.1.1) does not react or significantly interact with HF up to 306K.

The Reaction of the $\text{Ir}_2\text{SF}_{2}^+$ Complex (3.1.1) with 2,2,2-Trifluoroethanol ($\text{CF}_3\text{CH}_2\text{OH}$)

The reaction has been attempted between (3.1.1) and an equimolar amount of freshly distilled $\text{CF}_3\text{CH}_2\text{OH}$, with a view to examining the effect on the chemical shift of the fluorines of the $-\text{CF}_3$ group, as a result of the alkoxy-group being incorporated into an iridium complex.
Results

The $^{19}\text{F}(^1\text{H})$ n.m.r. spectrum of the solution, at 178K, contains the three resonances of (3.1.1) and a singlet, at $\delta$-77.1 p.p.m. for the three equivalent fluorines of the $-\text{CF}_3$ group in the unreacted alcohol.

As the solution is warmed, the signals of both species remain intact up to 306K.

Conclusions

When (3.1.1) is treated with CF$_3$CH$_2$OH in d$_2$-dichloromethane, there is no chemical reaction observed between 178K and 306K. This is confirmed by the $^{19}\text{F}(^1\text{H})$ n.m.r. spectra of the solution. The stability of (3.1.1) to reaction with CF$_3$CH$_2$OH is thought to arise from the inductive effect of the $-\text{CF}_3$ group reducing the nucleophilicity of the alcohol sufficiently to preclude attack on the iridium complex with resulting displacement of fluoride.

The Reaction of the Ir-SF$_2^+$ Complex (3.1.1) with some other Alcohols

This section discusses the $^{19}\text{F}(^1\text{H})$ n.m.r. spectra of d$_2$-dichloromethane solutions containing (3.1.1) and equimolar amounts of some alcohols with differing degrees of dissociation and steric properties. Firstly, the case of propan-2-ol ((CH$_3$)$_2$CHOH) will be considered.

This reaction was investigated with a view to
confirming that the previous reactions involving CH$_3$OH and CH$_3$CH$_2$OH were straightforward nucleophilic substitutions at sulphur in (3.1.1). Any rearrangement involving the larger isopropyloxy- group is likely to be kinetically slow relative to the smaller CH$_3$O- and CH$_3$CH$_2$O- groups. It was hoped that any rearrangement would be sufficiently slow, on the n.m.r. timescale, to obtain data for both the intermediate and final products.

The spectrum of the solution has been recorded over the temperature range 178–306K.

Results

At 178K, the $^{19}$F($^1$H) n.m.r. spectrum of the solution contains a set of resonances similar to those of the products of the reactions between (3.1.1) and CH$_3$OH and CH$_3$CH$_2$OH. It shows little change as the solution is warmed to 306K and there is no evidence for any rearrangement, or that the reaction is slow at 178K.

The $^{19}$F($^1$H) n.m.r. data of the product are given in table 3.6.
Table 3.6
$^{19}$F($^1$H) n.m.r. Data of (3.9.2) in d$_2$-dichloromethane at 178K.

<table>
<thead>
<tr>
<th>$F_X$</th>
<th>δ/p.p.m</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>-70.6</td>
<td>$^3J(F_C) = 21$ $^3J(P, P') = 16$</td>
</tr>
<tr>
<td>$F_B$</td>
<td>-149.4</td>
<td>$^2J(F_A) = 28$ $^3J(P, P') = 21$</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-353.9</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

On the basis of this data it is concluded that propan-2-ol reacts with (3.1.1) in a similar manner to CH$_3$OH and CH$_3$CH$_2$OH, to form a complex containing an $-SOCH(CH_3)_2$ group.

A similar conclusion is formed when (3.1.1) is treated with benzyl alcohol (PhCH$_2$OH). The n.m.r. data of the product are given in Table 3.7.

Table 3.7
$^{19}$F($^1$H) n.m.r. data of (3.9.3) in d$_2$-dichloromethane at 178K.

<table>
<thead>
<tr>
<th>$F_X$</th>
<th>δ/p.p.m</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>-76.3</td>
<td>$^3J(F_C) = 17$ $^3J(P, P') = 14$</td>
</tr>
<tr>
<td>$F_B$</td>
<td>-150.2</td>
<td>$^2J(P, P') = 27$ $^3J(F_A) = 17$</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-350.1</td>
<td></td>
</tr>
</tbody>
</table>
For clarity and ease of comparison of the results, the n.m.r. data on the products of each of the four reactions are tabulated below:

Table 3.8

$^{19}$F($^1$H) n.m.r. Data for the Products of Reaction of (3.1.1) with Alcohols

<table>
<thead>
<tr>
<th>R</th>
<th>FA/p.p.m.</th>
<th>FB/p.p.m.</th>
<th>FC/p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>-79.1</td>
<td>-151.1</td>
<td>-356.1</td>
</tr>
<tr>
<td>CH₃CH₂</td>
<td>-74.8</td>
<td>-149.7</td>
<td>-351.0</td>
</tr>
<tr>
<td>i-Pr</td>
<td>-70.6</td>
<td>-149.4</td>
<td>-353.9</td>
</tr>
<tr>
<td>PhCH₂</td>
<td>-76.3</td>
<td>-150.2</td>
<td>-350.1</td>
</tr>
</tbody>
</table>

In addition to CF₃CH₂OH, there are other alcohols or thiols which do not undertake nucleophilic substitution at sulphur, in (3.1.1). CH₃CH₂SH does not displace a fluorine bound to sulphur. In this case the reaction is believed to be disfavoured by the unlikely formation of a sulphur-sulphur single bond.

Treatment of (3.1.1) with (2,4,6)-trinitrophenol yields no product over the temperature range 178-273K. However, at 306K, the peaks denoting the Ir-F and -S-F's of (3.1.1) have disappeared. There is no evidence that substitution has occurred and the appearance of a singlet of high intensity, at $\delta +44.0$ p.p.m., is thought to be due to a decomposition product. Two other resonances are
observed, both of which are of low intensity. A singlet at $\delta$-310.7 p.p.m., indicates that an Ir-F species may be formed, but the origin and structure of this species could not be determined. A further singlet (which is a triplet when $^1H$-coupling is retained), at $\delta$-282.5 p.p.m., is thought to arise from fluorination of the aromatic ring at the hydroxyl site with splitting due to coupling to two protons of the ring.

3.13 The Reaction of the Ir-SF$_2^+$ Complex (3.1.1) with a 100% Excess of CH$_3$OH

In an attempt to displace the second fluorine bound to sulphur, in (3.1.1), the complex was treated with a 100% excess of CH$_3$OH in d$_2$-dichloromethane. The $^{19}$F($^1$H) n.m.r. spectrum has been recorded over the temperature range 178K-306K.

Results

The $^{19}$F($^1$H) n.m.r. spectrum of the solution at 178K contains the three resonances assigned to (3.8.1) and the peak denoting the fluorine of HF. There is, in addition, a new triplet resonance of low intensity, in the Ir-F region of the spectrum, at $\delta$-343.3 p.p.m. As the solution is warmed to 306K, the intensity of this new signal increases above 273K. At the same time the resonances assigned to the -S-F and Ir-F of (3.8.1) become less
Diagram 3.9

$^{19}$F n.m.r spectrum of (3.10.1) at

178K with expansion of $F_C$ at 306K
intense (see diagram 3.9).

At 306K, the resonance at $\delta-343.3$ p.p.m. is the only one remaining in the Ir-F region of the spectrum. There are no peaks in the -S-F region of the spectrum.

These spectroscopic changes are irreversible as the solution is recooled to 178K.

Conclusions

The data are consistent with (3.8.1) undergoing reaction with CH$_3$OH as indicated by the eqn. 3.10 below:

$$\text{Eqn. 3.10}$$

$$\begin{align*}
\text{PET}_3 & \quad | \quad F \\
\text{Cl} & \quad \text{Ir} & \quad \text{SFOMe}^+\text{[BF}_4^-] & \quad + \text{MeOH} \\
\text{OC} & \quad \text{PET}_3 & \quad \rightarrow & \quad \text{Cl} & \quad \text{Ir} & \quad \text{S(OMe)}_2^+\text{[BF}_4^-] \\
& & & \quad \text{OC} & \quad \text{PET}_3
\end{align*}$$

$$(3.10.1)$$

The triplet splitting in the new signal, $[^2J(F\text{C}_P)=31\text{Hz}]$, is the result of coupling between the Ir-F and the mutually trans phosphorus nuclei, as indicated. This is supported by a doublet of equal magnitude in the $^{31}\text{P}(^1\text{H})$ n.m.r. spectrum. The resonance assigned to the fluorines of the [BF$_4$]$^-$ anion is sharp.

The disappearance of the resonances assigned to (3.8.1) is thought to arise from the presence of unreacted CH$_3$OH. From previous experiments the $^{19}\text{F}(^1\text{H})$ n.m.r. spectrum of (3.8.1) does not decrease in intensity in solutions containing no excess of CH$_3$OH as they are warmed.
to 306K. Also, in these spectra there is no peak at \( \delta = 343.3 \) p.p.m.

This spectroscopic data support the idea that the new product is the result of a reaction between (3.8.1) and excess \( CH_3OH \). A complex of the form (3.10.1) is consistent with this data. However, there are other plausible products in agreement with the n.m.r. data.

3.14 The Reaction Between the Ir-SF\(_2^+\) Complex (3.1.1) and \((H_3C)_2NSi(CH_3)_3\) (3.14.1)

In addition to \( CH_3OSi(CH_3)_3 \), there are a wide range of silicon reagents which may undertake a nucleophilic substitution reaction at sulphur in (3.1.1). One such species is \((H_3C)_2NSi(CH_3)_3\) (3.14.1).

In order to investigate if (3.14.1) would displace a fluorine bound to sulphur in (3.1.1) with an \(-N(CH_3)_2\) group, a sample of the complex was treated with an equimolar amount of the silicon reagent in \( d_2 \)-dichloromethane. The purple solution turned yellow indicating that a reaction had taken place.

Results

The \( ^{19}F\{^{1}H\} \) n.m.r. spectrum of the solution, at 178K, (see diagram 3.10) confirms that the resonances assigned to (3.1.1) are absent. These have been replaced by a new signal in the Ir-F region of the spectrum, at \( \delta = 345.4 \)
Diagram 3.10

$^{19}$F n.m.r spectrum of (3.11.1) at 178K
p.p.m. and another in the \(-S-F\) region at \(\delta-45.3\) p.p.m. The intensities of these are the same.

There is a sharp peak at \(\delta-151.2\) p.p.m. which confirms the presence of [BF\(_4\)]\(^-\) and a singlet at \(\delta-157.6\) p.p.m. with satellites arising from \(^1J(F_{Si})\) which indicate that \((H_3C)_3SiF\) has been formed.

The \(^{31}P(\text{H})\) n.m.r. spectrum at 178K is an ABXY pattern.

Conclusions

When \((3.1.1)\) is treated with an equimolar amount of \((3.14.1)\) in \(d_2\)-dichloromethane, a reaction takes place at 178K. \((H_3C)_3SiF\) is eliminated and the resulting iridium complex contains one fluorine bound to iridium (\(F_C\)) and another bound to sulphur (\(F_A\)). The resonances corresponding to these fluorines indicate that they are from the same species, because each contains a doublet with matching coupling in the other. In addition both signals contain a triplet due to equal coupling between each fluorine and the phosphorus nuclei. It is thought coincidental that \(^2J(F_CP)\) and \(^2J(F_CP')\), \(^3J(F_AP)\) and \(^3J(F_AP')\) are the same, because the phosphine ligands are chemically non-equivalent, as indicated by the \(^{31}P(\text{H})\) n.m.r. spectrum.

The data are consistent with \((3.1.1)\) undertaking a nucleophilic substitution reaction with \((3.14.1)\) at sulphur to generate a complex containing an \(\text{Ir-SFN(CH}_3)_2^+\)
group. This is illustrated in eqn. 3.11.

Eqn. 3.11

\[ \text{Cl} - \text{Ir} - \text{SF}_2^*[\text{BF}_4^-] + \text{Me}_3\text{N} \text{SiMe}_3 \rightarrow \text{Cl} - \text{Ir} - [\text{SF}_A(\text{NMe}_2)]^+[\text{B(\text{BF})}_4]^- \]

The n.m.r. data of (3.11.1) are given in table 3.9 below:

Table 3.9

$^{19}$F n.m.r. Data of (3.11.1) at 178K

<table>
<thead>
<tr>
<th>$^\text{F}_X$</th>
<th>$\delta$/p.p.m.</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^\text{F}_A$</td>
<td>-45.3</td>
<td>$^3J(P,P')=18$ $^3J(F_C)=17$</td>
</tr>
<tr>
<td>$^\text{F}_B$</td>
<td>-151.2</td>
<td></td>
</tr>
<tr>
<td>$^\text{F}_C$</td>
<td>-345.4</td>
<td>$^2J(P,P')=34$ $^3J(F_A)=17$</td>
</tr>
</tbody>
</table>

Note: When the $^{19}$F n.m.r. spectrum is recorded with retention of $^1$H-coupling the peak assigned to $^\text{F}_A$ is broad and without any structure due to unresolved couplings to the protons of the $-\text{N(CH}_3)_2$ group.

As the solution is warmed, all resonances remain sharp and $^3J(\text{PF}), ^3J(\text{FF})$ and $^2J(\text{PF})$ are resolved up to 306K. This is consistent with the complex not being susceptible to significant intermolecular fluorine exchange, on the n.m.r. timescale, at 306K and concurs with the stability of (3.8.1) to such exchange under the
same conditions. It is also apparent from the retention of $^{1}J(FSi)$ that $(\text{H}_3\text{C})_3\text{SiF}$ does not significantly interact with the complex up to this temperature.

The reaction was repeated using (3.1.1) with 99% $^{13}\text{C}$-enrichment at carbonyl and $(\text{H}_3\text{C})_2\text{NSi(\text{CH}_3)_3}$ to establish the ligand arrangement at iridium in the product on the basis of $^{2}J(\text{F}_\text{C})$.

The resonance assigned to $\text{F}_\text{C}$ in the product contains an additional doublet splitting ($^{2}J(\text{F}_\text{C}) \approx 71\text{Hz}$). The magnitude of this coupling implies that the carbonyl is trans to $\text{F}_\text{C}$ in the complex, as illustrated at (3.11.1).

In an attempt to dislodge the sole remaining fluorine bound to sulphur ($\text{F}_\text{A}$) or $\text{F}_\text{C}$ in (3.11.1) the reaction was attempted between (3.11.1) and an equimolar amount of (3.14.1) in d$_2$-dichloromethane.

The $^{19}\text{F}(^1\text{H})$ n.m.r. spectrum was recorded between 178K and 306K and the resonances of (3.11.1) were present throughout. This indicates that the complex is stable to further substitution of fluoride by an $-\text{N(\text{CH}_3)_2}$ group under these experimental conditions.

3.15 Conclusions on the Formation and Reactivity of the Ir-$\text{SF}_2^+$ Complex (3.1.1).

When the Ir-$\text{SF}_3$ complex (2.1.1) is treated with an equimolar amount of BF$_3$, fluoride is transferred from the sulphur to boron. This generates a novel Ir-$\text{SF}_2^+$ complex
(3.1.1). When the reaction is repeated with 99% $^{13}$C-enrichment at carbonyl in (2.1.1) the value of $^2J(F_C C)$ in the product suggests that the ligand arrangement at iridium is not changed after the fluoride transfer.

The Ir-SF$_2^+$ complex (3.1.1) is stable to intermolecular fluorine exchange in d$_2$-dichloromethane, up to 306K, in the presence of HF and does not undertake a chemical reaction with the acid.

When (3.1.1) is treated with an equivalent of BF$_3$, a co-ordinated [BF$_4$]$^-$ group via a fluorine bridge is formed. This rearranges on warming the sample to form an isomer in which the sulphur group is believed to be trans to the fluoride and carbonyl trans to the chloride.

When the salt is reacted with N(CH$_3$)$_3$, P(CH$_3$)$_3$ or NH(CH$_3$)$_2$, the bases attack the [BF$_4$]$^-$ counter ion forming an adduct with BF$_3$ and releasing a fluoride ion. This combines with sulphur to regenerate the Ir-SF$_3$ complex (3.1.1).

When (3.1.1) is treated with an equimolar amount of anhydrous CH$_3$OH one of the -S-F's is displaced by a CH$_3$O-group forming a complex with an Ir-SFOCH$_3^+$ group. The value of $^2J(F_C C)$ obtained when this reaction is repeated with 99% $^{13}$C-enrichment at carbonyl in (3.1.1), indicates that the ligand arrangement at iridium is not affected as a result of this substitution reaction.

When a 100% excess of CH$_3$OH is reacted with (3.1.1) there is no soluble product which contains an -S-F bond.
This is consistent with the alcohol displacing the sole remaining fluorine bound to sulphur with a CH$_3$O- group, to give a complex containing an Ir-S(OCH$_3$)$_2^+$ group.

A species with identical $^{19}$F($^1$H) n.m.r. parameters to the product of the reaction of (3.1.1) with CH$_3$OH is obtained when the reaction is repeated between (3.1.1) and CH$_3$OSi(CH$_3$)$_3$. The product of elimination in this case is $(H_3C)_3SiF$

Other alcohols can also displace a fluorine bound to sulphur in (3.1.1). However, (2,2,2)-trifluoroethanol is believed to be too weakly nucleophilic to participate in this reaction. (2,4,6)-trinitrophenol is thought to be too bulky to displace a fluorine bound to sulphur in (3.1.1) and CH$_3$CH$_2$SH is believed not to displace one of these fluorines because of the disfavoured formation of a S-S single bond in the product.

The complex (3.1.1) will react with $(H_3C)_2NSi(CH_3)_3$ to generate a complex with an Ir-SF(N(CH$_3$)$_2^+$ group. However the reaction with a 100% excess of the silicon reagent does not cause displacement of the second fluorine bound to sulphur, presumably because of steric blocking or kinetic considerations.

When this reaction is repeated using (3.1.1) with 100% $^{13}$C-enrichment at carbonyl, the ligand arrangement at iridium is not affected as a result of this substitution reaction.

In all of the substituted -S-F derivatives the
resonance of the \([\text{BF}_4]^-\) anion is sharp relative to that of (3.1.1). This may be explained by a greater degree of ion pairing between the cation and anion in (3.1.1) relative to the other complexes with resultant broadening due to quadrupolar relaxation by the boron.
Chapter 4

4.0 The Reaction of $t$-IrCl(CO)$[P(CH_3)_3]_2$ with SF₄.

$t$-IrCl(CO)$[P(CH_3)_3]_2$ (4.0.1), like $t$-IrCl(CO)$[P(CH_2CH_3)_3]_2$ (2.0.1), is a square planar Ir⁺ complex with the potential to undergo oxidative addition reactions. The main difference between these starting materials is the steric bulk of the phosphines.

The reaction between SF₄ and an equimolar amount of (4.0.1) was investigated in d₂-dichloromethane to study the effect of the small trimethylphosphine, P(CH₃)₃, ligands, relative to the bulkier triethylphosphine, P(CH₂CH₃)₃, on the course of this addition. CsF was added to remove HF from the solution.

Results

The $^{19}$F($^1$H) n.m.r. spectrum of the reaction solution, at 178K, (see diagram 4.1) indicates that the sole metal-based product (4.1.1) of reaction (see eqn. 4.1) gives rise to three resonances only, in contrast with the four of (2.1.1) at this temperature. The two signals at higher frequency, $\delta+68.4$ and $\delta-61.2$ p.p.m., are in the region associated with fluorine bound to a main group element, which in this case is sulphur. The one at $\delta+68.4$ p.p.m. is twice the intensity of the first. The third resonance, at $\delta-382.3$ p.p.m., has the same intensity as
Diagram 4.1

$^{19}\text{F}$-$^1\text{H}$ n.m.r. spectrum of (4.1.1) at 178K.
Diagram 4. 1 exp

Expansion of $F_A$, $F_E$ and $F_C$ in

(4.1.1)
Diagram 4.1a
Coalescence of peaks of $f_A$ and $f_E$
in (4.1.1)
the one at $\delta-61.2$ p.p.m. and is in the region of the
spectrum associated with an Ir-F.

The $^{31}$P($^1$H) n.m.r. spectrum of this complex at 178K
(see diagram 4.2) consists of one first order resonance at
$\delta+4.4$ p.p.m.

Conclusions

The data are consistent with SF$_4$ undergoing oxidative
addition with (4.0.1) to generate an -SF$_3$ complex.
However, there are only two -S-F environments, one of
which contains twice the number of fluorines as the other.
The two equivalent -S-F's are presumably those bound
axially to sulphur, as the three equatorial sites are
thought to be occupied by one fluorine, a lone pair and
the iridium fragment of the complex. The axial fluorines
are believed to be equivalent as the result of motion
about the Ir-S bond, which is fast on the n.m.r.
timescale. There is no static structure, with trigonal
bipyramidal geometry at sulphur, in which these fluorines
are chemically equivalent.

Resolved couplings show that all three fluorine
resonances assigned to (4.1.1) denote fluorines on the
same complex. The signal at $\delta+68.4$ p.p.m. is a resolved
doublet [$^2$J(F$_E$)= 67.5Hz] of triplets [$^3$J(P)= 23.8Hz] of
doublets [$^3$J(F$_C$)= 6.5Hz], due to couplings to F$_E$, P and
F$_C$, as shown. These couplings are matched in the other
resonances. In addition, the signal at $\delta-61.2$ p.p.m.
contains a doublet [$^3$J(F$_C$)= 8.3Hz], and equivalent to one
Diagram 4.2

$^{31}$P{$^1$H} n.m.r. spectrum of (4.1.1) at 178K.
in the resonance assigned to $F_C$, which has an additional triplet [$^{2}J(P)= 34.5\text{Hz}$] from coupling to the equivalent phosphorus nuclei.

The proposed structure of (4.1.1), which is substantiated later, has chloride trans to the fluoride and carbonyl trans to the $-\text{SF}_3$ group. This is illustrated in eqn. 4.1 and the n.m.r. data are listed in table 4.1:

Eqn. 4.1

\[
\begin{array}{c}
\begin{array}{c}
PMe_3 \\
\mid \\
OC - \text{Ir} - Cl \\
\mid \\
PMe_3
\end{array}
\end{array}
\quad + \text{SF}_4
\quad \begin{array}{c}
\begin{array}{c}
PMe_3 \\
\mid \\
OC - \text{Ir} - S \\
\mid \\
PMe_3
\end{array}
\end{array}
\]

(4.0.1) \quad (4.1.1)

$F_A$ and $F_A'$ denote the fluorines which are axially bound to sulphur. These are indistinguishable and will be referred to solely as $F_A$ in subsequent discussion of (4.1.1)

$F_E$ denotes the fluorine bound equatorially to sulphur

$F_C$ denotes the fluorine bound directly to the iridium
Table 4.1
The n.m.r. data of (4.1.1) in d$_2$-dichloromethane, at 178K.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>δ/p.p.m.</th>
<th>2J(FA)</th>
<th>3J(P)</th>
<th>3J(FC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>+68.4</td>
<td>67.5</td>
<td>23.8</td>
<td>6.5</td>
</tr>
<tr>
<td>FE</td>
<td>-61.2</td>
<td>67.5</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>FC</td>
<td>-382.3</td>
<td>34.5</td>
<td>8.3</td>
<td>6.5</td>
</tr>
<tr>
<td>P</td>
<td>+4.4</td>
<td>34.5</td>
<td></td>
<td>23.8</td>
</tr>
</tbody>
</table>

In the absence of a crystal of (4.1.1) which was suitable for an X-ray crystallographic study, or a viable synthesis of t-IrCl($^{13}$CO)[P(C$_3$H$_3$)$_3$]$_2$, a definitive assignment of the ligand arrangement was not possible. However, the $^{19}$F($^1$H) n.m.r. spectra of solutions of the product of the reaction between t-Ir(NCO)($^{13}$CO)[P(CH$_3$)$_3$]$_2$ and SF$_4$ illustrate that the chemical shifts of the Ir-F's in the isomeric products are sensitive to the trans ligand ($\delta$F = -385.5 p.p.m. when -NCO is trans, and -337.2 p.p.m. when carbonyl is trans). There are several complexes containing an Ir-F bond (see fig. 4.1) for which $^{19}$F n.m.r. data are available[27] (see table 4.2). Some are illustrated in fig. 4.1:
Fig. 4.1

Some Iridium Complexes Containing Fluoride Ligands

The complexes in fig. 4.1 are products of reaction of the respective t-IrCl(CO)[P]₂, (P= P(CH₂CH₃)₃ or P(C₆H₅)₃) with XeF₂. The ¹⁹F n.m.r. data of these species are listed in table 4.2:
Table 4.2

$^{19}$F n.m.r. data of the complexes in fig. 4.1

<table>
<thead>
<tr>
<th>$F_X$</th>
<th>$\delta$/p.p.m.</th>
<th>L</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>FB</td>
<td>-470.6</td>
<td>F</td>
<td>P(CH$_2$CH$_3$)$_3$</td>
</tr>
<tr>
<td>FD</td>
<td>-288.5</td>
<td>CO</td>
<td>P(CH$_2$CH$_3$)$_3$</td>
</tr>
<tr>
<td>FF</td>
<td>-400.7</td>
<td>Cl</td>
<td>P(CH$_2$CH$_3$)$_3$</td>
</tr>
<tr>
<td>FG</td>
<td>-299.1</td>
<td>CO</td>
<td>P(CH$_2$CH$_3$)$_3$</td>
</tr>
<tr>
<td>FH</td>
<td>-448.2</td>
<td>F</td>
<td>P(C$_6$H$_5$)$_3$</td>
</tr>
<tr>
<td>FI</td>
<td>-276.6</td>
<td>CO</td>
<td>P(C$_6$H$_5$)$_3$</td>
</tr>
<tr>
<td>FJ</td>
<td>-380.5</td>
<td>Cl</td>
<td>P(C$_6$H$_5$)$_3$</td>
</tr>
<tr>
<td>FK</td>
<td>-292.2</td>
<td>CO</td>
<td>P(C$_6$H$_5$)$_3$</td>
</tr>
</tbody>
</table>

L = ligand trans to $F_X$

In each of the complexes in fig. 4.1 the chemical shift of the fluoride trans to carbonyl is to high frequency of -300 p.p.m. This does not depend on whether the phosphines of the complex are P(CH$_2$CH$_3$)$_3$, or the bulkier and much less basic P(C$_6$H$_5$)$_3$. It suggests that the electronic properties of the phosphines have considerably less influence on the chemical shift of the Ir-F than the ligand trans to that fluoride. Thus the chemical shift of $F_C$ in (4.1.1), $\delta$-382.2 p.p.m. indicates that the fluoride is trans to the chloride and the carbonyl is therefore trans to the -SF$_3$ group, as
4.1 A Discussion of Exchange Processes Relating to (4.1.1)

The chemical equivalence of the fluorines bound axially to sulphur, as illustrated by the n.m.r. data, infer that (4.1.1) is subject to fluorine exchange at 178K. It is clear from the retention of couplings that the mechanism is intramolecular, either a rotation or a rocking motion about the Ir-S bond which is fast on the n.m.r. timescale. Whatever the nature of this motion, it is less restricted in (4.1.1) than in all -SF₃ complexes in which the phosphines are P(CH₂CH₃)₃. This strongly suggests that the steric properties of the phosphine ligands are important. The electronic properties of P(CH₃)₃ and P(CH₂CH₃)₃ are similar.

It is probable that the σ-accepting ability of the carbonyl results in the removal of electron density from σ-bonding orbitals of the Ir-S bond. However, the importance of such electrons in inhibiting motion around the Ir-S centre is not fully understood. In any case, in the major product of reaction between t-Ir(NCO)(CO)[P(CH₂CH₃)₃]₂ and SF₄ the two fluorines bound axially to sulphur are chemically distinct below 200K. The -SF₃ group in this complex is also thought to be trans to carbonyl.

As the solution is warmed, the two high frequency
resonances broaden and no couplings are resolved at 248K. On further warming they coalesce at 301K. The third signal, which denotes $F_C$, retains couplings to these fluorines at this temperature, illustrating that the broadening is due to intramolecular exchange.

The most likely cause of this broadening is a Berry-pseudorotation (see chapter 1). However, as the solution is warmed further the two high frequency peaks continue to broaden, and coalesce at 301K. At this temperature, the resonance which denotes $F_C$ has lost coupling to $F_A$ and $F_E$. This confirms that intermolecular fluorine exchange has become important.

The $^{31}P(\text{H})$ n.m.r. at 301K is a doublet due to coupling to $F_C$ only, which illustrates that $F_A$ and $F_E$ are undergoing a mechanism of exchange which is fast on the n.m.r. timescale, and $F_C$ is not affected by this process.

The activation energy of the exchange processes involved, excluding the component which renders the fluorines bound axially to sulphur equivalent, has been calculated by the method described in chapter 2.

$$\Delta G_{301} = 49 \pm 0.5 \text{kJmol}^{-1}.$$
4.2 The Reaction of \((4.0.1)\) with \(\text{SF}_4\) and \(\text{BF}_3\)

When \((4.1.1)\) is treated with an equimolar amount of \(\text{BF}_3\), the reaction proceeds in a similar manner to that of the analogous system with \(\text{P(CH}_2\text{CH}_3)\text{_3}\) ligands. The chemical shift of \(\text{F}_A\) in the sole \(\text{Ir-SF}_2^+\text{[BF}_4^-\) complex is \(-24.3\) p.p.m. and that of \(\text{F}_C\) is \(-370.1\) p.p.m.

In an attempt to establish the ligand arrangement at iridium in \((4.1.1)\) the complex was reacted with a 100% excess of \(\text{BF}_3\) to see if the formation of an \(-\text{Ir-F}\text{-BF}_3\) adduct would produce a rearrangement similar to that described for the analogous system with \(\text{P(CH}_2\text{CH}_3)\text{_3}\) ligands.

**Results**

The \(^{19}\text{F}^{(1)}\text{H}\) n.m.r. spectrum of a \(d_2\)-dichloromethane solution containing \(\text{t-IrCl(CO)[P(CH}_3)\text{_3]}_2\), a slight excess of \(\text{SF}_4\) and just over 100% excess of \(\text{BF}_3\) indicates that there are two complexes present which contain an \(-\text{SF}_2\) group. This is illustrated in eqn. 4.2. The n.m.r. data of these species are given in the tables below together with the corresponding data from the analogous experiment involving the complexes with \(\text{P(CH}_2\text{CH}_3)\text{_3}\) ligands.
Eqn. 4.2

\[
PMe_3 \quad \text{OC} - \text{Ir} - \text{Cl} \quad \text{OC} - \text{Ir} - \text{Cl}
\]

\[
\text{PMe}_3 \quad +\text{SF}_4 \quad \text{I}_2\text{BF}_3
\]

\[
\frac{2\text{BF}_3}{\text{PMe}_3} \quad \text{(4.0.1)} \quad \text{Cl} \quad \text{PMe}_3 \quad \text{S(FA)}_2
\]

\[
\text{PMe}_3 \quad \text{F}_2\text{C}:\text{B(FB)}_3 \quad \text{F}_2\text{C}:\text{B(FB)}_3
\]

\[
\text{S(FA)}_2 \quad \text{Cl} \quad \text{PMe}_3
\]

\[
\text{(4.2.1)} \quad \text{(4.2.2)}
\]

Table 4.3

\[1^9\text{F}^{(1H)}\text{n.m.r. data from the products in eqn. 4.2}\]

\[
\begin{align*}
\text{FX (4.2.1)} & \quad \delta/\text{p.p.m.} \\
\text{FA} & \quad -24.3 \\
\text{FC} & \quad -264.4 \\
\text{FX (4.2.2)} & \quad \delta/\text{p.p.m.} \\
\text{FA} & \quad -51.7 \\
\text{FC} & \quad -272.1
\end{align*}
\]

(4.2.1) = initial reaction product
(4.2.2) = product after rearrangement

The chemical shift of FA in (4.2.1) is comparable with the shift in the product of reaction between (4.0.1), SF₄ and an equimolar amount of BF₃.
Table 4.3(a)

$^{19}F(1H)$ n.m.r. data from section 3.4 (see chapter 3)

<table>
<thead>
<tr>
<th></th>
<th>$F_X$ (I.P.) $\delta$/p.p.m.</th>
<th>$F_X$ (R.P.) $\delta$/p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>-52.5</td>
<td>-13.3</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-280.6</td>
<td>-269.2</td>
</tr>
</tbody>
</table>

I.P. = initial reaction product
R.P. = product of rearrangement

Conclusions

When (4.1.1) is treated with a 100% excess of BF$_3$ a rearrangement takes place. The chemical shift of $F_A$ in the rearranged product is similar to the corresponding shift in the Ir-SF$_2^+$[BF$_4$]$^-$ complex with chloride $trans$ to the sulphur group. It is therefore concluded that the -SF$_2$ group is not $trans$ to chloride before rearrangement has taken place. This suggests that the -SF$_3$ group from which the Ir-SF$_2^+$ complex derives, is not $trans$ to chloride either. This shift is not affected by co-ordinating BF$_3$ to $F_C$.

It is interesting to note that rearrangement has taken place in this system at 178K without requiring heating of the solution. This contrasts with the complexes containing $P(CH_2CH_3)$ ligands in which no rearrangement was observed until 245K. This may also be
the result of the larger steric bulk of the P(CH₂CH₃)₃ ligands inhibiting rearrangement.

A further apparent anomaly in this system is the presence of resonances in the spectrum due to unreacted SF₄. In the case of the analogous Ir-P(CH₂CH₃)₃ system an adduct of the form Ir-F:BF₃ is not formed as long as unreacted SF₄ remains in the solution. This may be explained by BF₃ having a greater affinity for the formation of an adduct with SF₄ than an Ir-F. This implies that the steric bulk of the phosphines increases the energy barrier to formation of an adduct at the Ir-F by a sufficient amount to shift the balance in favour of an adduct formation between BF₃ and SF₄.

With P(CH₃)₃ bound to iridium, however, this barrier may be sufficiently reduced to shift the balance in the opposite direction.

4.3 The Reaction of t-IrCl(CO)[P(C₆H₅)₃]₂ (1.0.1) with SF₄.

The object of this experiment was to investigate the effect of the bulky P(C₆H₅)₃ ligands on the ease of formation and stereochemical arrangement of ligands in the product of reaction of SF₄ with (1.0.1), relative to the corresponding reactions involving SF₄ and t-IrCl(CO)[P]₂ (P= P(CH₃)₃ or P(CH₂CH₃)₃).
Results

Initial \(^{19}\text{F}(^{1}\text{H})\) n.m.r. studies of a solution of (1.0.1) and a 10% excess of SF\(_4\), over the temperature range 178K-298K, indicated that the resonances of unreacted SF\(_4\) and a trace amount of SOF\(_2\) were observed over the entire range. There was no evidence to suggest that an oxidative addition had taken place.

However, after the n.m.r. tube had been placed in warm water, at 323K, for two hours the solution turned paler. This suggested that a reaction had taken place.

The \(^{19}\text{F}(^{1}\text{H})\) n.m.r. spectrum was subsequently recorded at 178K and showed several changes to the initial one at this temperature.

Three signals of equal intensity, at \(\delta\) (+68.1, +44.3 and -74.2) p.p.m. in the region associated with -S-F's provide evidence that a complex containing an Ir-SF\(_3\) group has been formed. A further new resonance, at \(\delta\) -325.2 p.p.m., is in the Ir-F region and is equal in intensity to each of these three signals. From the appearance of common couplings it is clear that the three -S-F resonances are from the same complex. It is likely that the fourth peak also belongs to the same complex (4.3.1), although it is broad and structureless. All these signals are broad because of the low solubility of the complex.

There is also a sharp doublet, \([^{1}\text{J}(\text{FP})= 652\text{Hz}]\), at \(\delta\)-39.8 p.p.m., which indicates the presence of \(t\)-P(C\(_6\)H\(_5\))\(_3\)F\(_2\). This is believed to have formed as a result
of attack on the phosphines by SF$_4$ when the solution was warmed to 323K.

The $^{31}$P($^1$H) n.m.r. spectrum at 308K contains a triplet, [$^1$J(PF) = 652Hz], which confirms the presence of t-P(C$_6$H$_5$)$_3$F$_2$. The only other signal in the spectrum is a broad doublet [$^2$J(PF) = 31Hz].

Conclusions

When (1.0.1) is treated with SF$_4$ an oxidative addition reaction takes place, although more forcing conditions are required than for the analogous reactions between SF$_4$ and the complexes with smaller alkyl phosphines [P(CH$_3$)$_3$ and P(CH$_2$CH$_3$)$_3$]. This is consistent with the idea that bulky, $\pi$-accepting phosphine ligands do not favour oxidative addition reactions at transition metal centres.

The chemical shifts of the -S-F resonances in the product (4.3.1) are similar to those obtained for other -SF$_3$ complexes with P(CH$_2$CH$_3$)$_3$ ligands (see chapter 2). This suggests that the $\pi$-accepting phosphines do not have a radically different effect on these fluorines relative to the $\pi$-donating ones.

The chemical shift of F$_{C}$ more closely resembles those of other Ir-F's which are trans to a carbonyl (see table 4.1) than those which are trans to a halide. On this basis the metal fluoride of (4.3.1) is assigned trans to the carbonyl. The equation of the reaction is given below.
and n.m.r. data of the product are listed in table 4.4:

Eqn. 4.3

\[
\begin{align*}
\text{PPh}_3 & \quad \xrightarrow{\text{+ SF}_4} \quad \text{PPh}_3 \\
\text{OC} & \quad \text{Ir} \quad \text{Cl} \\
\uparrow & \quad \downarrow \\
\text{PPh}_3 & \quad \text{Cl} \quad \text{Ir} \quad \text{S} \\
\uparrow & \quad \downarrow \\
\text{PPh}_3 & \quad \text{OC} \quad \text{FA} \quad \text{FE} \\
\end{align*}
\]

Table 4.4

\[ {^{19}\text{F}}(^{1}\text{H}) \text{ n.m.r. data of (4.3.1) in d}_2\text{-dichloromethane at } 178\text{K} \]

<table>
<thead>
<tr>
<th>( \delta / \text{p.p.m.} )</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{FA} )</td>
<td>+ 68.1</td>
</tr>
<tr>
<td>( \text{FA}' )</td>
<td>+ 44.3</td>
</tr>
<tr>
<td>( \text{FE} )</td>
<td>- 74.2</td>
</tr>
<tr>
<td>( \text{FC} )</td>
<td>-325.2</td>
</tr>
</tbody>
</table>

Presumably couplings between the phosphorus nuclei and the \( -\text{S-F}'s \) are not resolved at 308K, because the spectral lines are broadened by exchange. There was no HF scavenger used in this reaction.

4.4 The Reaction of \( t\text{-IrF(CO)[P(C}_6\text{H}_5)_3]_2 \) with \( \text{SF}_4 \).

\( t\text{-IrF(CO)[P(C}_6\text{H}_5)_3]_2 \) (4.0.2) is the only known \( \text{Ir}^1 \) complex of the type \( t\text{-IrF(CO)[P]_2} \) (\( \text{P=} \) any phosphine ligand). This extra \( \text{Ir-F} \) may enable more substantial
characterization by $^{19}\text{F}(^1\text{H})$ n.m.r. spectroscopy of any reaction product.

The reaction between the analogous chloro-complex and $\text{SF}_4$ requires refluxing in $\text{d}_2$-dichloromethane before any product forms. The ease of formation of any $-\text{SF}_3$ derivative of (4.0.2) relative to the corresponding chloro-complex should determine if electronic or steric factors predominate in the rate determining step of the reaction.

If electronic considerations are the major factor, chloride is a better $\tau$-donor ligand than fluoride and therefore the chloro-complex should oxidatively add $\text{SF}_4$ more readily than the fluoro-analogue.

If steric factors control the rates of these reactions, the fluoro-complex will react with $\text{SF}_4$ faster than the chloro-analogue, as fluoride is smaller in size than chloride.

Results

In the $^{19}\text{F}(^1\text{H})$ n.m.r. spectrum of a $\text{d}_2$-dichloromethane solution of $t$-IrF(CO)[P(C_6H_5)_3]_2$ and a 10% excess of $\text{SF}_4$ at 178K (see diagram 4.3), there are three resonances of equal intensity. The shifts of these are: $\delta+66.3$, $+49.8$ and $-76.3$ p.p.m. These are assigned to the chemically distinct fluorines of an $-\text{SF}_3$ ligand. In addition, two resonances at $\delta-291.8$ and $-355.6$ p.p.m. in the Ir-F region of the spectrum are equal in intensity to
Diagram 4.3

$^{19}$F n.m.r spectrum of (4.4.1) at

178K

\[ \delta / \text{p.p.m.} \]
these three signals. This set of resonances is provisionally assigned to the product (4.4.1) of cis addition of SF$_4$, at the iridium centre, with both carbonyl and the sulphur group trans to a fluoride (see eqn.4.4):

Eqn. 4.4

\[
\begin{align*}
\text{PPh}_3 & \quad + \quad \text{SF}_4 \\
\text{OC} - \text{Ir} - F & \quad \xrightarrow{\text{FC}} \quad \text{FC} - \text{Ir} - \text{S} \\
\text{OC} & \quad \text{FA} \\
\text{PPh}_3 & \quad \text{FA} \\
\end{align*}
\]

Once again the low solubility of the complex and consequent broadness of the peaks has resulted in no direct coupling being observed between either of the Ir-F's and the -S-F's. However, the signals assigned FC and FC' each contain a doublet splitting, $[^{2}J(FCFC')=146\text{Hz}]$, which implies they belong to the same species. Each resonance is split into triplets as a result of each fluorine coupling equally to the mutually trans phosphorus nuclei. The magnitudes of these $^{2}J(FF)$'s are given in table 4.5.
Table 4.5

$^{19}$F($^1$H) n.m.r. data of (4.4.1), at 178K, in d$_2$-dichloromethane

<table>
<thead>
<tr>
<th>$F_x$</th>
<th>$\delta F$/ p.p.m.</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>+66.3</td>
<td>$^2J(F_A)$ = 181 $^2J(F_E)$ = 54</td>
</tr>
<tr>
<td>$F_A'$</td>
<td>+49.8</td>
<td>$^2J(F_A)$ = 181 $^2J(F_E)$ = 88</td>
</tr>
<tr>
<td>$F_E$</td>
<td>-76.3</td>
<td>$^2J(F_A')$ = 88 $^2J(F_A)$ = 54</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-291.8</td>
<td>$^2J(F_C)$ = 146 $^2J(P)$ = 30</td>
</tr>
<tr>
<td>$F_C'$</td>
<td>-355.6</td>
<td>$^2J(F_C')$ = 146 $^2J(P)$ = 28</td>
</tr>
</tbody>
</table>

Assignment of the chemical shifts to $F_C$ and $F_C'$ is based on the data obtained from the analogous complex containing two Ir-F's with P(CH$_2$CH$_3$)$_3$ ligands. This is one of the products (2.9.2) of reaction of t-Ir(NCS)(CO)[P(CH$_2$CH$_3$)$_3$]$_2$ and SF$_4$. The values of $^2J(FC)$ from $^{13}$C-enrichment at carbonyl in (2.9.2) indicate that the Ir-F to higher frequency is trans to the carbonyl (see chapter 2).

The $^{19}$F($^1$H) n.m.r. spectrum of the solution also contains a structureless peak at $\delta$ -5.3 p.p.m with peaks of matching intensity at $\delta$(-306.2 and -319.9) p.p.m. These resonances are assigned to an Ir-SOF complex which is thought to be the product of hydrolysis of the Ir-SF$_3$ species by moisture.

The peaks of unreacted SF$_4$ and its partial hydrolysis
product, SOF$_2$, are also present. The signals of SF$_4$ are unusually broad, compared with the spectrum of authentic samples of SF$_4$, at 178K.

Conclusions

The reaction between SF$_4$ and t-IrF(CO)[P(C$_6$H$_5$)$_3$]$_2$ in d$_2$-dichloromethane takes place at low temperature (below 195K). These are much milder reaction conditions than for the reaction between SF$_4$ and t-IrCl(CO)[P(C$_6$H$_5$)$_3$]$_2$ and this implies that the greater steric bulk of chloride, with respect to fluoride, inhibits that reaction.

In all studies of oxidative addition of SF$_4$ at unsaturated Ir$^+$ centres, displacement of the carbonyl ligand has not been observed. The ligands in the proposed structure of the product are no more likely to labilize or displace carbonyl. Accordingly, one of the coordination sites trans to a fluoride is assigned to carbonyl.

The other site must be occupied by a monoanionic ligand if the complex is to have no nett charge. This ligand cannot be chloride, as the $^{19}$F($^1$H) n.m.r. data for that complex are given in table 4.2. Neither is it thought to be hydride, because of the ease of reductive elimination of HF. In the absence of any other obvious candidate the ligand is deemed to be -SF$_3$. This gives the structure illustrated above and substantiated in the next section.

The broadness of the signals of SF$_4$ is thought to be
the result of fluorine exchange between the -S-F's and fluoride ions. These ions may be present as a result of decomposition of the Ir$^+$ starting complex. The resonances of the Ir-SF$_3$ complex are too sharp for this species to be involved in the exchange.

4.5 The Reaction of t-IrF(CO)[P(C$_6$H$_5$)$_3$]$_2$ with SF$_4$ and BF$_3$

The ability of BF$_3$ to remove a fluorine from an -SF$_3$ group to generate an -SF$_2^+$ species (see chapter 3) may be used to establish that both Ir-F's and the -SF$_3$ group in (4.4.1) are from the same complex. The conversion of an -SF$_3$ group to -SF$_2^+$ is also accompanied by a change in the chemical shift of the Ir-F resonance in the complex. It is therefore likely that F$_C$ and F$_C'$ belong to the same complex as the -SF$_3$ ligand if their chemical shifts are changed as (4.4.1) is converted to an Ir-SF$_2^+$[BF$_4$]$^-$ salt.

One possible complication is that BF$_3$ can also bind to an Ir-F to give a coordinated Ir-F:BF$_3$ group. This also causes a change to the chemical shift of the Ir-F. However, in section 4.4, BF$_3$ was shown to preferentially remove a fluorine from sulphur rather than forming any adduct with bound fluoride.

When an -F:BF$_3$ group is formed, the resonance of the Ir-F, at 178K, attains an extra quartet splitting, due to couplings to the three equivalent BF's.

t-IrF(CO)[P(C$_6$H$_5$)$_3$]$_2$ was treated with a 10% excess of
SF₄ in d₂-dichloromethane. The product was then treated with an equimolar amount of BF₃.

Results

The ¹⁹F(¹H) n.m.r. spectrum of the reaction solution at 178K indicates that there are no longer the resonances of an -SF₃ group present. These are replaced by a structureless peak in the region of the spectrum associated with the equivalent fluorines of an -SF₂ group (see table 4.6). In addition to this change, the signals corresponding to FC and FC' have changed their chemical shifts. These are given in table 4.6 and are believed to be from the salt (4.5.1) the formation of which is illustrated in eqn. 4.5:

Eqn. 4.5

\[
\begin{align*}
\text{PPh}_3 & \quad \text{PPh}_3 \\
\text{F}_C & \quad \text{F}_C \\
\text{F}_A & \quad \text{F}_A \\
\text{OC} & \quad \text{OC} \\
\text{PPh}_3 & \quad \text{PPh}_3
\end{align*}
\]

\[\text{F}_C - \text{Ir} - \text{S} - + \text{BF}_3 \quad \text{F}_C - \text{Ir} - [\text{S(F}_A)_2]^+ [\text{B(F}_B)_4]^-
\]

(4.4.1) (4.5.1)
Table 4.6

$^{19}$F($^1$H) n.m.r. data of (4.5.1) at 178K

<table>
<thead>
<tr>
<th>$F_X$</th>
<th>$\delta F$/p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>-47.2</td>
</tr>
<tr>
<td>$F_B$</td>
<td>-148.7</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-308.6</td>
</tr>
<tr>
<td>$F_C'$</td>
<td>-322.7</td>
</tr>
</tbody>
</table>

Conclusion

The conversion of the $-\text{SF}_3$ ligand to an $-\text{SF}_2^+$ group, with accompanying change in chemical shifts of $F_C$ and $F_C'$, is clear evidence that the $-\text{SF}_3$ group and both Ir-F’s of the product (4.4.1) in eqn. 4.4 are from the same complex.

4.6 The Reactions of $t$-Ir$X$(CO)[P(C$_6$H$_5$)$_3$]$_2$ ($X=\text{Br}$, NCO, NCS) with SF$_4$.

A study of the reactions of the series of complexes $t$-Ir$X$(CO)[P(C$_6$H$_5$)$_3$]$_2$ ($X=\text{Br}$, NCO, NCS) with SF$_4$ should help to establish if electronic or steric factors provide the main driving force in this type of reaction. In the case of ($X=\text{Br}$) an enhanced rate of reaction would be expected (relative to $X=\text{Cl}$) if electronic considerations are the predominant factor. However, if steric factors
are more important, the greater steric bulk of bromide would diminish the rate of reaction. On the basis of the relative rates of reaction of \( t\text{-IrF}(CO)[P(C_6H_5)_3]_2 \) and \( t\text{-IrCl}(CO)[P(C_6H_5)_3]_2 \) with \( SF_4 \), it would seem that steric factors predominate.

The solubilities of the chloro- and bromo-starting materials are comparable in each of the reaction solvents, \( d_2\)-dichloromethane and \( d_8\)-toluene. This factor is therefore not regarded as being significant.

In the cases of the complexes \( (X=\text{NCO or NCS}) \), both of which are nitrogen-bound to iridium, the rate of addition of \( SF_4 \) should be slower than for \( (X=\text{Cl}) \), if electronic factors provide the main driving force, because both \(-\text{NCO}\) and \(-\text{NCS}\) are \( \pi\)-acceptor ligands. However, the steric bulk around iridium is less when linear nitrogen-bonded ligands replace chloride.

Results

The n.m.r. data for each of the above reaction mixtures (which were studied in both \( d_2\)-dichloromethane and \( d_8\)-toluene) establish that, for each of the starting complexes \( t\text{-IrX}(CO)[P(C_6H_5)_3]_2 \) \( (X=\text{Br, NCO, NCS}) \), there is no reaction with \( SF_4 \). This remains the case after the solutions have been heated to reflux temperature for several hours.
Conclusions

There are thought to be two separate factors which result in the failure of the complexes \( t-IrX(CO)[P(C_6H_5)_3]_2 \) to react with \( SF_4 \).

1. In the case of \( X = Br \) this is explained by steric blocking by the ligands around iridium in the starting material. This supports the theory that steric hindrance due to increasing the size of the halide slows the rate of reaction.

2. In the cases of \( X = NCO \) and \( NCS \) the failure of the iridium complexes to react with \( SF_4 \), may result from a combination of electronic factors and steric blocking. In the reactions between the analogous iridium complexes with \( P(CH_2CH_3)_3 \) ligands and \( SF_4 \) (see chapter 2), the \( \pi \)-accepting properties of the pseudohalides is not sufficient to prevent the addition of \( SF_4 \). However, the starting complexes in those reactions have phosphine ligands which are \( \pi \)-donor ligands. In both \( t-Ir(NCO)(CO)[P(C_6H_5)_3]_2 \) and \( t-Ir(NCS)(CO)[P(C_6H_5)_3]_2 \) all four ligands around iridium are \( \pi \)-acceptors. This could render the iridium centres sufficiently electropositive to preclude addition of \( SF_4 \).

The other possibility is that the reactions are prevented by steric interactions involving the aryl groups of the phosphines and the pseudohalides. These could
4.7 The Reaction of \( t\)-IrCl(CO)[P(C₆H₁₁)₃]₂ with SF₄.

\( t\)-IrCl(CO)[P(C₆H₁₁)₃]₂ (4.0.3), like (1.0.1), contains bulky phosphine ligands. However, the P(C₆H₅)₃ ligands in (1.0.1) possess electron-withdrawing properties, while the tricyclohexylphosphine, P(C₆H₁₁)₃, ligands of (4.0.3) are strongly electron-releasing. This should promote oxidative addition at the iridium centre in (4.0.3) relative to (1.0.1).

SF₄ was treated with (4.0.3) in d₂-dichloromethane in order to investigate how the large, basic P(C₆H₁₁)₃ ligands would affect the formation of an Ir-SF₃ complex and also the effect they may have on the fluxionality at sulphur.

The \( ^{19}\)F(\(^{1}\)H) n.m.r. spectrum of the solution, at 178K, contains the signals of unreacted SF₄ and SOF₂ only.

The solution was heated at reflux temperature for two hours to try and induce a reaction. However, there was no apparent change in the solution. The subsequent \( ^{19}\)F(\(^{1}\)H) n.m.r. spectrum confirmed that no reaction took place.

Similar results are obtained when the reaction is carried out in d₈-toluene and heated to 373K for two hours.

The conclusion drawn from this experiment is that there is insufficient space around iridium to permit
bonding to two $\text{P(C}_6\text{H}_{11})_3$ ligands and an $-\text{SF}_3$ group.

4.8 The Reaction of $t$-$\text{IrCl}_2(\text{CO})[\text{P(CH}_2\text{CH}_3)_2(\text{C}_6\text{H}_5)]_2$ with $\text{SF}_4$.

In order to investigate how phosphine ligands containing both alkyl- and aryl- groups affect the formation of $\text{Ir-SF}_3$ complexes, $t$-$\text{IrCl}_2(\text{CO})[\text{P(CH}_2\text{CH}_3)_2(\text{C}_6\text{H}_5)]_2$ (4.6.0) was prepared and reacted with an equimolar amount of $\text{SF}_4$ in $d_2$-dichloromethane.

Results

The $^{19}\text{F}(^{1}\text{H})$ n.m.r. spectrum of the solution, at 178K, (see diagram 4.4) resembles the one from the reaction between $t$-$\text{Ir(NCO)}_2(\text{CO})[\text{P(CH}_2\text{CH}_3)_3]_2$ and $\text{SF}_4$, at this temperature. There are two sets of resonances assigned to $-\text{SF}_3$ groups, each of which is accompanied by a signal denoting an Ir-F. The ratio of the major (4.6.1) to the minor product (4.6.2) is approximately 5:2. These complexes are believed to be isomeric.

The three $-\text{S-F}$ resonances assigned to (4.6.1) are to high frequency of the corresponding ones of (4.6.2). The signal assigned to $\text{F}_C$ in (4.6.1) is shifted to low frequency, with respect to the comparable resonance of the (4.6.2). These trends are similar to the $^{19}\text{F}(^{1}\text{H})$ n.m.r. data of the products of reaction involving the $\text{Ir-NCO}$
Diagram 4.4

$^{19}$F n.m.r. spectrum of (4.6.1) and (4.6.2) at 178K
complex mentioned above. Similarly, the signals denoting $F_A$ and $F_A'$ of the major isomer are broad at 178K, whereas that of $F_E$ is a resolved triplet. The corresponding resonance of $F_E$ in the spectrum of (4.6.2) is a doublet of doublets, in which a smaller triplet is resolved. This triplet is due to equal coupling between $F_E$ and the mutually trans phosphorus nuclei.

The signals denoting $F_A$ and $F_A'$ in the spectrum of (4.6.2) are complex multiplets, as a result of resolved couplings to the other fluorines and phosphorus nuclei in the complex.

The equation for the reaction, proposed structures of the isomers and their $^{19}F(1H)$ n.m.r. data are given below:

Eqn. 4.6

\[
\begin{align*}
\text{PET}_2\text{Ph} & \quad \text{PET}_2\text{Ph} & \quad \text{PET}_2\text{Ph} \\
\text{OC} - \text{Ir} - \text{Cl} & \quad + \text{SF}_4 & \quad \text{OC} - \text{Ir} - \text{S}^+ + \text{Cl} - \text{Ir} - \text{S}^+ \\
\text{PET}_2\text{Ph} & \quad \text{PET}_2\text{Ph} & \quad \text{PET}_2\text{Ph} \\
\text{Cl} & \quad \text{F}_A & \quad \text{F}_E \\
\text{PET}_2\text{Ph} & \quad \text{PET}_2\text{Ph} & \quad \text{PET}_2\text{Ph} \\
\text{F}_C & \quad \text{F}_A & \quad \text{F}_C \quad \text{F}_A \\
\text{Cl} & \quad \text{F}_A & \quad \text{F}_E \\
\text{PET}_2\text{Ph} & \quad \text{PET}_2\text{Ph} & \quad \text{PET}_2\text{Ph} \\
(4.6.1) & \quad (4.6.2)
\end{align*}
\]
Table 4.7

$^{19}F(1\,^1H)$ n.m.r. data of (4.6.1) at 178K

<table>
<thead>
<tr>
<th>$F_X$</th>
<th>δ/p.p.m.</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>+76.7</td>
<td>2$J(F_E)$ = 63</td>
</tr>
<tr>
<td>$F_A'$</td>
<td>+58.7</td>
<td>2$J(F_E)$ = 63</td>
</tr>
<tr>
<td>$F_E$</td>
<td>-59.9</td>
<td>2$J(F_A,A')$ = 63</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-384.1</td>
<td>2$J(P)$ = 24</td>
</tr>
</tbody>
</table>

Table 4.7(a)

$^{19}F(1\,^1H)$ n.m.r. data of (4.6.2) at 178K

<table>
<thead>
<tr>
<th>$F_X$</th>
<th>δ/p.p.m.</th>
<th>Coupling/Hz (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>+65.3</td>
<td>2$J(F_A')$ = 182 2$J(F_E)$ = 53</td>
</tr>
<tr>
<td>$F_A'$</td>
<td>+48.1</td>
<td>2$J(F_A)$ = 182 2$J(F_E)$ = 88</td>
</tr>
<tr>
<td>$F_E$</td>
<td>-65.9</td>
<td>2$J(F_A')$ = 88 2$J(F_A)$ = 53</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-328.6</td>
<td></td>
</tr>
</tbody>
</table>

(*) - other couplings between $F_A$, $F_A'$, $F_E$ and $F_C$ and the phosphorus nuclei are resolved in this isomer, but for clarity these have been omitted.

Conclusions

When (4.6.0) is reacted with SF$_4$ in d$_2$-dichloromethane, there are two reaction products which
contain an \(-\text{SF}_3\) group. The proposed structures of these complexes are given in eqn. 4.6.

It is evident that motion around the Ir-S bond in (4.6.1) is more significant than in (4.6.2) at 178K. This is based on the relative broadness of the peaks of \(F_A\) and \(F_A'\), as well as the difference between \(J(F_EF_A)\) and \(J(F_EF_A')\) in each isomer (for values see tables 4.7 and 4.7(a)). This is thought to be related to the influence of the ligand \textit{trans} to the \(-\text{SF}_3\) group (see earlier).

Although there is no known viable synthesis of \(t\text{-IrCl}(^{13}\text{CO})\left[P(\text{CH}_2\text{CH}_3)\right]_2(\text{C}_6\text{H}_5)]_2\), and therefore no values of \(2J(F_C)\) available, the structures proposed for each complex are based on the similarities of each set of resonances with the corresponding set in the \(19\text{F}^{(1\text{H})}\) n.m.r. spectrum of the reaction between \(t\text{-Ir(NCO)}(\text{CO})\left[P(\text{CH}_2\text{CH}_3)\right]_3\) and \(\text{SF}_4\) (see earlier) for which \(^{13}\text{CO}\) data is available.

4.9 The Reaction of \(t\text{-IrCl}(\text{CO})\left[P(\text{CH}_2\text{CH}_3)(\text{C}_6\text{H}_5)\right]_2\) with \(\text{SF}_4\).

The reaction between \(t\text{-IrCl}(\text{CO})\left[P(\text{CH}_2\text{CH}_3)\right]_2(\text{C}_6\text{H}_5)]_2\) and \(\text{SF}_4\) is anomalous amongst chloro-iridium complexes, because it results in the formation of isomeric products. The reasons for this are not immediately apparent. However, it may be related to the mixed alkyl/aryl phosphine ligands. In order to investigate this further,
another iridium complex, \( t\text{-IrCl(CO)[P(CH_2CH_3)(C_6H_5)_2]} \) (4.7.0), has been prepared and treated with SF\(_4\) and the reaction studied in d\(_2\)-dichloromethane.

**Results**

The \(^{19}\text{F}(^{1}\text{H})\) n.m.r. spectrum of the reaction solution, at 178K, contains only one set of resonances which denote an \(-\text{SF}_3\) group bound to iridium. There is an associated Ir-F signal, at \( \delta -321.8 \) p.p.m. and the combined data are assigned to the fluorines of the product (4.7.1) of a \( \text{cis} \) addition of SF\(_4\) at the metal centre, with FC \( \text{trans} \) to the carbonyl ligand. It is clear that FC is from the same complex as the \(-\text{SF}_3\) group, because the signal assigned to this fluoride contains a resolved coupling to FA', \( [^3J(\text{FCFA}')= 8\text{Hz}] \), which is also discernable in the resonance of FA'.

The equation of the reaction (eqn. 4.7) and the \(^{19}\text{F}(^{1}\text{H})\) n.m.r. chemical shifts and main coupling constants of (4.7.1) are listed in table 4.8:

Eqn. 4.7

\[
\begin{array}{c}
\text{PEtPh}_2 \\
\text{OC} \quad \text{Ir} \quad \text{Cl} \\
\text{PEtPh}_2
\end{array} \quad + \text{SF}_4 \quad \begin{array}{c}
\text{Cl} \\
\text{OC}
\end{array} \quad \text{Ir} \quad \begin{array}{c}
\text{S} \\
\text{Cl}
\end{array} \\
\begin{array}{c}
\text{F}_A \\
\text{PEtPh}_2
\end{array} \quad \begin{array}{c}
\text{F}_C \\
\text{PEtPh}_2
\end{array}
\]

\[
(4.7.1)
\]
Table 4.8

$^{19}F(1H)$ n.m.r. Data of (4.7.1) at 178K

<table>
<thead>
<tr>
<th>$F_X$</th>
<th>$\delta$/p.p.m.</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>+ 64.9</td>
<td>$2J(F_A') = 190$  $2J(F_E) = 57$</td>
</tr>
<tr>
<td>$F_A'$</td>
<td>+ 47.1</td>
<td>$2J(F_A) = 190$  $2J(F_E) = 88$  $3J(F_C) = 8$</td>
</tr>
<tr>
<td>$F_E$</td>
<td>- 66.4</td>
<td>$2J(F_A') = 88$  $2J(F_A) = 57$</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-321.8</td>
<td>$3J(F_A') = 8$</td>
</tr>
</tbody>
</table>

Conclusions

The reaction between (4.7.0) and SF$_4$ proceeded in a manner similar to those involving SF$_4$ and the complexes $t$-IrCl(CO)[P(CH$_2$CH$_3$)$_3$]$_2$ and $t$-IrCl(CO)[P(C$_6$H$_5$)$_3$]$_2$. In the absence of a viable synthesis of the complex with $^{13}$C-enrichment at carbonyl, assignment of the ligand order in (4.7.1) has been based on the chemical shift of $F_C$.

The presence of only one Ir-SF$_3$ complex, as a result of this reaction, suggests that the mixed alkyl/aryl phosphines are not the sole reason for the formation of isomers in the related reaction between $t$-IrCl(CO)[P(CH$_2$CH$_3$)$_2$(C$_6$H$_5$)]$_2$ and SF$_4$. 
4.10 The Reaction of \( t\)-Ir(NCO)(CO)[P(CH₂CH₃)(C₆H₅)₂]₂ with SF₄.

In the two previous reactions attempted between SF₄ and Ir-NCO complexes, the results have been contrasting. \( t\)-Ir(NCO)(CO)[P(CH₂CH₃)₃]₂ reacts readily with SF₄, at 178K, to give two isomeric products, whereas \( t\)-Ir(NCO)(CO)[P(C₆H₅)₃]₂ is stable to this oxidative addition after refluxing the solution for several hours.

\( t\)-Ir(NCO)(CO)[P(CH₂CH₃)(C₆H₅)₂]₂ (4.8.0) is intermediate between these other Ir-NCO complexes. Perhaps the manner of reactivity of this species with SF₄ will help to explain the outcomes of the other reactions involving the NCO-complexes.

Results

The \(^{19}\text{F}(^1\text{H})\) n.m.r. spectrum of the reaction solution, at 178K, confirms that a reaction has taken place by this temperature. There are two sets of resonances, which are assigned to -SF₃ groups bound to iridium, each of which is accompanied by a signal denoting an Ir-F. The ratio of major (4.8.1) to minor product (4.8.2) is approximately 3:1. The proposed structures of these species, which are believed to be isomeric, are given in eqn. 4.8, together with their \(^{19}\text{F}(^1\text{H})\) n.m.r. data in (table 4.9).
Eqn. 4.9

\[
\begin{align*}
\text{PEtPh}_2 & \quad \text{PEtPh}_2 \\
\mid & \quad \mid \\
\text{OC} - \text{Ir} & \quad \text{Ir} - \text{NCO} + \text{SF}_4 \\
\mid & \\
\text{PEtPh}_2 & \quad \text{PEtPh}_2
\end{align*}
\]

(4.8.1) \quad (4.8.2)

Table 4.9

$^{19}\text{F}(^1\text{H})$ n.m.r. data of (4.8.1), at 178K

<table>
<thead>
<tr>
<th>$F_X$</th>
<th>$\delta$/p.p.m.</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>68.7</td>
<td>$2J(F_A') = 177 \quad 2J(F_E) = 66$</td>
</tr>
<tr>
<td>$F_{A'}$</td>
<td>52.4</td>
<td>$2J(F_A) = 177 \quad 2J(F_E) = 66$</td>
</tr>
<tr>
<td>$F_E$</td>
<td>-72.4</td>
<td>$2J(F_{A,A'}) = 66$</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-383.2</td>
<td>$2J(P) = 25$</td>
</tr>
</tbody>
</table>

Table 4.9(a)

$^{19}\text{F}(^1\text{H})$ n.m.r. data of (4.8.2), at 178K

<table>
<thead>
<tr>
<th>$F_X$</th>
<th>$\delta$/p.p.m.</th>
<th>Coupling/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_A$</td>
<td>55.6</td>
<td>$2J(F_A') = 183 \quad 2J(F_E) = 70$</td>
</tr>
<tr>
<td>$F_{A'}$</td>
<td>42.1</td>
<td>$2J(F_A) = 183 \quad 2J(F_E) = 92$</td>
</tr>
<tr>
<td>$F_E$</td>
<td>-76.8</td>
<td>$2J(F_{A,A'}) = 92 \quad 2J(F_A) = 70$</td>
</tr>
<tr>
<td>$F_C$</td>
<td>-319.0</td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

The major product of reaction (4.8.1) has the -SF₃ group trans to the carbonyl and the fluoride trans to -NCO. In the minor product (4.8.2), the -SF₃ group is assigned trans to -NCO, with the fluoride trans to carbonyl. Assignment is based on the chemical shift of F in each complex and the relative sharpness of the signals denoting \( F_A \) and \( F_A' \). For the complex in which the -SF₃ group is assigned trans to the stronger \( \pi \)-accepting carbonyl ligand, the resonances of the fluorines bound axially to sulphur are broader than in the isomer in which the -SF₃ group is trans to the less efficient \( \pi \)-accepting -NCO ligand. Perhaps this results from carbonyl removing \( \pi \)-electron density more effectively from the Ir-S bond than -NCO and hence rendering motion about this centre more facile.

The formation of isomeric products in this reaction suggests that steric parameters account for the absence of a second product in the reaction between SF₄ and \( t\text{-IrCl(CO)[P(CH_2CH_3)(C_6H_5)_2]}_2 \). It is clear from the reaction between SF₄ and \( t\text{-IrCl(CO)[P(CH_2CH_3)_2(C_6H_5)}]_2 \), that the halide can be trans to carbonyl in Ir-SF₃ complexes.

The similarity in the ratios of major to minor product in this reaction and the analogous one with \( P(CH_2CH_3)_3 \) ligands, also suggests that the steric bulk of the phosphines does not significantly affect the course of
these two reactions.

4.11 The Reaction Between t-Ir(NCS)(CO)[P(CH₂CH₃)(C₆H₅)₂]₂ and SF₄

It is clear from the preceding section, that the reactions between SF₄ and the complexes t-Ir(NCO)(CO)[P]₂ (P = P(CH₂CH₃)₃ or P = (CH₂CH₃(C₆H₅)₂) are not significantly affected by variation in P. The analogous reaction between t-Ir(NCS)(CO)[P(CH₂CH₃)₃]₂ and SF₄ remains unique, however, as there are several products, one of which contains an -SF₃ ligand with no accompanying Ir-F. In order to establish if P(CH₂CH₃)(C₆H₅)₂ ligands affect the course of this reaction, the complex t-Ir(NCS)(CO)[P(CH₂CH₃)(C₆H₅)₂]₂ (4.9.0) was prepared and reacted with SF₄ in d₂-dichloromethane.

Results

The ¹⁹F(¹H) n.m.r. spectrum of the reaction solution, at 178K, resembles that of the analogous solution for the Ir-NCS complexes with P(CH₂CH₃)₃ ligands, at this temperature. The ratios of the various products is slightly different, but there are still four Ir-SF₃ complexes present. One of these contains two Ir-F's and another has none. The solubilities of the complexes are low and hence, the peaks are poorly resolved, but this experiment has again illustrated that varying the
phosphine ligands from P(CH₂CH₃)₃ to P((CH₂CH₃)(C₆H₅))₂ does not significantly affect the addition of SF₄ at the iridium centre.

4.12 Conclusions on the Reactivity of SF₄ towards the Irᴵ Complexes t-Ir(CO)ₓ[P]₂ as a Function of P (P as listed below).

Varying the phosphine ligands on the Irᴵ starting material t-IrCl(CO)[P]₂ (P= P(CH₃)₃, P(CH₂CH₃)₃, P(CH₂CH₃)₂(C₆H₅), P(CH₂CH₃)(C₆H₅)₂, P(C₆H₅)₃, P(C₆H₁₁)₃) has produced some interesting results in terms of reactivity towards oxidative addition of SF₄. The complex which ought to be most reactive, on the basis of the donor properties of the phosphines i.e. the one containing P(C₆H₁₁)₃ ligands, is stable to this addition. The one which should be least reactive (of those investigated) i.e. the one with P(C₆H₅)₃ ligands does undertake this reaction although it requires heating above 313K for two hours. This discrepancy is best explained by steric blocking in the case of the complex with P(C₆H₁₁)₃ ligands. The other complexes of the series react with SF₄ under less forcing conditions.

One further interesting observation which has arisen out of these experiments relates to the series of complexes t-IrX(CO)[P(C₆H₅)₃]₂ (X= F, Cl, Br, NCO, NCS). This group is best split into two groups to explain the
experimental observations, the halides in one and F, NCO and NCS in the other.

In the case of the halo-complexes, the rate of addition (on electronic grounds) ought to increase with increasing donating ability of the halide i.e. the bromo-complex should be most reactive and fluoro-complex the least reactive to addition of SF$_4$. In practice, the reverse order is found, hence the reaction appears to be more influenced by the steric bulk of the halogen.

In the case of the pseudo-halide and fluoro-complexes, each of which has a similar steric effect at iridium, the reactivity is as expected on electronic grounds i.e. the complex with the $\pi$-donating fluoride reacts with SF$_4$ at 178K, whereas those with the $\pi$-accepting pseudohalides are stable to this reaction after a two hour reflux at 384K.

The formation of isomers in the reaction of SF$_4$ with t-IrCl(CO)[P(CH$_2$CH$_3$)$_2$(C$_6$H$_5$)]$_2$, which is unique amongst the chloro-complexes investigated, is less easily explained. Perhaps the alignment of the phosphine ligands allows for the accommodation of a chloride cis to the -SF$_3$ group, which in all other chloro-complexes (excluding the one with P(CH$_3$) ligands) is sterically prohibited.

Another unexpected observation is the absence of isomers in the products of reaction of t-IrF(CO)[P(C$_6$H$_5$)$_3$]$_2$ with SF$_4$. The sole product containing an -SF$_3$ group has the two metal fluorides
arranged mutually cis. Perhaps the isomer with these ligands mutually trans is disfavoured, because these ligands are \( \pi \)-electron donors and each would prefer to be trans to a ligand which is a \( \pi \)-electron acceptor.
Chapter 5

Adducts Involving SF₄

5.0 Introduction

The synthetic value of SF₄ in the formation of a wide variety of mainly organic fluoro-compounds has been covered in section 1.12 of chapter 1. Also, the ability of SF₄ to introduce fluorine into certain iridium complexes and an account of how further derivatives of these fluoro-iridium species may be obtained have been discussed in chapters 2, 3 and 4.

There is another aspect to the versatility of SF₄ chemistry, namely its ability to form adducts with Lewis acids and bases. This is the consequence of a lone pair and coordinative unsaturation at sulphur.

The work described in this chapter reviews the nature of adducts in which SF₄ acts as a Lewis base, and confirms the existence and structure of its adduct with N(CH₃)₃. There is also an account of the exchange processes relating to this adduct.

5.1 Adducts of Lewis Acids with SF₄.

Adducts between SF₄ and inorganic fluorides such as BF₃, PF₅ and AsF₅ are best understood. The specific case of the adduct between SF₄ and BF₃, which is similar to the
others, is now discussed in some detail.

Initially, SF₄·BF₃ was thought to be a simple molecular complex resulting from donation of the sulphur lone pair to boron (see fig. 5.1):

Fig. 5.1
The Structure of SF₄·BF₃ Involving Donation of the Sulphur Lone Pair to the Boron

At the time there was a lack of experimental evidence to support this structure, owing to the facile reactivity of the species with moisture and its general insolubility in solvents apart from anhydrous HF. Hence, solution n.m.r. studies were effectively precluded. However, Azeem et al. investigated systems with selectively ¹⁸F-labelled SF₄ and BF₃. They reported that B¹⁸F₃ transferred 56% activity to SF₄ and that S¹⁸F₄ transferred 43% activity to BF₃ on dissociation of the adduct at room temperature. These figures concur with complete exchange taking place. This suggested that the adduct was either ionic, of the form SF₃⁺[BF₄]⁻, or an infinite chain with each unit linked by fluorine bridges. However, the sulphur lone pair is not involved. The exchange would be occurring on dissociation of the adduct. Several possible structures are illustrated in figs. 5.2(a-d):
Fig. 5.2
Possible Structures of \( \text{SF}_4 \cdot \text{BF}_3 \) with Bridging Fluorines

(a)

(b)

(c)

(d)

Fluorine-exchange results from breaking of the chain and this is most likely to involve the weakest links. This implies that fig. 5.2(a) cannot be the structure of the adduct, because breaking of these bonds produces the initial \( \text{BF}_3 \) and \( \text{SF}_4 \) monomers.
In order to confirm the nature of the structure of SF$_4$.BF$_3$, Azeem et al. carried out conductivity measurements on the adduct in anhydrous HF. It was found to have conductivity which is very similar to K$^+$(BF$_4$)$^-$. This suggests that the adduct is ionic. Similar results have been obtained from adducts of SF$_4$ and SbF$_5$, PF$_5$ and AsF$_5$.

5.2 Adducts of Lewis Bases with SF$_4$.

The other type of adducts involving SF$_4$ are those in which it acts as a Lewis acid. Azeem[78], in 1966, reported that the $^{19}$F($^1$H) n.m.r. spectrum of SF$_4$ was affected by the presence of diethylether or tetrahydrofuran (t.h.f.). It was still two triplets, but the magnitude of $^2$J(FF) was somewhat reduced, relative to that in free SF$_4$. From the data it was concluded that the ethers were forming adducts with SF$_4$ by lone pair donation from oxygen to sulphur. However, it was not possible at that time to establish a definitive structure for these complexes on the basis of the spectroscopic data alone.

A structure in which the ether moiety is trans to the lone pair results in all four fluorines being equivalent. Equally, an arrangement with the ether cis to the sulphur lone pair produces three fluorine environments. The proposed structure of the adduct formed between diethylether and SF$_4$ is shown at fig. 5.3. However, this
is unsatisfactory, because it requires two fluorines with a different ligand trans to each to have the same chemical shift. The mutually trans fluorines are labelled $F_A$. The equatorial ones are labelled $F_{E'}$ (for the one trans to the ether) and $F_{E''}$, for the other.

Fig. 5.3
A Proposed Structure for the Adduct Formed Between $SF_4$ and Diethylether

$$
\begin{array}{c}
F_A \\
\mid \\
F_{E'} \\
\mid \\
F_{E''}
\end{array}
\begin{array}{c}
\text{S} \\
\cap
\end{array}
\begin{array}{c}
\text{Et}_2\text{O} \\
\mid \\
F_A
\end{array}
$$

The mutually trans fluorines remain equivalent. However, the equatorial fluorines are distinct. $F_{E'}$ is trans to the ether moiety and $F_{E''}$ is trans to the sulphur lone pair.

An alternative explanation of the data is that $F_{E'}$ and $F_{E''}$ are rendered equivalent by a mechanism of exchange which is fast on the n.m.r. timescale (see later).
5.3 The Adduct Formed Between N(CH₃)₃ and SF₄.

This section confirms conclusively the formation and structure of the adduct formed between SF₄ and N(CH₃)₃. It also discusses fluorine exchange relating to this species and a possible mechanism is proposed.

The first reports of an adduct formed between SF₄ and N(CH₃)₃ appeared in the 1950's. E.L. Muetterties[79] claimed that the amine formed a 1:1 molecular complex with SF₄. This was based on the ¹⁹F(¹H) n.m.r. spectrum of SF₄, in the presence of the amine, being a single structureless peak over the temperature range 173K to 300K. This contrasts with the two triplets observed for SF₄ at the lower end of this temperature range, when the amine is absent. The conclusion derived from these spectroscopic observations was that the resulting adduct had octahedral geometry at sulphur, with the amine trans to the lone pair. This is illustrated at fig. 5.4:

Fig. 5.4
A Proposed Structure of the Adduct Formed Between SF₄ and N(CH₃)₃

\[
\begin{array}{c}
\text{F} \\
\text{S} \\
\text{F} \\
\text{NMe₃} \\
\text{F} \\
\text{F}
\end{array}
\]
The Formation and Actual Structure of SF<sub>4</sub>.N(CH<sub>3</sub>)<sub>3</sub>

The structure of this adduct was determined by the $^{19}$F($^1$H) n.m.r. spectrum of N(CH<sub>3</sub>)<sub>3</sub> and a 100% excess of SF<sub>4</sub>, in d<sub>8</sub>-toluene/diethylether solvent at 143K (see diagram 5.1). Three resonances are assigned to the adduct, implying the geometry at sulphur is octahedral with the nitrogen located cis to the lone pair. This is illustrated at fig. 5.5:

Fig. 5.5

The Structure of SF<sub>4</sub>.N(CH<sub>3</sub>)<sub>3</sub>

\[
\begin{array}{c}
\text{FA} \\
\text{F}_{E''} \quad \text{S} \quad \text{NMe}_3 \\
\text{F}_{E'} \quad \text{F}_A
\end{array}
\]

The resonance assigned to the axial fluorines, F<sub>A</sub>, at δ+56.4 p.p.m. is a triplet, [2J(FF) = 37Hz], arising from equal coupling to the two equatorial fluorines, F<sub>E'</sub> and F<sub>E''</sub>. These are chemically distinct, because one of them, F<sub>E''</sub>, is trans to the lone pair, and the other, F<sub>E'''</sub>, is trans to the amine. The signals corresponding to F<sub>E'</sub> and F<sub>E''</sub> appear as pseudoquartets, because 2J(F<sub>E'</sub>F<sub>E''</sub>), 2J(F<sub>A</sub>F<sub>E'</sub>) and 2J(F<sub>A</sub>F<sub>E'''</sub>) are all equal to within ca. 2Hz. The n.m.r. data are listed in table 5.1.
Table 5.1

$^{19}$F($^1$H) n.m.r. Data of SF$_4$.N(CH$_3$)$_3$ at 123K

<table>
<thead>
<tr>
<th>$^{19}$F</th>
<th>$^6$/p.p.m.</th>
<th>Couplings/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_X$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$F_A$</td>
<td>+56.4</td>
<td>$2J(F_{E''}) = 37$</td>
</tr>
<tr>
<td>$F_{E'}$</td>
<td>+47.8</td>
<td>$2J(F_A) = 37$</td>
</tr>
<tr>
<td>$F_{E''}$</td>
<td>+38.5</td>
<td>$2J(F_{E''}) = 37$, $2J(F_{E''}) = 37$</td>
</tr>
</tbody>
</table>

When the $^{19}$F n.m.r. spectrum of the adduct is recorded under the same conditions, but with retention of $^1$H coupling, the lower frequency quartet is significantly broadened, relative to the other, although no extra couplings are resolved. On this basis, the lower frequency resonance was tentatively assigned to the fluorine, $F_{E''}$, trans to the amine.

The Formation of SF$_4$.$^{15}$N(CH$_3$)$_3$

In order to establish the locations of $F_{E'}$ and $F_{E''}$, the $^{19}$F n.m.r. experiment was subsequently repeated using $^{15}$N(CH$_3$)$_3$ and a 100% excess of SF$_4$.

Results

The $^{19}$F($^1$H) n.m.r. spectrum of the solution at 123K (see diagram 5.1a) indicates that the resonance assigned to the axial fluorines remains as a triplet with no extra couplings resolved. Given the sharpness of the spectrum,
Diagram 5.1

$^{19}$F n.m.r. spectrum of SF$_4$ NMe$_3$ at 123K

Diagram 5.1a

$^{19}$F n.m.r. spectrum of SF$_4$ $^{15}$NMe$_3$ at 123K

$\delta$/p.p.m.
$2J(\text{NFA})$ must be less than ca. 2Hz. However, each of the other signals contains an additional splitting. The one assigned to $F_E''$, at $\delta+47.8$ p.p.m., is a doublet of quartets, [$2J(\text{FBN}) = 18\text{Hz}$], whereas the remaining one at $\delta+38.5$ p.p.m., which corresponds to $F_C$ is a pseudoquintet, because $2J(F_E''',N)$ is equal to the other $2J(F_E'',F)$ couplings to within ca. 2Hz.

Conclusions

The data obtained from SF$_4$.^{15}\text{N(CH}_3)_3$ are entirely consistent with the structure of the adduct proposed from the n.m.r. experiments with the $^{14}\text{N(CH}_3)_3$/SF$_4$ system. It is interesting to note that $2J(15\text{NF}_A)$ is not resolved. If the geometry at sulphur is a regular octahedron, $2J(\text{FA}_N)$ and $2J(\text{FE}_N,N)$ would be expected to be similar on the basis that they both occupy coordination sites cis to the nitrogen. However, there are many factors involved in determining the mechanism of two-bond couplings and unravelling the various factors relevant in molecules like this is not simple. The values of $2J(\text{NF}_E')$ and $2J(\text{NF}_E''')$ are larger than $2J(\text{NF}_A)$. However, those of $2J(\text{FA}_F'E')$, $2J(\text{FA}_F'E')$ and $2J(\text{F}_E'F_E''')$ are all similar, indicating that the couplings involved are unlikely to be simply related to parameters like s-character in sulphur orbitals. There is no satisfactory explanation for the similar coupling constants at this stage.
5.4 Discussion of Exchange Processes involved in SF$_4$.N(CH$_3$)$_3$

In order to understand the exchange processes involved in the adduct, a series of experiments were performed in which the relative amounts of SF$_4$ and N(CH$_3$)$_3$ were varied. These ranged from a 300% excess of SF$_4$ through an equimolar mixture to a solution of SF$_4$ (0.05mmol) in N(CH$_3$)$_3$ solvent. The actual ratios used were: 4SF$_4$:1N(CH$_3$)$_3$, 3SF$_4$:1N(CH$_3$)$_3$, 2SF$_4$:1N(CH$_3$)$_3$, 4SF$_4$:3N(CH$_3$)$_3$, 20SF$_4$:19N(CH$_3$)$_3$, 1SF$_4$:1N(CH$_3$)$_3$, 19SF$_4$:20N(CH$_3$)$_3$, 1SF$_4$:2N(CH$_3$)$_3$, 1SF$_4$:3N(CH$_3$)$_3$ and SF$_4$ in N(CH$_3$)$_3$ solution.

When N(CH$_3$)$_3$ and a 300% excess of SF$_4$ [4SF$_4$:1N(CH$_3$)$_3$] are dissolved in d$_8$-toluene/diethylether the SF$_4$.N(CH$_3$)$_3$ adduct forms.

The $^{19}$F($^1$H) n.m.r. spectrum at 123K (see diagram 5.2) shows the three resonances for the adduct, two triplets, \([^{2}J(FF)= 68\text{Hz}]\), for free SF$_4$ and a singlet corresponding to SOF$_2$, which is present as a result of hydrolysis of SF$_4$.

As the sample is warmed, the resonances of free SF$_4$ broaden and lose all structure by 143K, at which temperature those of the adduct remain sharp. On further warming the peaks of the complex start to broaden. At 165K, the two low frequency quartets have lost their structure. The high frequency resonance, although
Diagram 5.2

$^{19}$F n.m.r spectrum of 4SF$_4$:1NMe$_3$ at 123K
Diagram 5.2a

$^{19}$F n.m.r spectrum of 4SF$_4$:1NM$_3$ at 168 K
Diagram 5.2b

$^{19}\text{F n.m.r. spectrum of } 4\text{SF}_4:1\text{NMe}_3 \text{ at } 177K$
broader, is still a clearly resolved triplet, which retains its structure up to 171K. The two low frequency resonances coalesce at 177K. The high frequency signal is very broad at this temperature. Coalescence of the resonances due to $F_A$ and $F_E$ ($F_E$ denotes the coalesced form of $F_{E'}$ and $F_{E''}$) occurs at 190K, leaving all fluorines equivalent.

Similar observations are revealed in all cases where there is an excess of $SF_4$, and the exchange processes involved are found to be entirely reversible as the samples are recooled to 123K.

An attempt was also made to prepare an exactly equimolar mixture of $SF_4$ and $N(CH_3)_3$, under the same experimental conditions, by forming the adduct with an excess of $SF_4$ and then removing the excess of this reagent, under vacuum at 195K. In this case, the $^{19}F$ n.m.r. spectrum contains only the peaks of the adduct.

The situation is different when $SF_4$ is reacted with a 5% excess of $N(CH_3)_3$. The $^{19}F$ n.m.r. spectrum of the adduct at 123K (see diagram 5.3) is two well-resolved triplets, $[^2 J(FF)= 37\text{Hz}]$. As the temperature of the system is increased, the triplets begin to broaden. They lose all structure by 195K. Further warming of the system causes continued broadening of the resonances until, at 205K, they coalesce. Once again the exchange processes are found to be reversible as the sample is recooled to 123K. The spectra of the other samples containing an
Diagram 5.3

$^{19}$F n.m.r spectrum of SF$_4$ and 100% excess NMe$_3$ at 123K
Diagram 5.3a

$^{19}F$ n.m.r spectrum of SF$_4$ and 100% excess NMe$_3$ at 200K
Diagram 5.3b

$^{19}$F n.m.r spectrum of SF$_4$ and 100% excess NMe$_3$ at 230K
excess of amine reveal that the coalescence temperature is 205K, irrespective of the amine concentration.

Discussion of the Spectra of the Adduct in the Presence of an Excess of SF₄

When the adduct is formed in the presence of excess SF₄, the ¹⁹F(¹H) n.m.r. data confirms that it contains three distinct fluorine environments, Fₐ, Fₑ, and Fₑ', at 123K. This is shown in table 5.2, together with the coalescence temperatures, Tₐ, of the processes which render a) Fₑ, and Fₑ', and b) Fₐ and Fₑ (where Fₑ is defined as above) equivalent.

Table 5.2

<table>
<thead>
<tr>
<th>Fₓ</th>
<th>δ/p.p.m.</th>
<th>T/K</th>
<th>Tₑ(Fₑ,Fₑ')</th>
<th>Tₑ(FₐFₑ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fₐ</td>
<td>56.4</td>
<td>123</td>
<td>—</td>
<td>190</td>
</tr>
<tr>
<td>Fₑ</td>
<td>47.8</td>
<td>123</td>
<td>177</td>
<td>190</td>
</tr>
<tr>
<td>Fₑ'</td>
<td>38.5</td>
<td>123</td>
<td>177</td>
<td>190</td>
</tr>
</tbody>
</table>

The conclusion drawn from the ¹⁹F n.m.r. spectra is that the adduct has a static structure, at 123K, on the n.m.r. timescale. The most facile exchange process involves only the equatorial fluorines. It is thought that Fₑ and Fₑ' are rendered chemically equivalent by a weakening of the S-N bond, which leads to interchange of
the amine and lone pair coordination sites. This is illustrated diagramatically at fig. 5.6. The amine must remain associated with the sulphur throughout, because in solutions with excess amine $F_{E'}$ and $F_{E''}$ are chemically indistinguishable.

Mech. 5.1

A Possible Mechanism of Fluorine Exchange in the Adduct

\[
\begin{align*}
F_A & \\
F_{E'} & \xrightleftharpoons{S} \leftrightarrow \text{NMe}_3 \\
F_{E''} & \\
F_A & 
\end{align*}
\]

As the rate of exchange between the lone pair and amine becomes fast, on the n.m.r. timescale, $F_{E'}$ and $F_{E''}$ are rendered chemically equivalent, although they remain chemically distinct from $F_A$.

Further warming of the solution, results in coalescence of $F_A$ and $F_E$ at 190K. The nature of the process responsible for this is not fully understood, but it appears not to involve free $SF_4$, as the amount of excess $SF_4$ present in the solution does not affect the coalescence temperature.

As the solution is warmed to room temperature, the single structureless peak sharpens and contains no resolved couplings, up to 308K.
Discussion of the Spectra of the Adduct in the Presence of an Excess of N(CH₃)₃

The $^{19}$F($^1$H) n.m.r. spectrum of SF₄.N(CH₃)₃, at 123K, in the presence of an excess of the amine, consists of two triplets only. This contrasts with the three signals, at this temperature, when SF₄ is present in excess. An explanation of the spectroscopic data is that a trace excess of the amine causes $F_E$ and $F_E'$ to become chemically equivalent by a fast intermolecular exchange, on the n.m.r. timescale, as illustrated below:

Mech. 5.2

It is interesting to note that the fluorines bound axially to sulphur, $F_A$, are not directly affected by the presence of excess amine, at 123K. The chemical shift and value of $^{2}J(F_AF_E)$ remain the same in either case.

Another interesting feature is that the coalescence temperature of $F_A$ and $F_E$, in the absence of excess amine, is 15K lower than when excess amine is present, irrespective of the concentrations of the various species involved. The reasons for this are not fully understood.

Perhaps the exchange process involving $F_A$ and $F_E$ arises from the reversible dissociation of the adduct (see eqn. 5.1) and the presence of excess amine alters the
equilibrium constant in favour of the adduct.

Eqn. 5.1

\[
\begin{align*}
\text{FA} & \quad \text{F} \\
\text{F}_{\text{A}} & \quad \text{S} - \text{NMe}_3 \\
\text{F}_{\text{E}} & \quad + \text{NMe}_3 \\
\text{F} & \quad \text{S} - + \text{NMe}_3
\end{align*}
\]

This mechanism does not adequately account for the absence of a concentration dependence on the coalescence temperature or why excess SF\textsubscript{4} does not similarly favour adduct formation. Further experiments are required to confirm the nature of the processes involved.

5.5 The Effect of [NH(CH\textsubscript{3})\textsubscript{3}]\textsuperscript{+}F\textsuperscript{-} on SF\textsubscript{4}.

During the experiments involving N(CH\textsubscript{3})\textsubscript{3} and an excess of SF\textsubscript{4}, it became apparent from the \textsuperscript{19}F n.m.r. spectra, that the coalescence temperature of the triplets of free SF\textsubscript{4} was many degrees lower than expected. The reason for this is not understood. One possible explanation is an interaction between the fluoride of [NH(CH\textsubscript{3})\textsubscript{3}]\textsuperscript{+}F\textsuperscript{-}, present from reaction of the amine with HF, and SF\textsubscript{4}. In order to investigate this, SF\textsubscript{4} was treated with an equimolar amount of the tertiary ammonium salt, in a 1:1 mixture of d\textsubscript{2}-dichloromethane/diethylether. The coalescence temperature of the triplets was the same as for SF\textsubscript{4}, in the absence of the salt or HF. It is therefore clear that the salt is not significantly
interacting with SF₄ in solution, up to 288K.

The triplets of SF₄ in solutions containing SF₄·N(CH₃)₃ may be broadened by the presence of fluoride ion, with exchange via an associative mechanism which is inhibited in the adduct by steric considerations.

5.6 The Reaction of SF₄ with NH(CH₃)₂

The results describing adduct formation between SF₄ and N(CH₃)₃ suggested that other amines may similarly bind to the sulphur site. One possible candidate is NH(CH₃)₂. However, a recent literature report[84] indicated that this amine, when reacted with SF₄, produced an oil, the nature of which was not determined.

In order to establish if the literature reports were correct, equimolar amounts of SF₄ and NH(CH₃)₂ were dissolved in d₂-dichloromethane and the ¹⁹F(¹H) n.m.r. spectrum was recorded at 178K (see diagram 5.4).

It is apparent that SF₄ has reacted with the amine to form the known species, SF₃N(CH₃)₂, by a mechanism involving elimination of HF. This, in turn forms a secondary ammonium salt with some unreacted amine (see eqn. 5.2).
Diagram 5.4

$^{19}$F n.m.r. spectrum of reaction of $\text{SF}_4$ with $\text{NHMe}_2$
Eqn. 5.2

\[
2\text{SF}_4 + 2\text{NH(CH}_3)_2 \rightarrow \text{SF}_4 + \text{SF}_3\text{N(CH}_3)_2 + \text{HF} \\
\text{NH(CH}_3)_2 + \text{HF} \rightarrow [\text{NH}_2(\text{CH}_3)_2]^+ \text{F}^- 
\]

The solution was warmed to investigate the fluxional behaviour of SF4 in the presence of SF3N(CH3)2. It is apparent, from 19F n.m.r. data of the solution at 300K, that fluorine exchange in SF4 is more facile than in SF3N(CH3)2. There is no significant intermolecular fluorine exchange, on the n.m.r. timescale, between these two species as the resonances of SF3N(CH3)2 are too sharp.

5.7 The Interaction of Triethylamine (N(CH2CH3)3) with SF4.

In order to establish if the SF4 adduct with N(CH3)3 was unique to this amine, a further solution of SF4 was treated with a 50% deficiency of N(CH2CH3)3 in a 1:1 mixture of d2-dichloromethane/diethylether. The 19F(1H) n.m.r. spectrum of the solution, at 130K, produced a similar pattern to that of SF4.N(CH3)3, as well as the triplets of unreacted SF4. On the basis of this observation, it is clear that other amines can form an adduct similar to SF4.N(CH3)3. There was no further investigation of SF4.N(CH2CH3)3.
5.8 The Interaction of Pyridine (NC₅H₅) with SF₄.

Literature reports[79] have suggested that pyridine also forms a 1:1 adduct with SF₄. This was based on the ¹⁹F n.m.r. spectrum of solutions of SF₄ in the amine being a single structureless peak over a wide temperature range.

In order to confirm this, NC₅H₅ and a 100% excess of SF₄ were dissolved in a 1:1 d₂-dichloromethane/diethylether mixture. The ¹⁹F(¹H) n.m.r. spectrum of the solution at 150K (see diagram 5.5), comprises two triplets and a singlet only. The chemical shifts of the triplets are δ+68.3 p.p.m. and δ+31.2 p.p.m. The value of 2J(FF) in each is 44Hz. Clearly, these resonances are not assigned to free SF₄. This suggests the amine is in some way interacting with the sulphur. In fact, these spectroscopic observations are similar those determined by Azeem during his work on adducts of SF₄ with ethers (see earlier).

The absence of the signals of unreacted SF₄ implies that NC₅H₅ is affecting all of the SF₄ in solution. There are two plausible explanations for this.

Firstly, an adduct forms between SF₄ and NC₅H₅. In the presence of excess SF₄, there is fast intermolecular exchange, on the n.m.r. timescale, between the amine and sulphur, which renders both equatorial fluorines on any one sulphur and also all sulphur environments equivalent.

Alternatively, the amine forms an adduct with the
Diagram 5.5

$^{19}$F n.m.r spectrum of NC$_5$H$_5$ and 100% excess of SF$_4$ at 150K with a reference spectrum of SF$_4$ at this temperature.
sulphur sites of two molecules and there is a fast interchange between the sulphur lone pairs and the nitrogen of the amine.

In order to exclude this possibility, the reaction was repeated using NC₅H₅ and a 200% excess of SF₄. The $^{19}$F($^1$H) spectrum, at 150K, is very similar to the one from the solution containing only a 100% excess of SF₄. It is therefore clear that fast intermolecular exchange on the n.m.r. timescale is taking place.

Note: the singlet at δ+66.4 p.p.m. is assigned to the fluorines of SOF₂. As this is shifted to low frequency of the normal position (+73.5 p.p.m.) for these fluorines, there may also be an interaction between the amine and sulphur of the sulfoxide.

5.9 Reaction of P(CH₃)₃ with SF₄.

Another possible adduct, similar to SF₄.N(CH₃)₃, is between SF₄ and P(CH₃)₃. Such a species would have the added advantage, in terms of structure determination, of the phosphorus n.m.r. handle. However, phosphorus, unlike nitrogen, has the potential to readily adopt 5-coordination and SF₄ may fluorinate the phosphine to generate P(CH₃)₃F₂. In order to reduce the likelihood of fluorination at phosphorus, equimolar amounts of SF₄ and P(CH₃)₃ were dissolved in a 1:1 mixture of
d₂-dichloromethane/diethylether. The sample was kept frozen at 77K, until the ¹⁹F n.m.r. spectrum was recorded at 123K. Care was taken to ensure that the sample was not warmed above this temperature.

It is clear from the n.m.r. data that SF₄ has fluorinated the phosphine to generate P(CH₃)₃F₂, with the fluorines occupying the axial sites of the trigonal bipyramid.

The reaction is illustrated in eqn. 5.3:

\[
\text{Eqn. 5.3}
\]

\[
\text{SF}_4 + \text{P(CH}_3\text{)}_3\text{P(CH}_3\text{)}_3\text{F}_2 + \text{SF}_2
\]

\[
\text{2SF}_2 \rightarrow \text{SF}_4 + \text{S}
\]

There was no evidence for any stable adduct of the form SF₄.P(CH₃)₃. It may be possible to form such an adduct, at low temperature with a phosphine containing bulky alkyl or aryl groups, but this is beyond the scope of this work.

5.11 The Interaction of t.h.f. with SF₄.

In order to check the results of Azeem, mentioned earlier, t.h.f. and a 100% excess of SF₄ were dissolved in a 1:1 d₂-dichloromethane/diethylether mixture. The ¹⁹F n.m.r. spectrum of the solution, at 150K, contains two
triplets which are indistinguishable from free SF$_4$.

The experiment was repeated using equimolar amounts of the two reagents. The results are no different to the case of a 100% excess of SF$_4$.

When SF$_4$ in dissolved in t.h.f. solvent, the difference in chemical shifts and constants of the triplets, in the $^{19}$F n.m.r. spectrum more closely resemble the results reported by Azeem.

A possible interpretation of the data is that an adduct forms between the oxygen of the ether and sulphur. In solutions containing similar concentrations of the ether and SF$_4$, the equilibrium position lies on the side of free SF$_4$ and t.h.f. However, when the concentration of t.h.f. vastly exceeds that of SF$_4$, formation of the adduct is favoured.

There is also fast intermolecular exchange on the n.m.r. timescale between the oxygen and sulphur. This renders both equatorial fluorines on sulphur equivalent and is similar to the case of SF$_4$ and NC$_5$H$_5$. However, the equilibrium constants for formation of the two adducts are different.

5.12 Conclusions

In the presence of strong bases such as N(CH$_3$)$_3$ or N(CH$_2$CH$_3$)$_3$, SF$_4$ forms a 1:1 adduct. When the sulphur reagent is in excess of the base, there are three fluorine
environments in the adduct (i.e. the two equatorial fluorines are distinct). However, when less basic reagents i.e. diethylether or NC₅H₅ are used, the equatorial fluorines of the adduct are chemically equivalent, on the n.m.r. timescale, down to 123K.

This may be due to the lower basicities of these latter species rendering bonding to sulphur susceptible to cleavage.

However, in the case of NH(CH₃)₂ [which is of comparable basicity to N(CH₃)₃], the elimination of HF is favoured to adduct formation.

Also, unsaturated phosphines, like P(CH₃)₃, are fluorinated by SF₄ as opposed to forming an adduct at sulphur.
Chapter 6
Experimental Section

The Vacuum Line

All gaseous reagents were handled using conventional pyrex-glass tubing with ground glass joints and high vacuum taps at appropriate positions in the line. The joints and taps were greased with Apiezon (L) and (N) greases respectively.

A vacuum of approximately $10^{-6}$ torr was maintained by a glass mercury diffusion pump with oil rotary pump as a back-up.

The line was calibrated for volume using a molecular weight bulb and pressures subsequently measured by a glass spiral gauge with spotlight mirror as a null zero device.

Volatile compounds were separated by normal fractionation techniques through slush baths at standard temperatures.

All involatile substrates were prepared by published syntheses and were handled and stored under dry nitrogen. The nitrogen source was dried and deoxygenated by passing through columns containing $\text{P}_2\text{O}_5$ and BASF catalyst, R3-11.

N.m.r. tubes were attached to the vacuum line by B10 ground glass cones and were sealed with a hot flame when filled.
N.m.r. Machines

N.m.r. spectra were obtained from the following Fourier-transform spectrometers.
Jeol FX90Q. $^{31}P\{^1H\}$.
Bruker WP80. $^{19}F$ and $^{31}P\{^1H\}$.
Bruker WH360. $^{31}P\{^1H\}$.

I.R. Spectra

All volatile reagents were checked by I.R. spectroscopy for purity prior to use. These were recorded on Perkin-Elmer 577 or 598 double-beam spectrometers. The samples were in the gas phase in a cell fitted with KBr disks.

Spectra of solids were obtained from nujol mulls between KBr plates.

Solvents

N.m.r. solvents were dried over molecular sieve and distilled prior to use.

Non-n.m.r. solvents used in this work were treated as follows:

dithylether: distilled from LiAlH$_4$ and stored over Na wire.
dichloromethane: distilled from P$_2$O$_5$ and stored over CaH$_2$.
hexane: stored over and distilled from Na wire.
pyridine: dried over CaH$_2$. 
cyanomethane: refluxed over and distilled from P₂O₅.
methanol/ethanol: distilled from and stored over CaH₂.
benzene/toluene: obtained commercially and used without further purification.
propanone: degassed, stored over and distilled from A₄ molecular sieve.
tetrahydrofuran: refluxed over and distilled from Na/benzophenone.
trimethylamine: stored over and distilled from powdered KOH.

Note: unless specifically referenced all other materials were obtained commercially and used without further purification.

Materials

Preparation of BF₃[80]

A 3-necked round-bottomed flask (250ml) equipped with an N₂-inlet and CO₂/propanone condenser is attached to a vacuum line via swivel links. A mixture of previously ground together sodium tetrafluoroborate (NaBF₄)(18g) and boric oxide (B₂O₃)(3g) are added and dissolved in conc. H₂SO₄ (20ml). The flask is heated gently with a yellow flame to maintain a steady flow rate of the product. The impure BF₃ is condensed into traps on the vacuum line at 77K and purified BF₃ is obtained by collecting the fraction which passes through a trap at 153K. The purity
of the reagent is established by I.R. and \(^{19}\text{F}\) n.m.r. spectroscopic methods.

**SF\(_{4}\) Preparation**[39]

NaF(42g) and SCl\(_2\)(52g) are dissolved in cyanomethane(500ml) in a 3-necked flask (11) equipped with a mechanical stirrer, dropping funnel with side arm and N\(_2\)-inlet and an extensive H\(_2\)O condenser. The mixture is stirred at room temperature for 15 minutes and gently warmed to 348K at which temperature it is maintained for 3 hours. During this time the crude SF\(_{4}\) is collected at 120K in a large test-tube. This vessel is then isolated and the crude SF\(_{4}\) is transferred onto the vacuum line for purification.

**Purification of SF\(_{4}\)**[77]

The main impurities present in SF\(_{4}\) are the product of partial hydrolysis by water (SOF\(_2\) and HF) and some Cl\(_2\) from SCl\(_2\). SF\(_{4}\) cannot be separated from SOF\(_2\) by fractionation. A chemical method is employed and this is outlined below.

The crude mixture is placed in a thoroughly dried flask, which is attached directly to a vacuum line. A stoichiometric amount of BF\(_3\) is condensed onto the mixture at 77K and the system allowed to warm slowly to room temperature, during which time an SF\(_{4}\).BF\(_3\) adduct forms. The other unwanted species do not react with BF\(_3\) under
these conditions. The mixture is then cooled to 195K and the volatile impurities and excess BF₃ removed under vacuum. The vapour pressure of the adduct is negligible at this temperature.

Diethylether is then condensed onto the adduct at 77K and the mixture again warmed to room temperature. The ether liberates SF₄ from the adduct and generates F₃B:O(CH₂CH₃)₂. The mixture is recooled to 195K and the liberated SF₄ removed under vacuum and stored.

The purity of SF₄ is determined from gas phase I.R. spectroscopy and ¹⁹F n.m.r. spectroscopic methods.

Preparation of P(CH₂CH₃)₃[⁸¹]

A 3-necked flask (41) equipped with a dropping funnel, intensive reflux condenser and a mechanical stirrer is charged with ethyl bromide (CH₃CH₂Br) in diethylether (1.5l) under an N₂ atmosphere. Triphenylphosphite, P(OC₆H₅)₃, (410g; 1.32mol) in diethylether (500ml) is added to the flask slowly while the system is maintained at 273K. After complete addition of the phosphite, the mixture is refluxed for 3 hours. A creamy mixture is obtained. This is washed with water (3x300ml) and sodium hydroxide (NaOH) (5M) (4x250ml) and further aliquots of water (3x200ml). The solution containing P(CH₂CH₃)₃ is dried over MgSO₄ (overnight) and the product distilled at atmospheric pressure.

The purity of the phosphine is established by ³¹P
Pretreatment of IrCl₃

In order to ensure that the IrCl₃ is in the trihydrated form, IrCl₃·3H₂O, the raw IrCl₃ powder is treated with acid. IrCl₃ (2g) are placed in a clean, dry 100ml Schlenk bulb containing a magnetic stirrer bar. N₂ gas is passed through the system and conc. HCl (25ml) added with stirring. The bulb is then heated to 373K and maintained at this temperature until the HCl is driven off, leaving the desired product as a shiny black solid.

Preparation of Ir₂Cl₂(C₈H₁₄)₄[82]

This dimeric iridium complex is the precursor to the formation of t-IrCl(CO)[P(CH₂CH₃)₂]. Its preparation is carried out under a flow of N₂.

IrCl₃·3H₂O (2g) is dissolved in propan-2-ol (22ml) and deionized water (8ml) in a 100 ml Schlenk bulb. Cyclooctene, C₈H₁₄, (4 ml) is added to the solution via a syringe. The mixture is then stirred at room temperature for 10 minutes then refluxed for 3 hours, during which time an orange solid (the product) forms.

The solution is filtered using a Schlenk filtration apparatus, the residue washed three times with chilled methanol and stored under a reduced pressure of N₂. The first washings are maintained under N₂ whence more of the product crystallizes out.
Preparation of $t$-IrCl(CO)[$P(CH_2CH_3)_2$]$_2$[83]

$Ir_2Cl_2(C_8H_{14})_4$ (0.447g) is dissolved in degassed propanone (5ml) in a Schlenk tube. Carbon monoxide is bubbled through the solution for a few minutes with continuous agitation, during which time a blue-black slurry forms. A solution of $P(CH_2CH_3)_3$ (0.24g) in degassed propanone is added to the slurry and stirred at room temperature for ca. 3 hours, when a greenish-yellow solution forms. This solution is heated to 393K and the solvent and displaced $C_8H_{14}$ removed under vacuum. The product is sublimed, as yellow crystals, onto a water-cooled cold finger at 413K and transferred to a storage Schlenk and kept under a reduced pressure of N$_2$.

The purity of the reagent is ascertained by $^{31P}$ n.m.r. and I.R. spectroscopic methods.

Preparation of $t$-IrBr(CO)[$P(CH_2CH_3)_3$]$_2$[83]

$t$-IrCl(CO)[$P(CH_2CH_3)_2$]$_2$ (0.15g) is dissolved in degassed propanone and stirred, with a 200% excess of oven-dried LiBr, for 1 hour. The solvent is removed under vacuum and the product sublimed, at 414K, onto a water-cooled cold finger, then transferred to a storage Schlenk and kept under a reduced pressure of N$_2$.

The purity of the reagent is determined spectroscopically as in the case of the analogous chloro-complex.
Preparation of $t$-IrI(CO)[$P(CH_2CH_3)_3)_2$\[83]\n
$t$-IrCl(CO)[$P(CH_2CH_3)_3)_2$ (0.15g) is dissolved in degassed propanone and stirred with a 200% excess of NaI for 1 hour at room temperature under $N_2$. The solvent is removed under vacuum and the product sublimed onto a water-cooled probe. The apparatus is then placed in a dry-box to enable the yellow crystals to be transferred to a storage Schlenk and maintained under a reduced pressure of $N_2$.

The purity of this species is determined spectroscopically as with the chloro- and bromo-analogues.

Note: all operations involving this Ir$^+$ complex are performed in an $O_2$-free environment.

Preparation of $t$-IrCl(CO)[$P(C_6H_5)_3)_2$\[85]\n
A mixture of IrCl$_3$.3H$_2$O (1g) and $P(C_6H_5)_3$ (3.72g) is heated at reflux in dimethylformamide (50ml), under $N_2$, for 15 hours. The yellow solution is left to cool and combined with methanol (100ml). After cooling, the yellow crystals are collected on a filter and washed with methanol (3x10ml). The air-stable crystals are transferred to a glass bottle for storage.

The purity of the reagent is established spectroscopically.
Preparation of [Ir(CO)[P(CH₃)₃]₄]⁺Cl⁻[86]

A Schlenk tube containing t-IrCl(CO)[P(C₆H₅)₃]₂ (0.56g; 0.71mmol) suspended in benzene (5ml) and equipped with a magnetic stirrer bar is attached to a vacuum line. The solution is frozen in liquid N₂ and evacuated. P(CH₃)₃ (0.22g; 2.84 mmol) is condensed into the tube, which is then isolated and allowed to warm to room temperature with stirring. The resulting suspension is filtered (in air) and the white solid washed with benzene to remove traces of the unreacted Ir⁺ starting material. The product is then dried under vacuum and stored under a reduced pressure of N₂.

The purity of this cationic complex is ascertained by I.R. spectroscopy.

Preparation of t-IrCl(CO)[P(CH₃)₃]₂[86]

A sublimation apparatus (with a water-cooled probe) is charged with [IrCO[P(CH₃)₃]₄]⁺Cl⁻, evacuated and heated to 403K. Initially a white film appears on the probe, followed by the growth of bright yellow crystals. After nearly all the solid has sublimed, the product is scraped from the probe (in air) and resublimed once or twice, until the sublimate consists of pure yellow crystals with no visible white contaminant.

The purity of this iridium complex is determined by ³¹P n.m.r. and I.R. spectroscopic methods.
Preparation of \( t\text{-IrF(CO)}[P(C_6H_5)_3]_2 \) \(^{[87]} \)

\( t\text{-IrCl(CO)}[P(C_6H_5)_3]_2 \) (1g) is added to a saturated solution of ammonium fluoride (NH\(_4\)F) (10g; 300ml) in a 500ml Schlenk bulb. The resulting yellow suspension is stirred by manual swirling and heated to boiling point, on a steam bath. When most of the complex is in solution (after ca. 15 minutes), solid silver carbonate (Ag\(_2\)CO\(_3\)) (0.177g) is added in small quantities, over a period of 1 minute. Some effervescence is observed during this addition. The mixture is boiled until all the Ag\(_2\)CO\(_3\) has dissolved, then the hot suspension is filtered through a medium porosity fritted disk, under reduced pressure, onto a vigorously stirred solution of NH\(_4\)F (0.1M). The pale yellow crystals are dried under vacuum and stored under a reduced pressure of N\(_2\).

The purity of this fluoro-iridium complex is determined by \( ^{19}\text{F n.m.r. spectroscopy} \).

Preparation of \( t\text{-IrBr(CO)}[P(C_6H_5)_3]_2 \) \(^{[88]} \)

\( t\text{-IrCl(CO)}[P(C_6H_5)_3]_2 \) (0.21g) and LiBr (0.24g) are dissolved in degassed propanone (20ml) in a Schlenk tube equipped with a magnetic stirrer bar. The mixture is stirred at room temperature for 1 hour, after which time the solvent is removed under vacuum. Degassed water (5ml) is added to the residue and the solution pipetted off leaving the product as a yellow solid. Two further aliquots of degassed water (2x5ml) are added (to remove
any last traces of lithium salts) and the product is dried under vacuum. The yellow solid is stored under a reduced pressure of N₂.

The purity of this reagent is established by $^{31}$P n.m.r. spectroscopy.

Preparation of $t$-IrX(CO)[P(C₆H₅)₃]₂ (X= NCO, NCS)[89]

$t$-IrCl(CO)[P(C₆H₅)₃]₂ and a 10-fold excess of the potassium salt (K⁺NCO⁻ or K⁺NCS⁻) are placed in a Schlenk tube equipped with a magnetic stirrer bar. The tube is then filled with degassed propanone (50ml) and the contents stirred at reflux temperature under N₂ for 1 hour. After this time the solvent is removed under vacuum. Degassed water (10ml) is added to the mixture and the contents transferred under N₂ to a Schlenk filtration apparatus, from which the water is pipetted off. The yellow solid is washed with a further aliquot (5ml) of degassed water to remove any remaining potassium salts. The product is stored under a reduced pressure of N₂.

The purity of each of these complexes is ascertained by I.R. spectroscopy.

Preparation of $t$-IrCl(CO)[P(CH₂CH₃)(C₆H₅)₂]₂[90]

$t$-IrCl(CO)[P(C₆H₅)₃]₂ and a 10-fold excess of P(CH₂CH₃)(C₆H₅)₂ are stirred in a Schlenk bulb in toluene for 5 minutes at room temperature. The solvent is removed under high vacuum and the oily residue washed with ethanol
The yellow solid is dried and stored under a reduced pressure of N₂.

The purity of this reagent is determined by ⁴ⁱP n.m.r. spectroscopy.

**Preparation of t-IrCl(CO)(P(C₆H₁₁)₃)₂[^91]**

The procedure is similar to that of t-IrCl(CO)(P(CH₂CH₃)(C₆H₅)₂)₂. A 10-fold excess of P(C₆H₁₁)₃ is used instead of P(CH₂CH₃)(C₆H₅)₂.

The purity of the complex is ascertained by ⁴¹P n.m.r. spectroscopy.

**Preparation of t-IrX(CO)(P(CH₂CH₃)₃)₂ (X=NCO, NCS)**

t-IrCl(CO)(P(CH₂CH₃)₃)₂ and a 10-fold excess of the oven-dried potassium salt (K⁺NCO⁻, K⁺NCS⁻) are dissolved in degassed propanone in a Schlenk tube, equipped with a magnetic stirrer bar. The mixture is stirred under N₂ for 30 minutes and the solvent removed under vacuum. Benzene or dichloromethane is added to the residue and the mixture is filtered using a Schlenk filtration apparatus. The filtrate is dried under vacuum, leaving the product as a yellow solid, which is stored under a reduced pressure of N₂.

The purity of these complexes is established by n.m.r. and I.R spectroscopic techniques and by C.H.N analysis.
Preparation of $t$-IrX(CO)$_2$[P(CH$_2$CH$_3$)(C$_6$H$_5$)$_2$]$_2$ ($X=\text{NCO, NCS}$)

$t$-IrCl(CO)$_2$[P(CH$_2$CH$_3$)(C$_6$H$_5$)$_2$]$_2$ and an excess of oven dried potassium salt ($\text{K}^+\text{NCO}^-\text{ or K}^+\text{NCS}^-\text{)}$ are dissolved in degassed propanone and stirred at room temperature under a flow of $N_2$ in a Schlenk tube for 30 minutes. The solvent is removed under vacuum leaving a mixture of the desired product and an excess of the potassium salts ($\text{K}^+\text{Cl}^-\text{ and K}^+\text{NCO}^-\text{ or K}^+\text{NCS}^-\text{)}$). The mixture is dissolved in dry dichloromethane and filtered through a sintered frit under $N_2$. The solvent is removed under vacuum leaving a yellow solid. Hexane is added to this product and refluxed with stirring under $N_2$ for 60 minutes. As the solution is cooling diethylether is added and then pipetted off while hot. The yellow solid is washed three times with diethylether and the product dried under vacuum.

The purity of each complex is determined by n.m.r. and I.R spectroscopic techniques.

Preparation of $t$-IrCl($^{13}\text{CO}$)[P(CH$_2$CH$_3$)$_3$]$_2$

This complex can be prepared by treating its synthetic precursor with $^{13}\text{CO}$.

Ir$_2$Cl$_2$(C$_8$H$_{14}$)$_4$ (0.2g) is placed in a Schlenk tube equipped with a magnetic stirrer bar and degassed propanone (5ml). The vessel is cooled to 77K and evacuated on the vacuum line. $^{13}\text{CO}$ from a commercially obtained bulb is allowed to fill the tube, which is slowly warmed to room temperature. The mixture is left stirring
for 120 minutes to allow for sufficient absorption of $^{13}$CO. After this time, the tube containing the iridium mixture is isolated and worked up as in the case of the Ir-$^{12}$CO complex.

The degree of $^{13}$C-enrichment in this complex and all others derived from it determined by $^{31}$P n.m.r. spectroscopy.
Note: The other Ir-$^{13}$CO complexes are derived from the chloride by the procedures adopted for the non-enriched analogues.

Preparation of H$_3$COSi(CH$_3$)$_3$

Equimolar amounts of anhydrous CH$_3$OH and commercial (H$_3$C)$_3$SiCl are stirred in NC$_5$H$_5$ in a Schlenk tube for 60 minutes during which time [H$_5$C$_5$NH]$^+$Cl$^-$ forms as a white solid. The desired product is distilled off under vacuum using a vacuum line. It is purified by fractionation which removes any excess NC$_5$H$_5$.

The purity of this silicon reagent is determined by $^1$H n.m.r. and I.R. spectroscopic analysis.

Note: I wish to thank Dr. Ruth Sorbie for supplying some samples of P(CH$_2$CH$_3$)$_2$(C$_6$H$_5$) and P(CH$_2$CH$_3$)(C$_6$H$_5$)$_2$ and Neil Robertson for providing some t-IrCl($^{13}$CO)[P(CH$_2$CH$_3$)$_3$]$_2$. 
Monitoring Temperatures of N.m.r. Experiments

Where a series of experiments are used to establish accurate coalescence n.m.r. data, the temperatures at which the spectra are recorded are monitored by placing a non-spinning thermocouple in the probe of the magnet and a steady reading is noted on a digital readout thermometer.

The accuracy of such readings from the thermocouple is confirmed by ascertaining the freezing point of pure liquids.

The use of a thermocouple is essential as the thermometer reading in its absence varies significantly from the actual probe temperature during the n.m.r. accumulations.
References


List of Courses Attended

Solving and Refining Crystal Structures, by Drs. R.O. Gould and A.J. Blake

Multipulse N.M.R., by Dr. I.H. Sadler

Electronic Structures of Inorganic Molecules, by Drs. L.J. Yellowlees and A.J. Welch

Organometallic Catalysis, by Dr. J.V. Laurie

Lanthanides and Actinides, by Dr. S. Craddock

Mass Spectrometry, by Prof. K.R. Jennings

Business Studies Course, by University of Edinburgh Economics Department

R.S.C. Dalton Group Meeting (1987)

University of Strathclyde Inorganic Club Conferences (1987, 1988, 1989)

Departmental Inorganic Colloquia and Friday Discussion Group (4 years)
Vaska's Compound* – Dichloromethane Solvate (1/2)

BY ALEXANDER J. BLAKE,† E. A. V. EBSWORTH,‡ HENRY M. MURDOCH AND LESLEY J. YELLOWLEES

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(Received 2 April 1990; accepted 17 August 1990)

Abstract. C₃₇H₃₀ClIrOP₂.2CD₂Cl₂, Mᵣ = 954.14, orthorhombic, Pcab (alternative Pbca, No. 61), a = 8.0054(21), b = 20.669 (6), c = 23.170 (5) Å, V = 3834 Å³, Z = 4, Dᵣ = 1.649 Mg m⁻³, λ(Mo Kα) = 0.71073 Å, μ = 3.94 mm⁻¹, F(000) = 1872, T = 298 K, R = 0.0253 for 1176 unique observed reflections. Despite disordering of the Cl⁻ and CO ligands, it was possible to resolve the affected atoms and finally to refine without the need for geometric constraints. The solvate molecules associate with the metal complex via O···H and Cl···H contacts of 2.415 (25) and 2.672 (16) Å respectively.

Experimental. Crystals were obtained from a CD₂Cl₂ solution of IrH(CO)(PPh₃)₃. Yellow columnar crystal, 0.31 x 0.31 x 0.77 mm, Stoe STADI-I four-circle diffractometer, graphite-monochromated Mo Kα radiation, cell parameters from 2θ values of 46 reflections measured at ±ω (28 < 2θ < 30°). For data collection, ω-2θ scans with ω-scan width (1-65°) 0108-2701/91/030657-03$03.00 © 1991 International Union of Crystallography

Molecular geometry calculations were performed using CALC (Gould & Taylor, 1985).

Related literature. During the structure determination on unsolvated Vaska's compound, trans-IrCl(CO)(PPh₃)₂, Cl/CO disorder was also identified and successfully resolved (Churchill, Fettinger, Buttrey, Barkan & Thompson, 1988). The solvated and unsolvated forms show similar structures for the metal complex.

We thank the SERC for funding towards the purchase of a diffractometer. HMM thanks the University of Edinburgh for support.

References

* trans-Carbonylchlorobis(triphenylphosphine)iridium.
† Author for correspondence.
‡ Presently Vice-Chancellor, University of Durham, Old Shire Hall, Durham DH1 3HP, England.


using this information indicated the Ir to lie on an inversion centre and 
$F > 6 \sigma(F)$ factors $0.203$, $0.253$ respectively. $3844$ reflections 
during data processing, initial absorption correction 
using $\cdot fr$ scans (minimum, maximum transmission 
$\pm 0.000237 F^2$ gave satisfactory agreement analyses. Scattering 
factors were inlaid (Sheldrick, 1976) except for Ir (Cromer & Mann, 1968). Atomic 
coordinates and equivalent isotropic thermal parameters are given in Table 1, while selected bond 
lengths and angles appear in Table 2.* The atom- 
numbering scheme is shown in Fig. 1, which was 
generated using ORTEP (Mallinson & Muir, 1985).

* Lists of structure factors, anisotropic thermal parameters and 
$H$-atom coordinates have been deposited with the British Library 
Document Supply Centre as Supplementary Publication No. SUP 
53494 (10 pp.). Copies may be obtained through The Technical 
Editor, International Union of Crystallography, 5 Abbey Square, 
Chester CHI 2HU, England.

Fig. 1. A general view showing atom-numbering scheme: thermal 
ellipsoids are drawn at the $30\%$ probability level, excepting 
those of C and H/D which have artificial radii of $0.15$ and 
$0.10$ Å respectively for clarity.

Table 1. Atomic coordinates with e.s.d.'s in Table 2. Selected bond lengths (Å), angles ($) and 
torsion angles ($\phi$) with e.s.d.'s in parentheses

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Table 2. Bond lengths (Å), angles (°) and parentheses 
torsion angles (°) with e.s.d.'s in parentheses

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