THE PREPARATION OF ALKENE-ALKyne
COMPLEXES OF RHODIUM, AND
SOME PLATINACYCLES

A thesis presented for the
Degree of Doctor of Philosophy
in the
Faculty of Science
by
MICHAEL DAVID SCHILLING
University of Leicester
August 1978
STATEMENT

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester, between October 1975 and August 1978, under the supervision of Dr. R. D. W. Kemmitt. The work has not been, and is not concurrently being presented for any other degree.

August 1978
ACKNOWLEDGEMENTS

To my supervisor, Dr. R. D. W. Kemmitt, I owe a great deal. His guidance, optimistic enthusiasm and advice have greatly contributed to my knowledge and understanding of organometallic chemistry, and to the enjoyment of my work, here in Leicester.

I am also most grateful to Dr. D. R. Russell and Mr. J. Barlow, who carried out the X-ray crystal structure determinations.

Similarly, my thanks are extended to Mrs. D. Sutherland and Mrs. B. Rughani, who spent many hours patiently recording $^1H$, $^{19}F$ and $^{31}P$ n.m.r. spectra.

I am especially grateful to Miss P. Perkins who, voluntarily, devoted many painstaking hours to typing this thesis.

Mention must be made of the many varied and stimulating discussions with my colleague Dr. M. Howden, both in and out of the laboratory.

That my course at the School of Education has been successful is due to the understanding, and efforts, of Mr. M. Galton and Mr. E. Davies, and I am very grateful to them.

Finally, I would like to thank the Science Research Council for providing the grant which enabled me to do this research.
CONTENTS

CHAPTER 1 THE PREPARATION AND REACTIONS OF SOME MONO-ALKENE-ALKyne COMPLEXES OF RHODIUM(I)

1.1 Introduction 1

1.2 Results and discussion
   A. The preparation of new mono-alkene-alkyne complexes of rhodium(I) 6
   B. Reactions of alkene-alkyne complexes involving diene formation 18
   C. Reactions of phosphines, arsines and stibines with alkene-alkyne complexes 33
   D. Reactions of pyridines 42
   E. Attempted preparations of hexafluoroacetylacetonato(alkene)(alkyne)rhodium(I) complexes 54

1.3 Experimental 56

CHAPTER 2 REACTIONS OF HEXAFLUOROPROPANONE WITH ALKYNEDIOL COMPLEXES OF PLATINUM(0)

2.1 Introduction
   Alkyne complexes of zerovalent platinum 91

2.2 Results and discussion
   A. Reactions of hexafluoropropanone with alkynediolbis-(triphenylphosphine)platinum(0) complexes 114
   B. Reactions of electrophilic alkenes and alkynes with but-2-yne-1,4-diolbis(triphenylphosphine) platinum(0) 122

2.3 Experimental 125
CHAPTER 3 THE PREPARATION OF SOME NOVEL METALLACYCLOBUTANE COMPLEXES

3.1 Introduction

The preparation and reactions of metallacyclobutane complexes of palladium and platinum

3.2 Results and discussion

3.3 Experimental

REFERENCES

Chapter 1 165
Chapter 2 169
Chapter 3 173
SUMMARY

In chapter one, the series of complexes of the type [Rh(dpm)(alkene)(C\textsubscript{4}F\textsubscript{6})] is extended by alkene displacement reactions of [Rh(dpm)(\text{C}_{2}H_{4})(C\textsubscript{4}F\textsubscript{6})]. The reaction of some of these alkene-alkyne complexes with cyclopropane, propene and tetramethyallallene, to give 1,4-diene complexes of rhodium is described, together with the X-ray crystal structure of the tetramethyallalene derivative. Complexes of the type [Rh(acac)(L)\textsubscript{2}(C\textsubscript{4}F\textsubscript{6})] (L=PPh\textsubscript{3}, PPh\textsubscript{2}Me, AsPh\textsubscript{3}, SbPh\textsubscript{3}) and [Rh(dpm)(L)(C\textsubscript{4}F\textsubscript{6})] (L=PPh\textsubscript{3}, P(C\textsubscript{6}H\textsubscript{11})\textsubscript{3}, AsPh\textsubscript{3}) are characterised, and rhodacyclopentene complexes \([\text{Rh}\{CH\textsubscript{2}CH\textsubscript{2}C(CF\textsubscript{3})=C(CF\textsubscript{3})\}](dpm)(L)\textsubscript{2}\) are isolated from the reaction of pyridine derivatives (L=C\textsubscript{5}H\textsubscript{5}N, 3-MeC\textsubscript{5}H\textsubscript{4}N, 3,5-Me\textsubscript{2}C\textsubscript{5}H\textsubscript{3}N) with [Rh(dpm)(\text{C}_{2}H_{4})(C\textsubscript{4}F\textsubscript{6})]. The X-ray crystal structure of the complex, where L=pyridine, is described.

Chapter two presents a review of the preparation, physico-chemical properties and reactions of platinum(0)-alkyne complexes. This is followed by a description of the characterisation of some platinaacyclic complexes which are isolated from the reactions of hexafluoropropanone with alkynediolbis(triphenylphosphine)platinum(0) complexes. The result of the X-ray crystal structure determination of the but-2-yne-1,4-diol derivative is discussed. A series of alkyne displacement reactions is described, for the reactions of some electrophilic alkenes and alkynes with \([\text{Pt}(H_{2}C(OH)C\equiv CCH_{2}OH)(PPh\textsubscript{3})\textsubscript{2}]\), and the $^{31}$P n.m.r. spectroscopic data for the products are reported.
After a review of the preparation and reactions of metallacyclobutane complexes of palladium and platinum, chapter three describes the preparation and characterisation of a series of metallacyclobutanone complexes, from the reactions of acetonedicarboxylic acid dimethyl ester with the complexes ML₄ (M=Pt, L=PPh₃, PPh₂Me, PPhMe₂; M=Pd, L=PPh₃).
### ABBREVIATIONS

#### General

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Angström unit</td>
</tr>
<tr>
<td>ac</td>
<td>alkyne</td>
</tr>
<tr>
<td>acac</td>
<td>anion of acetylacetone</td>
</tr>
<tr>
<td>ACADME</td>
<td>acetonedicarboxylic acid dimethyl ester</td>
</tr>
<tr>
<td>apemino</td>
<td>anion of 4-aminopent-3-ene-2-imine</td>
</tr>
<tr>
<td>cod</td>
<td>cis-cis-cyclo-octa-1,5-diene</td>
</tr>
<tr>
<td>cp</td>
<td>anion of cyclopentadiene</td>
</tr>
<tr>
<td>diphos</td>
<td>1,2-bis(diphenylphosphino)ethane</td>
</tr>
<tr>
<td>dpm</td>
<td>anion of dipivaloylmethane(2,2,6,6-tetramethyl-3,5-heptanedione)</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>hfacac</td>
<td>anion of hexafluoroacetylacetone</td>
</tr>
<tr>
<td>HFP</td>
<td>hexafluoropropanone</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>Ph</td>
<td>phenyl</td>
</tr>
<tr>
<td>py</td>
<td>pyridine</td>
</tr>
<tr>
<td>tBu</td>
<td>tertiary butyl</td>
</tr>
<tr>
<td>thf</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMA</td>
<td>tetramethylallene</td>
</tr>
</tbody>
</table>

#### Experimental data

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>br</td>
<td>broad</td>
</tr>
<tr>
<td>d</td>
<td>doublet</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>i.r.</td>
<td>infra-red</td>
</tr>
<tr>
<td>m</td>
<td>multiplet (n.m.r.); medium (i.r.)</td>
</tr>
<tr>
<td>M⁺</td>
<td>molecular ion</td>
</tr>
<tr>
<td>MHz</td>
<td>mega-hertz</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>mmol</td>
<td>millimole</td>
</tr>
<tr>
<td>M.P.</td>
<td>melting point</td>
</tr>
<tr>
<td>n.m.r.</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>p.p.m.</td>
<td>parts per million</td>
</tr>
<tr>
<td>q</td>
<td>quartet</td>
</tr>
<tr>
<td>quin</td>
<td>quintet</td>
</tr>
<tr>
<td>s</td>
<td>singlet (n.m.r.); strong (i.r.)</td>
</tr>
<tr>
<td>sh</td>
<td>shoulder</td>
</tr>
<tr>
<td>t</td>
<td>triplet</td>
</tr>
<tr>
<td>T.M.S.</td>
<td>tetramethyilsilane</td>
</tr>
<tr>
<td>w</td>
<td>weak</td>
</tr>
</tbody>
</table>
For Heather
CHAPTER ONE
THE PREPARATION AND REACTIONS OF SOME MONO-ALKENE-ALKYNE COMPLEXES OF RHODIUM(I).

1.1 Introduction

The reaction of hexafluorobut-2-yne with the rhodium(I) complexes \([\text{Rh(\(\beta\)-ketoenolate)(alkene)}_2]\) at room temperature can give one of two types of complex (I) and (II) depending on the ligands attached to the metal,\(^{1-4}\) as shown in Figure 1.1.

In both complexes (I) and complexes (II), one molecule of hexafluorobut-2-yne has added 1,4 across the rhodium-\(\beta\)-ketoenolate ring. In complexes (I) cyclocotrimisation has occurred between two molecules of the alkyne and one molecule of ethene, to form 1,2,3,4-tetrakis(trifluoromethyl)cyclohexa-1,2-diene, which is co-ordinated to the rhodium through the diene system, and one molecule of ethene has been lost. In complexes (II), three molecules of the alkyne have cyclotrimerised to form hexakis(trifluoromethyl)benzene, which is rigidly co-ordinated to the rhodium as a diene. Both molecules of ethene, or the cyclo-octa-1,5-diene molecule, have been lost in the reaction.

In an analogous reaction to that in which complex (I) is formed, hexafluorobut-2-yne was found to react with

![Diagram of complex (III)](image-url)
[\text{Rh}(\text{acac})(\text{cis-C}_8\text{H}_{14})_2] \text{ at room temperature to give complex (III).}^4 \text{ One molecule of cyclo-octene has been incorporated in the bicyclo[6.4.0]dodeca-9,11-diene ring.}

The metal catalysed cyclocotramerisation of two molecules of alkyne with one molecule of alkene, to form derivatives of cyclohexa-1,3-diene has been the subject of a number of studies.\textsuperscript{5-14} The intermediacy of metallacyclopentadienes has been shown,\textsuperscript{5,8,10,11} as exemplified in Figure 1.2 for cobalt\textsuperscript{8}, and in Figure 1.3 for palladium\textsuperscript{10}.

A metallacyclopentene intermediate has been shown for cobalt\textsuperscript{9} (Figure 1.4).

\[\text{Co}(\eta^5-\text{C}_5\text{H}_5)(\text{PPh}_3)_2 \xrightarrow{R^1\text{C}==\text{CR}^2} \text{Co}(\eta^5-\text{C}_5\text{H}_5)(\text{PPh}_3)(R^1\text{C}==\text{CR}^2)]\]

\[R^3\text{C}==\text{CR}^4\]

\[R^5\text{CH}==\text{CHR}^5\]

\[\text{Co}(\eta^5-\text{C}_5\text{H}_5)(\text{PPh}_3)\]

\[\text{Figure 1.2} \quad [R=\text{H, Ph, CO}_2\text{Me.}]\]

\[\text{[Pd}_2(\text{dba})_3] \xrightarrow{\text{RC}==\text{CR}} \]

\[\text{Pd} \quad \longrightarrow \quad \text{RC}==\text{CR} \quad \longrightarrow \quad \text{RC}==\text{CR} \]

\[\text{Figure 1.3} \quad [\text{dba} = \text{dibenzylidene acetone; } R = \text{CO}_2\text{Me.}]\]
Recently, mono-alkene-alkyne complexes of rhodium(I) were isolated, and shown to be intermediates in the formation of the cyclohexadiene systems (I) and (III), (Figure 1.5):

\[ \text{[Rh(dpm)(C}_2\text{H}_4)_2] \xrightarrow{\text{C}_4\text{F}_6, -78^\circ\text{C}} \text{[Rh(dpm)(C}_2\text{H}_4)(\text{C}_4\text{F}_6)]} \]

\[ \text{C}_4\text{F}_6 \quad \text{Room temperature} \]

Figure 1.5
In the work presented here, the series of mono-alkene-alkyne complexes of rhodium(I) is extended, and their reactions are investigated.
1.2 Results and discussion

A. The preparation of new mono-alkene-alkyne complexes of rhodium(I).

The complexes (IV) were prepared by the low temperature (-78°C) reaction of hexafluorobut-2-yne with the complexes

![Chemical structure](image)

\[ \text{(IV)} \]

\[ \text{a)} R_2C:CR_2 = C_2H_4; \ R' = \text{CH}_3 \]
\[ \text{b)} R_2C:CR_2 = \text{cis-C}_8\text{H}_{14}; \ R' = \text{CH}_3 \]
\[ \text{c)} R_2C:CR_2 = C_2H_4; \ R' = \text{CM}_3 \]

[\text{Rh(β-ketoenolate)(alkene)}_2]. The crystal structures of the complexes (IVa) and (IVb) showed that the rhodium-alkene bond is longer, and therefore weaker, than the rhodium-alkyne bond.

The conclusion was reached, in a comparison of the X-ray structures of [\text{Rh(acac)}(C_2H_4)_2] and [\text{Rh(acac)}(C_2F_4)] \text{C}_2H_4 and later of [\text{Rh(cp)}(C_2H_4)(C_2F_4)] that the \(\pi\)-acceptor properties of the alkenes dominate the bonding to rhodium in these systems, and C_2F_4 was found to be more strongly bonded than C_2H_4. This confirmed earlier experimental results which had indicated that there is more \(\pi\)-back-bonding to C_2F_4 than to C_2H_4. These rhodium-alkene and rhodium-alkyne distances are given in Table 1.1.
Table 1.1

Rhodium-alkene and rhodium-alkyne interatomic distances for the complexes \([\text{Rh(L)(alkene)}]_2\) and \([\text{Rh(L)(alkene)(alkyne)}]\).

<table>
<thead>
<tr>
<th></th>
<th>Rh-C(_1)</th>
<th>Rh-C(_2)</th>
<th>Rh-C(_3)</th>
<th>Rh-C(_4)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh(acac)}(\text{C}_2\text{H}_4)]_2)</td>
<td>2.13(2)</td>
<td>2.14(2)</td>
<td>2.13(2)</td>
<td>2.14(2)</td>
<td>14</td>
</tr>
<tr>
<td>([\text{Rh(acac)}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)])</td>
<td>2.19(1)</td>
<td>2.19(1)</td>
<td>2.00(1)</td>
<td>2.02(1)</td>
<td>14</td>
</tr>
<tr>
<td>([\text{Rh(cp)}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)])</td>
<td>2.165(6)</td>
<td>2.169(5)</td>
<td>2.022(5)</td>
<td>2.026(5)</td>
<td>15</td>
</tr>
<tr>
<td>([\text{Rh(acac)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)])</td>
<td>2.142(14)</td>
<td>2.171(17)</td>
<td>2.016(10)</td>
<td>2.042(11)</td>
<td>13</td>
</tr>
<tr>
<td>([\text{Rh(acac)}(\text{C}<em>8\text{H}</em>{14})(\text{C}_4\text{F}_6)])</td>
<td>2.163(13)</td>
<td>2.196(11)</td>
<td>2.034(10)</td>
<td>2.059(10)</td>
<td>13</td>
</tr>
</tbody>
</table>

(a. \(C_1\) and \(C_2\) for \(\text{C}_2\text{H}_4\) or \(\text{C}_8\text{H}_{14}\); \(C_3\) and \(C_4\) for \(\text{C}_2\text{F}_4\) or \(\text{C}_4\text{F}_6\))
It is therefore consistent that the electron-withdrawing hexafluorobut-2-yne should exert a similar influence in the complexes (IV), and the consequent weakening of the rhodium-ethene bond in complex (IVc), for example, relative to the bis-ethene complex \([\text{Rh(dpm)(C}_2\text{H}_4)_2]\), suggested that it might be possible to displace the ethene with another alkene, to obtain complexes analogous to (IV), for which the bis-alkene precursors are unknown.

It was found that the alkenes \textit{cis}-cyclo-octene, cycloheptene, propene, \textit{cis}-but-2-ene and \textit{trans}-but-2-ene all displaced ethene from complex (IVc), to give complexes (IVd-h) respectively.

\[
\text{R}_2\text{C} \equiv \text{CR}_2 = \text{cis-C}_8\text{H}_{14} \quad (d) \\
\text{C}_7\text{H}_{12} \quad (e) \\
\text{C}_7\text{H}_6 \quad (f) \\
\text{cis-C}_4\text{H}_8 \quad (g) \\
\text{trans-C}_4\text{H}_8 \quad (h)
\]

No reaction was observed with the alkenes cyclohexene, bicyclo[2.2.1]hept-2-ene and 2,3-dimethylbut-2-ene.

Complexes (IVd-h) have infra-red spectra which are very similar to that for (IVc); the band for the C≡C stretching frequency of the co-ordinated alkyne in complexes (IVf-h) is split into two strong peaks, rather than one strong peak and a shoulder, as observed for the other
complexes (IV). The $^{19}$F n.m.r. spectra for all complexes show a single resonance, with coupling to rhodium observed in all cases except (IVf) and (IVh). In contrast to the $^1$H n.m.r. spectra for complexes (IVA-c), which were run in (CD$_3$)$_2$CO or CD$_2$Cl$_2$, the spectra for complexes (IVd-h), run in CDCl$_3$, show two separate resonances for the two t-butyl groups of the dpm ligand. Table 1.2 gives the n.m.r. data for the complexes [Rh(dpm)(alkene)(C$_4$F$_6$)].

The $^1$H n.m.r. spectrum of (IVc), [Rh(dpm)(C$_2$H$_4$)(C$_4$F$_6$)], was re-run in CDCl$_3$, and showed separate signals for the t-butyl groups, at 8.84 and 8.89$\tau$ [lit.value = 8.86$\tau$(s)\(^4\)]. The ethene protons were seen as a doublet, with coupling to the rhodium, (6.33$\tau$, $J_{\text{RhH}}$=2Hz)\(^4\) at room temperature. On cooling to -50°C, the signal was found to split into two doublets, centred at 5.80 and 7.06$\tau$.

This suggested that the ethene might be rotating about the rhodium-ethene axis, at room temperature, and that the low temperature $^1$H n.m.r. spectrum shows the "inner" and "outer" environments for the ethene protons, as shown in Figure 1.6.

![Figure 1.6](image)
<table>
<thead>
<tr>
<th>Complex</th>
<th>$^{19}$F n.m.r. $^a$</th>
<th>$^1$H n.m.r. $^b$</th>
<th>алкene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_4^F_6$</td>
<td>$J_{RhF}$(Hz)</td>
<td>$\text{CMe}_3$</td>
</tr>
<tr>
<td>[Rh(dpm)(C$_2$H$_4$)(C$_4^F_6$)]</td>
<td>55.02</td>
<td>2</td>
<td>8.84(s)</td>
</tr>
<tr>
<td>i) R. T.</td>
<td>Not recorded</td>
<td>8.84(s)</td>
<td>8.89(s)</td>
</tr>
<tr>
<td>ii) -50°C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Rh(dpm)(C$_3$H$_6$)(C$_4^F_6$)]</td>
<td>52.68</td>
<td>-</td>
<td>8.84(s)</td>
</tr>
<tr>
<td>[Rh(dpm)(cis-C$_4^H_8$)(C$_4^F_6$)]</td>
<td>52.91</td>
<td>1.6</td>
<td>8.85(s)</td>
</tr>
<tr>
<td>[Rh(dpm)(trans-C$_4^H_8$)(C$_4^F_6$)]</td>
<td>53.72</td>
<td>-</td>
<td>8.85(s)</td>
</tr>
<tr>
<td>[Rh(dpm)(C$<em>8$H$</em>{14}$)(C$_4^F_6$)]</td>
<td>52.66</td>
<td>2</td>
<td>8.83(s)</td>
</tr>
<tr>
<td>[Rh(dpm)(C$<em>7$H$</em>{12}$)(C$_4^F_6$)]</td>
<td>53.33</td>
<td>2</td>
<td>8.82(s)</td>
</tr>
</tbody>
</table>

$^a$ Measured in CDCl$_3$; chemical shifts (p.p.m.) relative to external CFCl$_3$.

$^b$ Measured in CDCl$_3$; chemical shifts (τ) relative to internal T.M.S.
The rotation of co-ordinated alkenes has been the subject of much study in recent years, and work has been performed to evaluate the effects of electronic and steric factors in determining the magnitude of the rotational energy barrier.

Thus, for example, bis-alkene complexes of rhodium(I)\textsuperscript{17-24}, five-co-ordinate cyanoalkene complexes of rhodium(I)\textsuperscript{25-28}, mono-alkene complexes of platinum(II)\textsuperscript{29-32} and various alkene complexes of iridium(I)\textsuperscript{33-35} have been studied, using variable-temperature \textsuperscript{1}H n.m.r. techniques.

There are two possible mechanisms for the alkene rotation, as shown in Figure 1.7. Mechanism A has been proposed in all these cases, because mechanism B would result in the breaking of both the σ- and π-components of the metal-alkene bond (using the bonding scheme proposed by Dewar\textsuperscript{36}, and Chatt and Duncanson\textsuperscript{37}), causing dissociation of the alkene. Mechanism A always leaves the σ-bond intact, and only the d-π*-orbital overlap is ruptured, so the "propellor-like" rotation seems more probable.
Direct evidence for this type of rotation has been shown, using the complex \([\text{Os(CO)(NO)(PPh}_3\lambda_2\text{C}_2\text{H}_4)]\text{PF}_6\)\(^{38}\), where each end of the co-ordinated ethene molecule is in a different chemical environment, by a study of its variable-temperature ^{13}\text{C} \text{n.m.r.} \text{ spectrum.}

The coalescence temperature for complex (IVc) was found to be -30\(^\circ\text{C}\), and using the approximate formula of Gutowsky and Holm\(^{39}\), as applied previously to these systems,\(^{21,29}\) the free energy of activation for the ethene rotation in complex (IVc) was calculated to be 11.4 kcal.mol\(^{-1}\).

\[
\Delta G^\ddagger = -RT_c \ln \left( \frac{\pi \Delta \nu h}{\sqrt{2} k T_c} \right)
\]

\(T_c\) = Coalescence temperature; \(\Delta \nu\) = maximum separation of the signals, in the absence of exchange of environments;
\(R\) = Gas constant; \(h\) = Planck's constant; \(k\) = Boltzmann's constant.
Substituting for the constants, the expression simplifies to:

\[
\Delta G^\ddagger = \frac{4.576T_c}{1000} \left\{ 9.9722 + \log_{10} T_c - \log_{10} \Delta \nu \right\} \text{ kcal.mol}^{-1}
\]

<table>
<thead>
<tr>
<th>(\Delta G^\ddagger)</th>
<th>(T_c)</th>
<th>(\Delta \nu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.4</td>
<td>-30</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>-50</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.3 compares the free energies of activation for a number of bis-alkene complexes of rhodium(I).

The \(^1\text{H} \text{n.m.r.} \text{ spectra for complexes (IVf) and (IVg) are temperature invariant, with a signal for the methyl protons on the alkenes at 8.27\(r\) (doublet) in both cases. The spectrum for the propene complexes (IVf) is very similar to that described for the bis-propene complex \([(\text{Rh(acac})(\text{C}_3\text{H}_6)\text{)}]^{16},\)
Table 1.3

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_a$ (kcal mol$^{-1}$)</th>
<th>$\Delta G$ (kcal mol$^{-1}$)</th>
<th>$T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="$%5Ctext%7BC%7D_2%5Ctext%7BH%7D_4$">Rh(dpm)$_2$</a>($\text{C}_2\text{F}_4$)$_2$]</td>
<td>-</td>
<td>11.4</td>
<td>-30°C</td>
</tr>
<tr>
<td><a href="$%5Ctext%7BC%7D_2%5Ctext%7BH%7D_4$">Rh($\text{C}_5\text{H}_5$)$_2$</a>($\text{C}_2\text{F}_4$)$_2$]</td>
<td>13.6</td>
<td>-</td>
<td>-10°C</td>
</tr>
<tr>
<td><a href="$%5Ctext%7BC%7D_2%5Ctext%7BH%7D_4$">Rh($\text{C}_5\text{H}_4$)CN</a>($\text{C}_2\text{F}_4$)$_2$]</td>
<td>14.1</td>
<td>14.1</td>
<td>22°C</td>
</tr>
<tr>
<td><a href="$%5Ctext%7BC%7D_2%5Ctext%7BH%7D_4$">Rh($\text{C}_5\text{H}_4$)($\text{CO}_2\text{Me}$)</a>$_2$]</td>
<td>-</td>
<td>&gt;16.9</td>
<td>22°C</td>
</tr>
<tr>
<td><a href="$%5Ctext%7BC%7D_2%5Ctext%7BH%7D_4$">Rh($\text{C}_5\text{Me}_5$)</a>$_2$]</td>
<td>15.0</td>
<td>15.7</td>
<td>&gt;60°C</td>
</tr>
<tr>
<td><a href="$%5Ctext%7BC%7D_2%5Ctext%7BH%7D_4$">Rh($\text{C}_5\text{Me}_5$)</a>$_2$]$^{2+}$]</td>
<td>11.02</td>
<td>12.26</td>
<td>55°C</td>
</tr>
<tr>
<td><a href="$%5Ctext%7BC%7D_2%5Ctext%7BH%7D_4$">Rh(acac)</a>$_2$]</td>
<td>16.17</td>
<td>-</td>
<td>-23°C</td>
</tr>
<tr>
<td><a href="$%5Ctext%7BC%7D_2%5Ctext%7BH%7D_3%5Ctext%7BF%7D_3$">Rh($\text{C}_5\text{H}_5$)$_2$</a>$_2$]</td>
<td>-</td>
<td>-</td>
<td>68°C</td>
</tr>
</tbody>
</table>
with an irregular quadruplet signal for the alkenic protons (6.03-6.88).

In order to determine whether the methyl groups on the alkenes were in "inner" or "outer" environments, single crystal X-ray structure determinations were attempted. Unfortunately, the crystal of complex (IVf) decomposed in the X-ray beam, but that of complex (IVg) was sufficiently stable for the orientation of cis-but-2-ene to be determined, although the data are not of very great accuracy, and have not therefore been refined. The methyl groups are, as predicted by steric arguments, directed away from the co-ordinated alkyne, as shown in Figure 1.8.

![Figure 1.8](image)

It is therefore proposed that the methyl group of the propene ligand in complex (IVf) is similarly directed away from the alkyne.

A more detailed investigation of the $^1H$ n.m.r. of the trans-but-2-ene complex (IVh) was consequently carried out, because a stationary alkene would necessitate having an
"inner" methyl group, and possibly result in distortion of the alkene. However, it was found that over several hours, at room temperature in CDCl₃ solution, the complex rearranged to give the cis-but-2-ene complex (IVg), identified by its ¹H n.m.r. spectrum.

It was found subsequently that the successful preparation of complex (IVh) from [Rh(dpm)(C₆H₄)(C₄F₆)] (IVc) and trans-but-2-ene depended upon a low temperature and a short reaction time, and often complex (IVg) only could be detected in the ¹H n.m.r. spectrum of the reaction product.

The phenomenon of metal-catalysed cis-trans, and trans-cis isomerisation has been noted previously, and metal hydride, ionic, or dipolar intermediates have been proposed. The mechanism for the conversion of complex (IVh) to (IVg) is uncertain, but it seems unlikely to involve a metal hydride intermediate, on the basis of the results reported in Section 1.2B, where the hexafluorobut-2-yne ligand abstracts a hydrogen atom to form a –C(CF₃)=C(H)CF₃ group.

It was also possible to prepare the cyclo-octene complex (IVd) by the low temperature (−78°C) reaction of hexafluorobut-2-yne with [Rh(dpm)(C₆H₁₄)₂]. Cyclocotramerisation occurred between one molecule of the cyclic alkene and two molecules of hexafluorobut-2-yne in the room temperature reactions of C₄F₆ with complexes (IVd) and (IVe), to give complexes (V) and (VI) respectively. These complexes were shown to be analogous to complex (III)⁴.
by their $^{19}$F n.m.r. spectra. The cyclocotramerised diene ligands are distinguished from the rigid hexakis(trifluoromethyl)-benzene ligand by having two, $^2,4$ instead of three $^2,4,48$ broad signals in their $^{19}$F n.m.r. spectrum. Table 1.4 contrasts the $^{19}$F n.m.r. data for complexes (III)$^4$, (V) and (VI), with that for some complexes containing a hexakis(trifluoromethyl)benzene moiety.

The reaction of hexafluorobut-2-yne with $[\text{Rh(dpm)}(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)]$ at $-78^\circ\text{C}$ was found to give complex (IVc) by displacement of the fluoroalkene. More
Table 1.4

$^{19}$F n.m.r. data for complexes (III), (V), (VI) and complexes with a rigid C$_6$(CF$_3$)$_6$ ligand$^a$

<table>
<thead>
<tr>
<th>Complex</th>
<th>RhC(CF$_3$)$_1$=C(CF$_3$)$_2$</th>
<th>C$_6$(CF$_3$)$_6$</th>
<th>{C$<em>8$H$</em>{14}$(C$_4$F$_6$)$_2$} or</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh(cp)]{C$_6$(CF$_3$)$_6$]$^b$</td>
<td>-</td>
<td>-</td>
<td>54.0, 57.1, 61.1</td>
<td>-</td>
</tr>
<tr>
<td>[Rh(apemino. C$_4$F$_6$)]{C$_6$(CF$_3$)$_6$]$^c$</td>
<td>55.1</td>
<td>64.23(15.6)</td>
<td>54.56, 57.25, 61.62</td>
<td>-</td>
</tr>
<tr>
<td>[Rh(acac. C$_4$F$_6$)]{C$_6$(CF$_3$)$_6$]$^d$</td>
<td>55.7</td>
<td>64.2 (16)</td>
<td>55.7, 57.5, 61.8</td>
<td>-</td>
</tr>
<tr>
<td>[Rh(dpm. C$_4$F$_6$)]{C$_6$(CF$_3$)$_6$]$^d$</td>
<td>55.86</td>
<td>59.17(15.8)</td>
<td>55.86, 57.54, 61.97</td>
<td>-</td>
</tr>
<tr>
<td>[Rh(acac. C$_4$F$_6$)]{C$<em>8$H$</em>{14}$(C$_4$F$_6$)$_2$} (III)</td>
<td>56.09</td>
<td>64.67(15.5)</td>
<td>-</td>
<td>58.68, 59.14</td>
</tr>
<tr>
<td>[Rh(dpm. C$_4$F$_6$)]{C$<em>8$H$</em>{14}$(C$_4$F$_6$)$_2$} (V)</td>
<td>52.70</td>
<td>56.19(15.9)</td>
<td>-</td>
<td>54.44, 54.92</td>
</tr>
<tr>
<td>[Rh(dpm. C$_4$F$_6$)]{C$<em>7$H$</em>{12}$(C$_4$F$_6$)$_2$} (VI)</td>
<td>53.61</td>
<td>57.54(15.2)</td>
<td>-</td>
<td>56.07$^g$</td>
</tr>
</tbody>
</table>

a) Chemical shifts (p.p.m.) are relative to CFCI$_3$.

b) Measured in tetrahydrofuran solution, at 56.4 MHz.

c) Measured in (CD$_3$)$_2$CO solution, at 94.1 MHz.

d) Measured in (CH$_3$)$_2$CO solution, at 56.4 MHz.

e) Measured in CDCl$_3$ solution, at 94.1 MHz.

f) Quartet resonances. J$_{FF}$(Hz) given in parentheses.

g) One broad signal (12F).
surprisingly, the room temperature reaction of an excess of tetrafluoroethene with complex (IVc) gave
\[ \text{[Rh(dpm)(C}_2\text{H}_4)(\text{C}_2\text{F}_4)] \] with displacement of the \( \text{C}_4\text{F}_6 \).

The reaction of cis-cis-cyclo-octa-1,5-diene with complex (IVc), at room temperature, also caused the \( \text{C}_4\text{F}_6 \) ligand to be displaced, along with \( \text{C}_2\text{H}_4 \), to give the known complex \([\text{Rh(dpm)}(\text{cod})] \).

The co-ordinated hexafluorobut-2-yn was reported to be displaced from the cyclo-octene complex (IVb), by cyclo-octene, at room temperature, to give
\[ \text{[Rh(acac)(C}_8\text{H}_{14})] \] \(^4\) However, it seems likely that this was unreacted starting material from the reaction:
\[ \text{[Rh(acac)(C}_8\text{H}_{14})]_{2} \xrightarrow{-78^\circ\text{C}} \text{[Rh(acac)(C}_8\text{H}_{14})(\text{C}_4\text{F}_6)] + \text{C}_8\text{H}_{14} \]
rather than the product of the reverse reaction, because no reaction was observed when complexes (IVd) and (IVe) were treated with an excess of cis-cyclo-octene, and cycloheptene, respectively, at room temperature.

A pure sample of \([\text{Rh(acac)(C}_8\text{H}_{14})(\text{C}_4\text{F}_6)] \) (IVb) was then treated with an excess of \( \text{C}_8\text{H}_{14} \), at room temperature, and no displacement of hexafluorobut-2-yne by cyclo-octene was observed.

B. Reactions of alkene-alkyne complexes involving diene formation.

Although no reaction was observed at room temperature, an excess of cyclopropane shaken with \([\text{Rh(dpm)(C}_2\text{H}_4)(\text{C}_4\text{F}_6)] \) (IVc) at 60°C gave an intractable red oil. The same complex was also isolated in the reaction of propene with complex (IVc).
at 50°C. This complex (VII) has been assigned a 1,2,4,5-\eta-penta-1,4-diene structure, on the basis of its $^1H$ and $^{19}F$ n.m.r. spectra. Microanalytical results and

![Chemical Structure](image)

the mass spectrum for complex (VII) indicate that one molecule of cyclopropane, or of propene, has replaced the molecule of ethene. Confirmation that there is no ethene in the complex was given by its preparation from complex (IVd), [Rh(dpm)(C$_8$H$_{14}$)(C$_4$F$_6$)] or complex (IVe), [Rh(dpm)(C$_7$H$_{12}$)(C$_4$F$_6$)] and cyclopropane, at 60°C.

The $^1H$ n.m.r. spectrum of complex (VII) is temperature invariant, and the six distinct environments for the six protons of the $\text{CH}_2=\text{CHCH}_2\text{C(CF}_3\text{)=C(H)CF}_3$ ligand which appear in the spectrum are reproduced in Figure 1.9.

The proton resonance at 7.49 ppm appears as a quartet, due to geminal coupling to three equivalent fluorines ($J_{HF}=11.0$ Hz) and is assigned to $H_4$. It appears at relatively high field, which is consistent with its being an alkenic proton, where the alkene is co-ordinated to a metal.\textsuperscript{18,49} The doublet resonance centred at 6.97 ppm is assigned to the other "inner" alkenic proton, $H_5$. 
A section of the $^1$H n.m.r. spectrum of complex (VII)
(Coupling constants (Hz) in parentheses)
and appears as a doublet due to trans coupling to H_3 (J_HH=12Hz). The "outer" proton, H_6, appears at lower field (6.75_1), as is generally observed^{18,49} and shows cis coupling to H_3 (J_HH=8 Hz). No coupling between H_5 and H_6 is observed, nor can any rhodium coupling be detected. Rhodium coupling to "inner" and "outer" protons in similar environments to H_5 and H_6 is sometimes observed^{49,60} (J_{RhH}=0.5-2.8Hz). The multiplet resonance at 5.50_1 is assigned to H_3. This proton shows couplings to H_1, H_2 and H_6 of similar magnitudes, together with a larger coupling to H_5. The signals at 6.38_1 and 7.96_1 can be assigned to H_1 and H_2, although unique assignments to H_1 and H_2 cannot be made. The signals appear as doublets of doublets (J_{H_1H_2}=13 Hz, J_{H_1H_3}=8 Hz, J_{H_2H_3}=6 Hz).

These assignments have been further substantiated by proton-proton decoupling experiments. (See experimental section (B)1(i)).

The^{19}F n.m.r. spectrum of complex (VII) shows a quartet signal at 60.48 p.p.m., relative to external fluorotrichloromethane, (J_{FF}=11.0 Hz) with coupling to the rhodium (J_{RhF}=1.2 Hz), and an apparent quintet formed by the overlap of two quartet signals, due to the proton-fluorine coupling being fortuitously identical in magnitude to the fluorine-fluorine coupling (53.46 p.p.m. relative to external fluorotrichloromethane, J_{FF}=J_{HF}=11.0 Hz). The cis arrangement of the CF_3 groups about the double bond is suggested by a comparison with the coupling constants for the known vinylic systems M-C(CF_3)=C(H)CF_3, where either cis^{50-52} or trans^{53,54} geometry is observed. The data are shown in Table 1.5.
Table 1.5.

$^{19}$F n.m.r. coupling constants for M-C(CF$_3$)=C(H)CF$_3$ systems

<table>
<thead>
<tr>
<th>Complex</th>
<th>$J_{12}$ (Hz)</th>
<th>$J_{13}$ (Hz)</th>
<th>$J_{23}$ (Hz)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ph$_3$P)$_2$Pt</td>
<td>12.2</td>
<td>0</td>
<td>9.6</td>
<td>50</td>
</tr>
<tr>
<td>(Ph$_3$P)$_2$Ru</td>
<td>14.4</td>
<td>0</td>
<td>11.0</td>
<td>51</td>
</tr>
<tr>
<td>(Ph$_3$P)$_2$(CO)Rh</td>
<td>11.2</td>
<td>2.5</td>
<td>10.7</td>
<td>52</td>
</tr>
<tr>
<td>(OC)$_2$Mn</td>
<td>2.3</td>
<td>2.3</td>
<td>9.6</td>
<td>53</td>
</tr>
<tr>
<td>(OC)$_2$Re</td>
<td>2.5</td>
<td>2.5</td>
<td>9.1</td>
<td>54</td>
</tr>
</tbody>
</table>
A possible mechanism for the formation of complex (VII) from propene and \([\text{Rh(dpm)}(C_2H_4)(C_4F_6)]\) is illustrated in Figure 1.10.
Some evidence for the formation of the $\eta^3$-allyl intermediate is given by the preparation of allyl complexes from the reaction of propene with $[\text{IrH}_2(\text{PPh}_3)_2]$ and with $[\text{Ru}(\text{PPh}_3)_4(\pi-\text{MeCN})].\text{MeCN}$, and by the observation of the temperature dependent equilibrium:

$$
\begin{align*}
\text{Ni} & \quad \text{PF}_3 & -40^\circ \text{C} & \quad \text{Ni} \quad \text{PF}_3 \\
\text{H} & \quad \text{H} & -50^\circ \text{C} & \quad \text{H} \quad \text{H}
\end{align*}
$$

Allyl complexes of rhodium(III) have been prepared from divinylcyclopropane derivatives. Bis-allyl complexes of rhodium(III) have been shown to give $\eta^4$-hexa-1,5-diene

$$
[Rh_{\text{III}}(\eta^3\text{-allyl})_2\text{Cl}]_2 \xrightarrow{\text{AgBF}_4/\text{thf}} [Rh_{\text{III}}(\eta^3\text{-allyl})_2(\text{thf})_2].\text{BF}_4
$$

Figure 1.11.

a) $R=H$, Arene = 1,3,5-C$_6$H$_3$Me$_3$

b) $R=H$, Arene = C$_6$Me$_6$

c) $R=H$, Arene = 1,2-C$_6$H$_4$(OMe)$_2$

d) $R=\text{Me}$, Arene = 1,3,5-C$_6$H$_3$Me$_3$

e) $R=\text{Me}$, Arene = C$_6$Me$_6$

complexes, by the reductive dimerisation of the two $\eta^3$-allyl ligands. In this way, the arene rhodium(I) complexes (VIII) were isolated, as shown in Figure 1.11.
Allyl palladium complexes have been prepared from substituted cyclopropanes, and a small amount of cyclopropane was isomerised to propene, in its reaction with PdCl₂. In the reaction of substituted cyclopropanes with [RhCl(CO)₂]₂, some evidence was found for the isomerisation of the cyclopropanes to alkenes, and an η³-allyl rhodium(III) hydride complex was proposed as an intermediate.

The reaction of cyclopropane with [Rh(dpm)(C₂H₄)⁻ \( \rightarrow \) \( (C₄F₆) \)] may therefore also involve a rhodium-allyl intermediate (Figure 1.10).

Tetramethylallene (TMA) reacts with [Rh(dpm)(C₂H₄)⁻ \( \rightarrow \) \( (C₄F₆) \)](IVc) at room temperature, to form yellow crystals of the substituted 1,2,4,5-η-penta-1,4-diene complex (IXa).

A section of the ¹H n.m.r. spectrum of complex (IXa) is reproduced in Figure 1.12, together with peak assignments.
A section of the $^1$H n.m.r. spectrum of complex (IXa)

(Coupling constants (Hz) in parentheses)
and coupling constants. As for complex (VII) the chemical shifts for the alkenic protons are consistent with data for \( \eta^2 \)-bonded alkene-metal complexes.\(^{18,49}\)

The \( ^{19}F \) n.m.r. spectrum for complex (IXa) is similar to that of complex (VII), and shows a quartet signal at 52.52 p.p.m. relative to external fluorotrichloromethane, \((J_{FF}=9.0\text{Hz})\), together with an apparent quintet at 53.86 p.p.m. \((J_{FF}=J_{HF}=9.0\text{Hz})\), formed, as for complex (VII) by the overlap of two quartets. No rhodium coupling is resolved. The magnitude of the fluorine-fluorine coupling constant is again consistent with a cis arrangement of the CF\(_3\) groups about the double bond (see Table 1.5).

Complex (IXa) was also prepared by the room temperature reactions of TMA with \([\text{Rh}(dpm)(C_8H_{14})(C_4F_6)](IVd)\) and with \([\text{Rh}(dpm)(C_7H_{12})(C_4F_6)](IVe)\).

In an identical reaction, the acetylacetonato analogue (IXb) of complex (IXa) was isolated by treating \([\text{Rh}(acac)(C_2H_4)(C_4F_6)](IVA)\) with TMA. Complex (IXb) is crystalline and has a \(^1H\) n.m.r. spectrum which is almost identical to that of complex (IXa), and its \(^{19}F\) n.m.r. spectrum too is similar, with a quartet signal at 53.22 p.p.m. \((J_{FF}=9.0\text{Hz})\) and a "quintet" at 54.51 p.p.m. \((J_{FF}=J_{HF}=9.0\text{Hz})\), relative to external fluorotrichloromethane.

The structure of complex (IXa) has been recently confirmed by a single crystal X-ray crystallographic study.\(^{40}\)

The crystals of (IXa), \(C_{22}H_{31}O_2F_6\text{-Rh}\), (molecular weight = 544.39) are monoclinic with space group P2\(_1\)/c, and

\[
a = 11.50\text{Å}, \quad b = 19.00\text{Å}, \quad c = 23.32\text{Å}, \quad \beta = 99.74^\circ, \\
U = 5022.0\text{Å}^3 \text{ and } Z = 8.
\]
Other penta-1,4-diene complexes of rhodium have been reported, and it is useful to make a comparison of the results. The crystal structure of the dibenzylideneacetone complex (X) has been reported, and a comparison of some of the bond lengths in the carbon skeletons of the 1,4-dienes in (IXa) and (X) is shown in Table 1.6.

The complexes (XI) were prepared for diene isomerisation studies, and were isolated as red oils.

\[ \text{(X)} \]

\[ \text{(XI)} \]

a) \( R=H; L=\eta^5-C_5H_5 \)
b) \( R=H, L=\eta^5-C_5H_4CO_2Me \)
c) \( R=Me, L=\eta^5-C_5H_4CO_2Me \).
Table 1.6

Some interatomic distances (Å) for complexes (IXa) and (X)

<table>
<thead>
<tr>
<th></th>
<th>(IXa)</th>
<th>(X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-C₁</td>
<td>2.185</td>
<td>2.241(6)</td>
</tr>
<tr>
<td>Rh-C₂</td>
<td>2.171</td>
<td>2.149(6)</td>
</tr>
<tr>
<td>Rh-C₅</td>
<td>2.155</td>
<td>2.230(6)</td>
</tr>
<tr>
<td>Rh-C₄</td>
<td>2.089</td>
<td>2.152(6)</td>
</tr>
<tr>
<td>C₁-C₂</td>
<td>1.469</td>
<td>1.406(8)</td>
</tr>
<tr>
<td>C₅-C₄</td>
<td>1.435</td>
<td>1.416(9)</td>
</tr>
<tr>
<td>C₃-C₆</td>
<td>1.380</td>
<td></td>
</tr>
<tr>
<td>C₃-O</td>
<td></td>
<td>1.236(7)</td>
</tr>
</tbody>
</table>

(IXa) $R_1=H$, $R_2=Me$, $R_3=R_4=CF_3$.

(X) $R_1=R_4=Ph$, $R_2=R_3=H$.

a. Refinement of the crystallographic data for complex (IXa) is not yet complete.
Their $^1$H n.m.r. data were reported, but no details of coupling constants were given. The $^1$H n.m.r. data for the 1,4-diene ligands in complexes (VII), (IXa), (IXb), (X) and (XIa-c) are presented in Table 1.7. The numbering scheme is that adopted earlier for complexes (VII) and (IX), and is shown in Figure 1.13.

![Diagram of complexes](image)

**Figure 1.13**

In their reactions with carbon monoxide, complexes (VII) and (IXa) both gave the known complex $[\text{Rh(dpm)}(\text{CO})_2]^+$ [ν(C=O) = 2080, 2011 cm$^{-1}$], with complete displacement of the 1,4-diene ligand. In an attempt to isolate a crystalline complex from the oil (VII), a solution of (VII) in diethyl ether was treated with triphenylphosphine. Unfortunately, this resulted only in the complete decomposition of the complex to rhodium metal.

The reaction of TMA with the acetylacetonato- and dipivalocylmethanato(alkene)(alkyne)rhodium(I) complexes reported here is in complete contrast with the reaction
<table>
<thead>
<tr>
<th>Complex</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(VII)</td>
<td>6.38(dd)</td>
<td>7.96(dd)</td>
<td>5.50(m)</td>
<td>7.49(q)</td>
<td>6.97(d)</td>
<td>6.75(d)</td>
<td>(CF₃)</td>
<td>(CF₃)</td>
<td>This work</td>
</tr>
<tr>
<td>(IXa)</td>
<td>8.40(s)[Me]</td>
<td>7.85(s)[Me]</td>
<td>7.64(qd)</td>
<td>6.74(s)</td>
<td>7.37(d)</td>
<td>(CF₃)</td>
<td>(CF₃)</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>(IXb)</td>
<td>8.40(s)[Me]</td>
<td>7.86(s)[Me]</td>
<td>7.60(qd)</td>
<td>6.74(s)</td>
<td>7.35(d)</td>
<td>(CF₃)</td>
<td>(CF₃)</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td>(X)</td>
<td>[C=O]</td>
<td>5.17(dd)</td>
<td>6.47(dd)</td>
<td>6.47(dd)</td>
<td>2.80(m)[Ph]</td>
<td>2.80(m)[Ph]</td>
<td>5.17(dd)</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>(XIa)</td>
<td>7.8(m)</td>
<td>6.9(m)</td>
<td>8.92(dd)</td>
<td>8.92(dd)</td>
<td>7.74(dt)</td>
<td>7.74(dt)</td>
<td>6.9(m)</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>(XIb)</td>
<td>7.8(m)</td>
<td>6.9(m)</td>
<td>8.7(dd)</td>
<td>8.7(dd)</td>
<td>7.68(dt)</td>
<td>7.68(dt)</td>
<td>6.9(m)</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>(XIC)</td>
<td>8.3(m)</td>
<td>8.5(d)[Me]</td>
<td>6.9(m)</td>
<td>8.75(dd)</td>
<td>8.75(dd)</td>
<td>7.69(dt)</td>
<td>7.69(dt)</td>
<td>6.9(m)</td>
<td>45</td>
</tr>
</tbody>
</table>

a. See Figure 1.13 for numbering of protons.
b. dd = doublet of doublets; dt = doublet of triplets; qd = quartet of doublets.
of allene with acetylacetonatobis(ethene)rhodium(I), which was performed at low temperature.\textsuperscript{69} A bis-allyl rhodium(III) complex was isolated, together with a 3,4-dimethylenerrhodacyclopentane complex, which was shown to be an intermediate in the reaction, as shown in Figure 1.14.

\[
[Rh(acac)(C_2H_4)_2] 
\xrightarrow{-78^\circ C} \text{H}_2\text{C} = \text{C} = \text{CH}_2
\]

\[
\xrightarrow{-35^\circ C} \text{H}_2\text{C} \equiv \text{C} \equiv \text{CH}_2
\]

\begin{center}
Figure 1.14
\end{center}

The room temperature reaction of hexafluorobut-2-yne with the bis-alkene complex \([\text{TMMe}_2]\text{Rh(acac)}\) has been reported,\textsuperscript{3} and a hexakis(trifluoromethyl)benzene complex (II) was isolated (cf. Figure 1.1). The result of a similar reaction, performed at \(-78^\circ C\) is awaited with interest.
C. Reactions of phosphines, arsines and stibines with alkene-alkyne complexes.

Complex (IVc), $[\text{Rh(dpm)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)]$, is known to react with triphenylphosphine, triphenylarsine, triphenylstibine$^{13}$ and 1,2-bis(diphenylphosphino)ethane$^4$ to give the complexes (XII).

\[
\text{(XII)}
\]

\begin{align*}
a) & \quad \text{L} = \text{PPh}_3 \\
b) & \quad \text{L} = \text{AsPh}_3 \\
c) & \quad \text{L} = \text{SbPh}_3 \\
d) & \quad \text{L-} \text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2
\end{align*}

This series of reactions has been extended, and complexes (XIIIe) and (XIIIh) have been prepared, where $\text{L} = \text{PPh}_2\text{Me}$ and $\text{PPh}_2\text{Et}$ respectively.

In a similar series of reactions, the analogous acetylacetonato complexes (XIII) were prepared from $[\text{Rh(acac)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)](\text{IVa})$. 
The equilibrium shown in Figure 1.15 has been proposed for complexes (XIIa-c) in solution, from evidence provided by variable-temperature $^{19}F$ n.m.r. studies.$^{4,13}$

\[
\text{Figure 1.15}
\]
The room temperature $^{19}\text{F}$ n.m.r. spectra all showed one signal, which appeared as a doublet due to coupling to the rhodium ($J_{\text{RhF}}=1.5-2\text{Hz}$). Coupling to phosphorus was not observed for the triphenylphosphine complex (XIIa). On cooling the solutions to $-58^\circ\text{C}$, the spectra then showed two signals, of equal intensity, and phosphorus coupling was observed on the low field signal for complex (XIIa), ($J_{\text{PF}}=16.8\text{Hz}$). This was attributed to coupling to a trans phosphorus atom, and the cis configuration was invoked for complexes (XII), as shown in Figure 1.15.

Although the possibility of rotation of the alkyne cannot be eliminated, this change in the spectra with temperature has been interpreted in terms of ligand dissociation (Figure 1.15) from the observation that the coalescence temperatures ($T_c$) for the spectra are increased by the addition to the solution of an excess of the ligand L.

The diphos complex (XIIId) showed two signals in its $^{19}\text{F}$ n.m.r. spectrum at room temperature, showing that the hexafluorobut-2-ynyl is rigidly bound, and that, as expected, the chelating phosphine ligand is not dissociating. The characterisation of this complex confirmed the assignment of a cis configuration to the complexes (XII).

Complexes (XIIe) and (XIIf) have room temperature $^{19}\text{F}$ n.m.r. spectra similar to that for (XIIId), showing that the phosphines $\text{PPh}_2\text{Me}$ and $\text{PPh}_2\text{Et}$ in these complexes are not dissociating in solution at room temperature.

The observed dissociation of the triphenylphosphine, triphenylarsine and triphenylstibine ligands in solution is probably due to steric effects. Methyldiphenylphosphine
and ethyldiphenylphosphine, which do not dissociate, are
generally regarded as stronger bases than triphenylphosphine
but recently it has been suggested that the donor ability
series should be: 70

\[
PPh_3 > PPh_2 Me > PPhMe_2 > PMe_3
\]

It seems likely that, in these complexes, the smaller
phosphines are more easily accommodated than PPh_3,
AsPh_3 or SbPh_3, to give the d^8 rhodium(I) complexes
\([\text{Rh(dpm)}(L)C_4F_6]^\text{-}, (L=PPh_2Me, PPh_2Et)\).

In the acetylacetonatorrhodium(I) complexes (XIII),
exactly the same situation is observed. One signal is
observed in the room temperature \(^{19}\text{F n.m.r.}\) spectrum
for complexes (XIIIa-c), showing that ligand dissociation
is occurring. Rhodium coupling (\(J_{\text{RhF}}=1.6-2.0\text{Hz}\)) causes
this signal to appear as a doublet. At lower temperatures,
two signals are observed, each of the same intensity,
although the spectrum for the triphenylphosphine complex
(XIIIa) is not sufficiently well resolved for the phosphorus
coupling on the low field signal to be measured.

The bis(methyldiphenylphosphine) complex (XIIIb)
does not show any signals at room temperature, with phosphorus coupling
observed on the low field signal (\(J_{\text{PF}}=12\text{Hz}\)), as for the
dipivaloylmethanato analogue (XIIe), and indicating that
the phosphine ligands are not dissociating at room
temperature.

The \(^{19}\text{F n.m.r.}\) data are shown in Table 1.8 for
complexes (XII) and (XIII), together with the temperatures
at which the two signals of the six co-ordinate complexes
coalesce into the one signal of the five co-ordinate complexes.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Room Temperature&lt;sup&gt;d&lt;/sup&gt;</th>
<th>Low Temperature</th>
<th>T&lt;sub&gt;c&lt;/sub&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(XIIa)</td>
<td>51.66(d, J&lt;sub&gt;Rhf&lt;/sub&gt;=2Hz)</td>
<td>51.62(d, 3F, J&lt;sub&gt;PF&lt;/sub&gt;=16.8Hz)</td>
<td>-19</td>
<td>13</td>
</tr>
<tr>
<td>(XIIb)</td>
<td>52.66(d, J&lt;sub&gt;Rhf&lt;/sub&gt;=2Hz)</td>
<td>51.03(s, 3F)</td>
<td>-44</td>
<td>13</td>
</tr>
<tr>
<td>(XIIc)</td>
<td>52.97(d, J&lt;sub&gt;Rhf&lt;/sub&gt;=1.5Hz)</td>
<td>51.62(s, 3F)</td>
<td>-21</td>
<td>13</td>
</tr>
<tr>
<td>(XIIId)</td>
<td>51.80(dx, 3F, J&lt;sub&gt;PF&lt;/sub&gt;=17.4Hz, J&lt;sub&gt;Rhf&lt;/sub&gt;=4.5Hz)</td>
<td>53.42(d, 3F, J&lt;sub&gt;Rhf&lt;/sub&gt;=3Hz)</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>(XIIe)</td>
<td>51.13(dx, 3F, J&lt;sub&gt;PF&lt;/sub&gt;=16.3Hz, J&lt;sub&gt;Rhf&lt;/sub&gt;=3.6Hz)</td>
<td>51.91(d, 3F, J&lt;sub&gt;Rhf&lt;/sub&gt;=2.2Hz)</td>
<td>-</td>
<td>This work</td>
</tr>
<tr>
<td>(XIIf)</td>
<td>50.66(d, 3F, J&lt;sub&gt;PF&lt;/sub&gt;=11Hz)</td>
<td>53.01(s, 3F)</td>
<td>-</td>
<td>&quot;</td>
</tr>
<tr>
<td>(XIIIa)</td>
<td>51.72(d, J&lt;sub&gt;Rhf&lt;/sub&gt;=1.6Hz)</td>
<td>50.98(s, 3F)</td>
<td>-28</td>
<td>&quot;</td>
</tr>
<tr>
<td>(XIIIb)</td>
<td>52.50(d, J&lt;sub&gt;Rhf&lt;/sub&gt;=1.8Hz)</td>
<td>52.01(d, 3F, J&lt;sub&gt;Rhf&lt;/sub&gt;=2.7Hz)</td>
<td>-57</td>
<td>&quot;</td>
</tr>
<tr>
<td>(XIIIc)</td>
<td>52.57(d, J&lt;sub&gt;Rhf&lt;/sub&gt;=2.0Hz)</td>
<td>52.12(s, 3F)</td>
<td>~ -25</td>
<td>&quot;</td>
</tr>
<tr>
<td>(XIIIId)</td>
<td>51.54(d, 3F, J&lt;sub&gt;PF&lt;/sub&gt;=12Hz)</td>
<td>51.96(s, 3F)</td>
<td>-</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

The infra-red spectra of complexes (XII) and (XIII) were run as nujol mulls, and not as solutions, and are therefore the spectra of the six co-ordinate complexes. They show two bands for $\nu(C=C)$; one at $1810-1832\text{cm}^{-1}$ and one at $1791-1794\text{cm}^{-1}$.

In an attempt to prepare the bis(tricyclohexylphosphine) analogue of complex (XIIa), the complex $[\text{Rh(dpm)}\{P(C_6H_{11})_3\}(C_4F_6)]$ (XIVa) was isolated. It is readily distinguished from the bis-phosphine complexes by its i.r. spectrum. This shows one strong band for the $C=C$ stretching frequency, at about $100\text{cm}^{-1}$ higher than for (XIIa) [$\nu(C=C) = 1924\text{cm}^{-1}$].

Subsequently it was found to be possible to prepare the complexes (XIVb) and (XIVc), from triphenylphosphine and triphenylarsine, in their reactions with $[\text{Rh(dpm)}(C_6H_4)(C_4F_6)]$ using equimolar quantities. However, the reaction of one

\[
\begin{align*}
F_3C & \quad L \quad \text{Rh} \quad \text{CMe}_3 \\
\quad C & \quad \text{O} & \quad \text{C} \\
F_3C & \quad \text{C} & \quad \text{H} \\
\end{align*}
\]

(XIV)

a) $L = P(C_6H_{11})_3$
b) $L = P(C_6H_5)_3$
c) $L = \text{As}(C_6H_5)_3$
molar equivalent of triphenylstibine with [Rh(dpm)(C$_{2}$H$_{4}$)(C$_{4}$F$_{6}$)] produced only the bis-stibine complex (XIIc), leaving some of complex (IVc) unreacted.

The incorporation of only one molecule of tricyclohexylphosphine, to form complex (XIVa) must be a consequence of the steric interference of two cis tricyclohexylphosphine ligands. The fact that only the bis(triphenylstibine) complex (XIIc) can be isolated is an indication of the low electron donating ability of this ligand, such that the d$^8$ rhodium(I) complex [Rh(dpm)(SbPh$_3$)(C$_4$F$_6$)] would be too electron deficient, in the solid state.

The $^{19}$F n.m.r. spectra for complexes (XIV) show one signal, with rhodium coupling ($J_{RhF}$ = 2Hz) in each case.

The infra-red stretching frequencies $\nu$(C=C) are shown in Table 1.9, for complexes (XII), (XIII) and (XIV).

The triphenylphosphine complex (XIVb) was also isolated from the reaction of [Rh(dpm)(C$_6$H$_{14}$)(C$_4$F$_6$)](IVd) or [Rh(dpm)(C$_7$H$_{12}$)(C$_4$F$_6$)](IVe) with an equimolar quantity of triphenylphosphine. Cycloheptene was also displaced from complex (IVe) by triphenylarsine, to give complex (XIVc).

The complexes (XIV) are analogues of the known tetrafluoroethene complexes (XV)$^{71}$. The complexes (XVb) and (XVc) react with hexafluorobut-2-yne at room
Table 1.9

Infra-red data for complexes (XII), (XIII) and (XIV)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Complex</th>
<th>( \nu (\text{C=O}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(XIIa)</td>
<td>[Rh(dpm)(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{4}F\textsubscript{6})] 1815s, 1787s</td>
</tr>
<tr>
<td>(XIIb)</td>
<td>[Rh(dpm)(AsPh\textsubscript{3})\textsubscript{2}(C\textsubscript{4}F\textsubscript{6})] 1821s, 1790s</td>
</tr>
<tr>
<td>(XIIc)</td>
<td>[Rh(dpm)(SbPh\textsubscript{3})\textsubscript{2}(C\textsubscript{4}F\textsubscript{6})] 1829s, 1790m</td>
</tr>
<tr>
<td>(XIID)</td>
<td>[Rh(dpm)(di.phos)(C\textsubscript{4}F\textsubscript{6})] 1829s, 1794m</td>
</tr>
<tr>
<td>(XIIe)</td>
<td>[Rh(dpm)(PPh\textsubscript{2}Me)\textsubscript{2}(C\textsubscript{4}F\textsubscript{6})] 1810m, 1781s</td>
</tr>
<tr>
<td>(XIII)</td>
<td>[Rh(acac)(PPh\textsubscript{2}Et)\textsubscript{2}(C\textsubscript{4}F\textsubscript{6})] 1829m, 1790m</td>
</tr>
<tr>
<td>(XIIIa)</td>
<td>[Rh(acac)(PPh\textsubscript{3})\textsubscript{2}(C\textsubscript{4}F\textsubscript{6})] 1820m, 1786m</td>
</tr>
<tr>
<td>(XIIIb)</td>
<td>[Rh(acac)(AsPh\textsubscript{3})\textsubscript{2}(C\textsubscript{4}F\textsubscript{6})] 1829m, 1791m</td>
</tr>
<tr>
<td>(XIIIc)</td>
<td>[Rh(acac)(SbPh\textsubscript{3})\textsubscript{2}(C\textsubscript{4}F\textsubscript{6})] 1832m, 1790m</td>
</tr>
<tr>
<td>(XIIIId)</td>
<td>[Rh(acac)(PPh\textsubscript{2}Me)\textsubscript{2}(C\textsubscript{4}F\textsubscript{6})] 1815m, 1782m</td>
</tr>
<tr>
<td>(XIVA)</td>
<td>[Rh(dpm){P(C\textsubscript{6}H\textsubscript{11})\textsubscript{3}}(C\textsubscript{4}F\textsubscript{6})] 1924s</td>
</tr>
<tr>
<td>(XIVb)</td>
<td>[Rh(dpm)(PPh\textsubscript{3})\textsubscript{3}(C\textsubscript{4}F\textsubscript{6})] 1940s</td>
</tr>
<tr>
<td>(XIVc)</td>
<td>[Rh(dpm)(AsPh\textsubscript{3})\textsubscript{3}(C\textsubscript{4}F\textsubscript{6})] 1934s</td>
</tr>
</tbody>
</table>

\textsuperscript{a}. Recorded as nujol mulls.
temperature to give the five co-ordinate rhodacyclopentadiene complexes (XVIa) and (XVIb) respectively. The reactions of hexafluorobut-2-yne with $[\text{Rh(dpm)}(\text{AsPh}_3)(C_4F_6)]$, (XIVc), and with $[\text{Rh(dpm)}(\text{SbPh}_3)_2(C_4F_6)]$, (XIIc), were consequently investigated. Complexes (XVIa) and (XVIb) respectively were isolated, in good yield.
The reaction of tetrafluoroethene with complex (XIVc) was performed, and it was found that an excess of the alkene, at -93°C, displaces the co-ordinated hexafluorobut-2-yne, as in the room temperature reaction with \([\text{Rh}(\text{dpm})(C_2\text{H}_4)(C_4\text{F}_6)]\) discussed in Section 1.2A, and \([\text{Rh}(\text{dpm})(\text{AsPh}_3)(C_2\text{F}_4)](\text{XVb})\) was isolated.

A summary of the reactions of the triphenylarsine and triphenylstibine complexes with tetrafluoroethene and with hexafluorobut-2-yne is presented in Figure 1.16.

The reaction of carbon monoxide with \([\text{Rh}(\text{acac})(\text{PPh}_3)^2](C_4\text{F}_6)]\), (XIIIa), also resulted in the displacement of the co-ordinated alkyne, to give yellow crystals of the known complex \([\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]\).72

D. Reactions of pyridines with alkene-alkyne complexes

In the course of investigating the reactions of \(\sigma\)-donor ligands with \([\text{Rh}(\text{dpm})(C_2\text{H}_4)(C_4\text{F}_6)](\text{IVc})\), the rhodium(III) complexes (XVII) were isolated. These

![Diagram](XVII)

- a) \(L = \text{pyridine}\)
- b) \(L = 3\)-methylpyridine
- c) \(L = 3,5\)-dimethylpyridine
complexes are prepared by the room temperature reaction of pyridines with a solution of complex (IVc) in diethyl ether, and form pale yellow-green crystals. These bis-pyridine rhodium(III) adducts were isolated from reactions of one and of two molar equivalents of pyridine with complex (IVc).

The $^1$H n.m.r. spectrum of complex (XVIIa) shows that the ethene molecule has been retained. The appearance of the C$_2$H$_4$ protons as a broad signal (6.80-7.87, 4H) suggests that the ethene is incorporated into a ring or chain system, by a comparison with the spectra of known rhodium complexes with ligands containing a $\text{C}=$C-CH$_2$-CH$_2$-C= ligand, for example. The spectrum also shows two singlet signals of unequal intensities (4.49 and 4.56), which are assigned to the CH of the dpm ligand, and a singlet for each t-butyl group of the dpm ligand (8.90 and 9.01), showing them to be in different chemical environments.

The $^{19}$F n.m.r. spectrum is more surprising, in that it shows three quartet signals (52.83, 54.72 and 57.93 p.p.m., relative to external fluorotrichloromethane). The two lower field quartets are rather poorly resolved, which suggests some rhodium coupling, and they are of unequal intensities. However, their combined intensities are about equal to the intensity of the high field quartet, which is well resolved ($J_{FF}=14.0$Hz) and for which no rhodium coupling is observed. The spectrum is unchanged by heating the CDCl$_3$ solution of complex (XVIIa) to 60°C, and the addition of an excess of pyridine to the CDCl$_3$ solution has no effect.
<table>
<thead>
<tr>
<th>Complex</th>
<th>(L)</th>
<th>(^{19}_F) n.m.r. (^a)</th>
<th>(^{1}_H) n.m.r. (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>52.83(q), 54.72(q)(3F); 57.93(q, 3F)</td>
<td>(4.49(s)) ((IH)) 4.56(s) 8.90(s, 9H) 9.01(s, 9H) 6.80-7.87(br)</td>
</tr>
<tr>
<td>(XVIIa)</td>
<td>(C_5H_5N)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(XVIIb)</td>
<td>3-MeC_5H_4N</td>
<td>53.87(q), 55.94(q)(3F); 59.19(5 lines, 3F)</td>
<td>(4.49(s)) ((IH)) 4.57(s) 8.87(s, 9H) 8.95(s, 9H) 6.78-7.68(br)</td>
</tr>
<tr>
<td>(XVIIc)</td>
<td>3,5-Me_2C_5H_3N</td>
<td>53.15(q), 55.26(q)(3F); 58.26(7 lines, 3F)</td>
<td>(4.51(s)) ((IH)) 4.61(s) 8.88(s, 9H) 8.99(s, 9H) 6.81-7.74(br)</td>
</tr>
</tbody>
</table>

\(^a\) Measured in CDCl\(_3\): Chemical shifts (p.p.m.) relative to external CFCl\(_3\).

\(^b\) Measured in CDCl\(_3\): Chemical shifts (\(\tau\)) relative to internal T.M.S.
Complexes (XVIIb) and (XVIIc) similarly show two unequal singlets in their $^1$H n.m.r. spectra, which are again assigned to the $\gamma$-CH of the dpm ligand. Their $^{19}$F n.m.r. spectra show three signals; two low field quartets with possible rhodium coupling and a higher field multiplet.

The n.m.r. data for complexes (XVII) are summarised in Table 1.10.

A single crystal X-ray diffraction study of complex (XVIIa) was undertaken to enable a structure to be assigned, and to assist in the interpretation of the n.m.r. data. The crystals of complex (XVIIa), C$_{27}$H$_{33}$N$_2$O$_2$F$_6$Rh, (molecular weight = 634.46) are monoclinic, with space group P2$_1$/n, and $a = 11.561\AA$, $b = 16.686\AA$, $c = 14.834\AA$, $\beta = 90.2^\circ$, $V = 2865.4\AA^3$ and $Z = 4$. The results show complex (XVIIa) to be an octahedral rhodium(III) complex, with the pyridine ligands in a cis configuration. Some details of the structure are shown in Figure 1.17.

It is relevant to consider the reactions of pyridine and of triphenylphosphine with the allene complex of rhodium(III), complex (XVIII), for which the following structure has been proposed:

![Diagram](XVIII)
\[
[Rh\{CH_2CH_2C(CF_3)=C(ClCF_3)\}CO(dpmp)(py)_2]
\]

Figure 1.17
This microcrystalline complex was formed by adding $[\text{Rh(acac)}(\text{C}_2\text{H}_4)_2]$ to liquid allene at $-78^\circ\text{C}$, but was found to be unstable at temperatures higher than $0^\circ\text{C}$. The reactions of complex (XVIII) with pyridine and with triphenylphosphine are outlined in Figure 1.18.

$$C_5H_5N_2[(\text{Acac})\text{Rh}(\text{C}_2\text{H}_4)_2(\text{C}_5\text{H}_5N)_2] + \text{C}_3\text{H}_4$$

(XIX)

$$[(\text{Acac})\text{Rh}(\text{C}_2\text{H}_4)_2] \rightarrow \text{PPh}_3 [(\text{Acac})\text{Rh}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)_2] + \text{C}_3\text{H}_4$$

(XX)

Figure 1.18

The single crystal X-ray structure of complex (XIX) has been reported, and it was shown to be an octahedral rhodium(III) complex, with cis pyridine ligands. The structure of complexes (XVII) is therefore very similar to that of complex (XIX). Complex (XX), however, was
assigned a trans configuration, on the basis of $^1H$ n.m.r. data. 69

It is therefore proposed that complexes (XVII) can exist in both cis and trans configurations, in solution, and that the chemical shifts observed for the CF$_3$ groups and for the $\gamma$-CH of the dpm ligand, in the n.m.r. spectra, will be different for the two isomers. The difference in intensity observed for the two singlet signals, in the $^1H$ n.m.r. spectrum, which are assigned to the $\gamma$-CH, can be attributed to the differing concentrations of the cis and trans isomers. Likewise, assigning the lower field quartet signals, in the $^{19}F$ n.m.r. spectrum, to the CF$_3$ group attached to the carbon atom adjacent to rhodium, the different intensities of these two quartets can be attributed to unequal concentrations of the cis and trans isomers.

For the bis-pyridine complex (XVIIa), the chemical shifts of the CF$_3$ group furthest from rhodium are fortuitously identical, for the two isomers. This gives
rise to only one quartet, with no rhodium coupling. However, for complexes (XVIIb) and (XVIIc), these chemical shifts are slightly different for the two isomers, and this gives rise to the observed multiplet, formed by two overlapping quartets, in the $^{19}\text{F n.m.r.}$ spectrum of each complex.

The pyridine ligands in complexes (XVII) do not appear to dissociate in solution, as was observed for the ligands $\text{EPh}_3$ (E=P,As or Sb) in complexes (XII) and (XIII) (Section 1.2C), because the addition of an excess of pyridine to a solution of $[\text{Rh}\{\text{CH}_2\text{CH}_2\text{C(CF}_3)\text{=C(CF}_3)\}_{2}\text{-(dpm)}(\text{py})_2] (XVIIa)$ does not affect the $^{19}\text{F n.m.r.}$ spectrum.

In the light of the reactions described earlier (see Figure 1.18), where the bis-pyridine complex (XIX) was isolated in the pure cis configuration, and the bis-phosphine complex (XX) was isolated in the pure trans configuration, complex (XVIIa) was treated with triphenylphosphine, in diethyl ether solution at room temperature, in an attempt to displace the pyridine ligands and form a pure trans bis-triphenylphosphine complex. A pale yellow crystalline complex (XXI) was isolated from the solution, which, according to microanalytical data, contains one molecule of pyridine and one of triphenylphosphine, per rhodium atom. The $^{1}\text{H}, ^{19}\text{F}$ and proton decoupled $^{31}\text{P n.m.r.}$ spectra suggest that complex (XXI) is the pure cis isomer:
A postulated mechanism for the formation of this pure cis complex from the mixture of cis and trans bis-pyridine complexes (XVIIa) is shown in Figure 1.19.
The $^1$H n.m.r. spectrum shows only one singlet resonance for the 7-CH of the dpm ligand, and the $^{19}$F n.m.r. spectrum shows only two signals, at 53.85 p.p.m. (multiplet, 3F) and 60.46 p.p.m. (quartet, 5F, $J_{PP} = 13.1$ Hz), relative to external fluorotrichloromethane. The low field multiplet is assigned to the CF$_3$ group attached to the carbon atom adjacent to rhodium, and arises from coupling to three equivalent fluorines and to the phosphorus.

The magnitude of the phosphorus coupling can be measured from the proton decoupled $^{31}$P n.m.r. spectrum.

![Diagram A](image1)

![Diagram B](image2)

Figure 1.20
which shows one signal centred at -14.6 p.p.m., relative to external phosphonium ion, (doublet of quartets, $J_{\text{RhP}}=82\text{Hz}$, $J_{\text{PP}}=11\text{Hz}$). This indicates that the triphenylphosphine ligand is trans to the carbon atom carrying a $\text{CF}_3$ group, to which the phosphorus couples, and that complex (XXI) has the cis configuration [A] rather than the trans configuration [B], shown in Figure 1.20. The rhodium-phosphorus coupling constant of 82Hz is typical of a rhodium(III) complex, and the chemical shift, too, (-14.6 p.p.m.) is typical for rhodium(III).

The characterisation of these rhodacyclopentene complexes (XVII) and (XXI) is of considerable interest to the continuing work on the cyclocotrimerisation of two molecules of an alkyne with one of an alkene, to form a cyclohexadiene system. Reference was made in Section 1.2A to work in which metallacyclopentenes have been postulated, or isolated, as intermediates in cyclocotrimerisation reactions.

Work is currently in progress to investigate the reaction of the bis-pyridine rhodacyclopentene complex (XVIIa) with hexafluorobut-2-yn-2-yn, and to try to extend this reaction to include other electrophilic alkynes.

Unlike the rhodium(I) complexes (VII) and (IXa), in which the 1,4diene ligands were displaced by carbon monoxide, to give $[\text{Rh(dpm)}(\text{CO})]_2$, (Section 1.2B), the rhodium(III) complex (XVIIa) showed no reaction, in solution with carbon monoxide.
The reaction of pyridine with the complex [Rh(dpm)$(\text{C}_2\text{H}_4)$]$(\text{C}_2\text{F}_4)$ was also investigated. The crystalline product was identified as dipivaloylmethanatobis(pyridine)(tetrafluoroethene)rhodium(I), complex (XXII). The analogous acetylacetonato complex, [Rh(acac)(py)$_2$(C$_2$F$_4$)]$^{76}$ is known, and the $^{19}$F n.m.r. spectrum of complex (XXII) shows four lines, at 64.69, 66.25, 67.75 and 69.06 p.p.m., relative to external fluorotrichloromethane, similar to that for the acac complex,$^{76}$ and characteristic of an AB system.

E. Attempted preparations of hexafluoroacetylacetonato-(alkene)(alkyne)rhodium(I) complexes.

The differences in stability of the alkene-alkyne complexes which have been isolated are quite marked. Whereas the dipivaloylmethanato complexes with co-ordinated ethene, cis-cyclo-octene or cycloheptene are stable in air for many weeks, the acetylacetonato analogues are found to decompose after a few days, even in an inert atmosphere.
Attempts to synthesise other alkene-alkyne complexes have all met with failure. The approach to these attempts has been based on electronic arguments, so that the "balance" of electron density is theoretically maintained.

It had been found previously that the treatment of \([\text{Rh(dpm)}(\text{C}_2\text{H}_4)_2]\) with electrophilic alkynes, other than hexafluorobut-2-yne, did not result in the isolation of mono-alkene-alkyne complexes, so an alternative approach was tried.

Hexafluoroacetylacetonatobis(ethene)rhodium(I) was treated, at room temperature, with some electron-rich alkynes. However, no reaction occurred with 3-bromophenyltrimethylsilylethylene, but-2-yne, or hex-3-yne, and the starting material was recovered unchanged.
1.3 Experimental

In this section, the melting points, microanalytical results, and infra-red and n.m.r. spectroscopic data are presented for all newly characterised compounds.

Microanalyses were carried out by D. Butterworth, The Butterworth Microanalytical Consultancy Ltd., 41 High Street, Teddington, Middlesex.

Melting points were recorded on a Reichart hot-stage apparatus, and are uncorrected.

Infra-red spectra were recorded as nujol mulls, using CsI plates, on a Perkin-Elmer 580 spectrophotometer, and were calibrated using a polystyrene film.

$^1$H n.m.r. spectra were recorded in CDCl$_3$ solution, unless stated otherwise, on a Jeol JNM-FS-100 spectrometer, operating at 100 MHz. Chemical shifts (τ) are reported relative to internal T.M.S.

$^{19}$F n.m.r. spectra were recorded in CDCl$_3$ solution, unless stated otherwise, on a Jeol JNM-FS-100 spectrometer, operating at 94.1 MHz. Chemical shifts (p.p.m.) are reported relative to external fluorotrichloromethane.

$^{31}$P n.m.r. spectra were recorded in CDCl$_3$ solution on a Jeol JNM-FX60 spectrometer, operating at 24.15 MHz. Chemical shifts (p.p.m.) are reported relative to external phosphonium ion ($\text{PH}_4^+$). The spectra were completely $^1$H decoupled.

Mass spectra were recorded on a VG Micromass 16B spectrometer, operating at 70 eV.

Reactions were performed at room temperature, unless stated otherwise, and under an atmosphere of dry dinitrogen, using previously dried and degassed solvents.
Reactions carried out in Carius tubes (150 cm$^3$) were
done in 15 cm$^3$ of the stated solvent.

Reactions performed at low temperature were carried out
in cold baths prepared from the following components:
Ice-sodium chloride solution (-10°C)
Solid carbon dioxide - chlorobenzene (-44°C)
Solid carbon dioxide - acetone (-78°C)
Liquid nitrogen - acetone (-95°C)

Ligands and reagents

The following materials were purchased:

- cis-cyclo-octene
- cyclo-octa-1,5-diene
- hex-3-yne
- 3,5-dimethylpyridine
- hexafluoroacetylacetone
- cycloheptene
- bicyclo[2.2.1]heptene
- 2,3-dimethylbut-2-ene
- tetramethylallene
- triphenylphosphine
- triphenylarsine
- triphenylstibine
- dipivalcymethane
- tricyclohexylphosphine
- methylidiphenylphosphine
- ethyldiphenylphosphine
- pyridine
- cyclohexene

Koch Light Labs. Ltd.
Aldrich Chemical Co. Ltd.
Fisons Ltd.
Maybridge Chemical Co. Ltd.
May and Baker Ltd.
propene

\textit{cis}-but-2-ene \quad \text{\textcopyright The Matheson Co.}

\textit{trans}-but-2-ene

carbon monoxide \quad \text{\textcopyright B.O.C.}

ethene

3-methylpyridine

acetylacetone \quad \text{\textcopyright B.D.H. Chemicals Ltd.}

cyclopropane

polytetrafluoroethene

but-2-yne \quad \text{\textcopyright B.A.S.F.}

hexafluorobut-2-yne \quad \text{\textcopyright Bristol Organics Ltd.}

Tetrafluoroethene was prepared by the thermal decomposition of polytetrafluoroethene, in a silica tube, under vacuum. It was trapped out by cooling in liquid dinitrogen.

A sample of 3-bromophenyltrimethylsilylethyne was kindly donated by Dr. I.M.T. Davidson, of this department.

Hydrated rhodium trichloride was obtained on loan from Johnson Matthey Ltd.

The following were prepared as described in the literature:

\[
\text{[Rh(dpm)(C}_2\text{H}_4)(C}_4\text{F}_6\text{)]}, \quad \text{[Rh(acac)(C}_2\text{H}_4)(C}_4\text{F}_6\text{]} \quad \text{and} \\
\text{[Rh(acac)(C}_8\text{H}_{14})(C}_4\text{F}_6\text{]} \quad \text{[Rh(dpm)(C}_2\text{H}_4)(C}_2\text{F}_4\text{]} \quad \text{[Rh(dpm)(C}_8\text{H}_{14})_2\text{]} \quad \text{[Rh(hfacac)(C}_2\text{H}_4)\text{]}}
\]
The preparation of new mono-alkene-alkyne complexes of rhodium(I)

I. Reactions of alkenes with dipivaloylmethanato(ethene)-(hexafluorobut-2-ylene)rhodium(I)

i) With cis-cyclo-octene

To a stirred solution of \([\text{Rh(dpm)}(\text{C}_2\text{H}_4)\text{(C}_4\text{F}_6)]\) (0.15g, 0.32mmol) in diethyl ether, cis-cyclo-octene (0.04g, 0.32mmol) was added. The yellow solution was stirred for 3 hours, and a yellow solid was obtained by evaporating the solvent under vacuum. The solid was recrystallised from diethyl ether/methanol, and identified as \([\text{Rh(dpm)}(\text{cis-C}_8\text{H}_{14})\text{(C}_4\text{F}_6)]\)

Yield = 0.13g, 74%

M.P. 140-2°C (decomp)

**Analysis**

Calculated for \(\text{C}_{23}\text{H}_{35}\text{O}_2\text{F}_6\text{Rh}\): C, 49.47%, H, 5.96%

Found: C, 49.24%, H, 5.95%

**Infra-red.** 1971m,sh, 1959s, 1570m, 1553s, 1538s, 1530m,sh, 1506s, 1321w, 1270s, 1251m,sh, 1226s, 1202w, 1189m, 1174w,sh, 1149s, 1138s, 1025w,br, 980w, 962w, 933w, 920w, 902m, 806m, 787m, 769m, 750w, 739w, 726w, 706m, 672m, 647m,sh, 641m, 522m, 509w, 497w.

**\(^1\text{H n.m.r.}\)** 4.20(s, 1H); 6.64 (quin.x d, 2H, \(J_{\text{HH}}=7\)Hz, \(J_{\text{RhH}}=2\)Hz); 7.67(m,4H); 8.22-8.76(br,8H); 8.83(s,9H); 8.95(s, 9H).

**\(^{19}\text{F n.m.r.}\)** 52.66(d, \(J_{\text{RhF}}=2\)Hz).
ii) With cycloheptene

Cycloheptene (0.03g, 0.32mmol) was added to a solution of $[\text{Rh(dpm)}(\text{C}_7\text{H}_8)(\text{C}_4\text{F}_6)]$ (0.15g, 0.32mmol) in diethyl ether. The yellow solution was stirred for 2 hours, and a yellow solid was obtained by evaporating the solvent under vacuum. The solid was recrystallised from diethyl ether/methanol and identified as $[\text{Rh(dpm)}(\text{C}_7\text{H}_{12})(\text{C}_4\text{F}_6)]$.

Yield = 0.15g, 87%.

M.P. 121-2°C (decomp)

Analysis Calculated for $\text{C}_{22}\text{H}_{31}\text{O}_2\text{F}_6\text{Rh}$: C, 48.54%; H, 5.74%

Found: C, 48.29%; H, 5.46%

Infra-red. 1974m, 1959s, 1546s, 1539s,sh, 1530m,sh, 1506s, 1323w, 1268s, 1249m,sh, 1224s, 1203w, 1185w, 1160s,sh, 1145s, 1062w, 1028w,br, 961w, 936w, 902m, 831w, 809w, 788w, 772w, 751w, 727w, 708w, 672m, 643m, 618w,sh, 534w, 516w, 498w, 468w, 454w, 442w, 431w.

$^1\text{H n.m.r.}$ 4.19(s,1H); 6.36 (quin.x d, 2H, $J_{HH}=6$Hz, $J_{RhF}=-2$Hz)

$^{19}\text{F n.m.r.}$ 53.33ppm (d, $J_{RhF}=2$Hz).

iii) With propene

An excess of propene (1.0cm$^3$) was condensed (-196°C) on to a solution of $[\text{Rh(dpm)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)]$ (0.20g, 0.42mmol) in diethyl ether, contained in a 50cm$^3$ "Quickfit" flask. The flask was allowed to warm up to -44°C and the solution was stirred for 30 minutes under a dry nitrogen atmosphere. The flask was then evacuated and cooled to -196°C again, and a further 1.0cm$^3$ of propene introduced, and allowed to react at -44°C. In this way 3 aliquots of propene were introduced
to the solution. Finally it was evaporated to an orange oil, which on careful addition of methanol gave a yellow solid, identified as $\text{[Rh(dpm)(CH}_3\text{C(H)=CH}_2\text{)(C}_4\text{F}_6]}$. Crystals were obtained by recrystallisation from diethyl ether/methanol.

**Yield** = 0.17g, 83%

**M.P.** 61-2°C (decomp)

**Analysis**

Calculated for $C_{18}H_{25}O_2F_6$Rh: C, 44.10%; H, 5.14%

Found: C, 44.34%; H, 5.18%

**Infra-red.** 1973s, 1960s, 1549s, 1535s, 1502s, 1276s, sh, 1267s, 1240m, sh, 1221s, 1201w, 1184m, 1161s, 1147s, 1132s, 1049m, 996w, 968w, 960w, 930w, br, 900m, 807w, 788w, 771w, 752w, 726w, 706w, 673m, 648m, 532w, 513w, 496w.

$^1$H n.m.r. 4.17(s,1H); 6.03-6.88(m,3H); 8.27(d,3H,J$_{HH}$=7Hz); 8.84(s,9H); 8.92(s,9H).

$^{19}$F n.m.r. 52.68(s).

iv) **With cis-but-2-ene**

An excess of cis-but-2-ene (1.0cm$^3$) was condensed (-196°C) on to a solution of $\text{[Rh(dpm)(C}_2\text{H}_4\text{)(C}_4\text{F}_6]}$ (0.10g, 0.21mmol) in diethyl ether, contained in a 50cm$^3$ "Quickfit" flask. The flask was allowed to warm up to -10°C and the solution was stirred for 1 hour at this temperature. Evaporation of the solvent gave a yellow solid, which was recrystallised from diethyl ether/methanol and identified as $\text{[Rh(dpm)(cis-CH}_2\text{C(H)=C(H)CH}_3\text{)(C}_4\text{F}_6]}$.

**Yield** = 0.07g, 71%

**M.P.** 57-58°C

**Analysis**

Calculated for $C_{19}H_{27}O_2F_6$Rh: C, 45.25%; H, 5.40%

Found: C, 45.28%; H, 5.35%
Infra-red 1972s, 1961s, 1555s, 1538s, 1532m, sh, 1506s, 1269s, 1248m, 1226s, 1199m, 1185m, 1164s, sh, 1151s, 1153m, sh, 1083w, sh, 1057w, 1040w, 968w, 937w, 900w, 841w, 806w, 789w, 772w, 751w, 726w, 708w, 672m, 649w, 640w, 531w, 511w, 497w.

$^1$H n.m.r. 4.20 (s, 1H); 6.38–6.78 (m, 2H); 8.27 (d, 6H, $J_{HH}$ = 6 Hz); 8.85 (s, 9H); 8.94 (s, 9H).

$^{19}$F n.m.r. 52.91 ($d, J_{Rhf}$ = 1.6 Hz).

v) With trans-but-2-ene

An excess of trans-but-2-ene (1.0 cm$^3$) was condensed (-196°C) on to a solution of [Rh(dpm)(C$_2$H$_4$)(C$_4$F$_6$)] (0.20 g, 0.42 mmol) in diethyl ether contained in a 50 cm$^3$ "Quickfit" flask. The flask was allowed to warm up to -10°C and the solution was stirred for 1 hour at this temperature. Evaporation of the solvent, and careful addition of methanol, gave a yellow solid, which was identified as [Rh(dpm)(trans-CH$_2$CH=CHCH$_3$)(C$_4$F$_6$)].

Yield = 0.16 g, 76%.

M.P. 102-3°C

Analysis Calculated for C$_{19}$H$_{27}$O$_2$F$_6$Rh: C, 45.25%; H, 5.40%

Found: C, 45.37%; H, 5.60%

Infra-red. 1972s, 1960s, 1570s, 1538s, 1504s, 1286s, 1247m, 1224s, 1187m, 1164m, sh, 1149s, 1137s, sh, 1039w, 966w, 934w, 899w, 840w, 805w, 788w, 770w, 725w, 706w, 672m, 649m, 642m, 532w, 511w, 496w.

$^1$H n.m.r. 4.22 (s, 1H); 6.58 (m, 2H); 7.83 (s, 6H); 8.85 (s, 9H); 8.94 (s, 9H).

$^{19}$F n.m.r. 53.72 (s)
With cyclohexene

Cyclohexene (0.03g, 0.32mmol) was added to a solution of [Rh(dpr)(C\textsubscript{6}H\textsubscript{6})(C\textsubscript{4}F\textsubscript{6})] (0.15g, 0.32mmol) in diethyl ether. The solution was stirred for 3 hours. The yellow solid obtained by evaporating the solvent was identified as unreacted starting material, by its \textsuperscript{1}H n.m.r. and i.r. spectra and its m.p.

In a similar reaction, carried out in benzene solution at 70°C for 24 hours, the starting material was again recovered unchanged.

With bicyclo[2.2.1]heptene

Bicyclo[2.2.1]heptene (0.03g, 0.32mmol) was added to a solution of [Rh(dpm)(C\textsubscript{6}H\textsubscript{6})(C\textsubscript{4}F\textsubscript{6})] (0.15g, 0.32mmol) in diethyl ether. The solution was stirred for 2 hours. The yellow solid obtained by evaporating the solvent was identified as unreacted starting material by its \textsuperscript{1}H n.m.r. and i.r. spectra, and its m.p.

In a similar reaction, carried out in benzene solution at 50°C for 20 hours, the starting material was again recovered unchanged.

With 2,3-dimethylbut-2-ene

2,3-dimethylbut-2-ene (0.03g, 0.32mmol) was added to a solution of [Rh(dpm)(C\textsubscript{6}H\textsubscript{6})(C\textsubscript{4}F\textsubscript{6})] (0.15g, 0.32mmol) in diethyl ether. The solution was stirred for 24 hours. A yellow solid was obtained by slow evaporation of the solvent, and identified as unreacted starting material by its i.r. and \textsuperscript{1}H n.m.r. spectra.
ix) **With tetrafluoroethene**

An excess of tetrafluoroethene (1.0 cm³) was condensed (-196°C) on to a solution of \([\text{Rh(dpm)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)]\) (0.15 g, 0.32 mmol) in diethyl ether, contained in a Carius tube. The tube was sealed and shaken for 19 hours. After opening the tube and removing the volatile material the yellow solution was evaporated to give a sticky yellow solid. This was recrystallised from diethyl ether/methanol, and identified as the known complex \([\text{Rh(dpm)}(\text{C}_2\text{F}_4)]\) by its i.r. and \(^{19}\text{F} \text{n.m.r. spectra. Yield = 0.10 g, 75\%}.\)

x) **With cis-cis-cyclo-octa-1,5-diene**

To a solution of \([\text{Rh(dpm)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)]\) (0.05 g, 0.11 mmol) in diethyl ether, **cis-cis-cyclo-octa-1,5-diene** (0.012 g, 0.11 mmol) was added, and the solution was stirred for 2 hours. Evaporation of the solvent, and careful addition of methanol gave yellow microcrystals which were identified as the known complex \([\text{Rh(dpm)}(\text{cod})]\), by their i.r. and \(^1\text{H} \text{n.m.r. spectra. Yield = 0.04 g, 92\%}.\)

II. **Reactions with hexafluorobut-2-yne at -78°C**

i) **Dipivaloylmethanatobis(cyclo-octene)rhodium(I)**

An excess of hexafluorobut-2-yne (1.0 cm³) was condensed (-196°C) on to a solution of \([\text{Rh(dpm)}(\text{C}_8\text{H}_{14})_2]\) (0.56 g, 1.11 mmol) in diethyl ether, contained in a 50 cm³ "Quickfit" flask. The flask was allowed to warm up to -78°C, and the solution was stirred for 12 hours at this temperature. Rapid evaporation of the solvent gave
a yellow solid, which was pumped on a vacuum line to remove any cyclo-octene. Recrystallisation from diethyl ether/methanol gave yellow crystals which were identified by their i.r. and $^1$H n.m.r. spectra as $[\text{Rh(dpm)}(C_8H_{14})(C_4F_6)]$, by comparison with the spectra of the sample prepared in (A) I.(ii). Yield = 0.56g, 90%.

ii) Dipivaloylmethanato(ethene)(tetrafluoroethene)(rhodium(I))

An excess of hexafluorobut-2-yne (1.0cm$^3$) was condensed (-196°C) on to a solution of $[\text{Rh(dpm)}(C_2H_4)(C_2F_4)]$ (0.20g, 0.48mmol) in diethyl ether, contained in a 50cm$^3$ "Quickfit" flask. The flask was allowed to warm up to -78°C and the solution was stirred for 2 hours at this temperature. The solvent was evaporated rapidly to give a yellow powder which was identified by its i.r. spectrum and m.p. as $[\text{Rh(dpm)}(C_2H_4)(C_4F_6)]$, by comparison with those of an authentic sample. Yield = 0.20g, 88%.

III. Reactions with hexafluorobut-2-yne at room temperature

i) Dipivaloylmethanatobis(cyclo-octene)rhodium(I))

An excess of hexafluorobut-2-yne (1.0cm$^3$) was condensed (-196°C) on to a solution of $[\text{Rh(dpm)}(C_8H_{14})_2]$ (0.20g, 0.40mmol) in diethyl ether contained in a Carius tube. The tube was sealed and shaken for 8 days. After opening the tube and removing the volatile material, the yellow solution was evaporated to give a yellow solid. Recrystallisation from diethyl ether/methanol gave yellow crystals which were identified as $[\text{Rh(dpm-C_4F_6})(C_8H_{14})(C_4F_6)_2]]$ Yield = 0.15g, 42%
M.P. 197-8°C (decomp)

Analysis

Calculated for C_{31}H_{33}O_{2}F_{18}Rh: C, 42.19%; H, 3.77%

Found: C, 42.13%; H, 4.06%

Infra-red. 1670s, 1646w, 1575m, 1309m, 1274s, sh, 1248s, 1229s, 1212s, sh, 1196s, 1172s, 1156s, br, 1140s, 1116s, 1082m, 1061m, 1035m, 1012m, 1000m, sh, 965m, 945m, 902w, 869w, 841w, 828w, 821w, 773w, 741w, 724w, 713m, 690m, 679m, 668m, 657m, 610w, 591w, 539w, 519w, 508w, 495w, 456w, 424w.

{\textsuperscript{1}}H n.m.r. 3.55(s, 1H); 7.54(m, 2H); 7.88-8.66(br, 12H);
8.77(s, 18H).

{\textsuperscript{19}}F n.m.r. 52.70(br, 3F); 54.44(br, 6F); 54.92(br, 6F);
56.19(q, 3F, J_{FF}=15.9Hz).

ii) Dipivaloylmethanato(cyclo-octene)(hexafluorobut-2-yne)rhodium(I)

An excess of hexafluorobut-2-yne (1.0 cm\textsuperscript{3}) was condensed (-196°C) on to a solution of [Rh(dpm)(C_{8}H_{14})(C_{4}F_{6})] (0.15 g, 0.27 mmol) in diethyl ether contained in a Carius tube. The tube was sealed and shaken for 6 days. After opening the tube and removing the volatile material, the solution was evaporated to give a yellow solid. Yellow crystals were obtained by recrystallisation from chloroform/methanol, and identified as [Rh(dpm,C_{4}F_{6})(C_{8}H_{14})] by comparing their {\textsuperscript{19}}F n.m.r. and i.r. spectra with those from the previous experiment. Yield = 0.16 g, 67%.

iii) Dipivaloylmethanato(cycloheptene)(hexafluorobut-2-yne)rhodium(I)

An excess of hexafluorobut-2-yne (1.0 cm\textsuperscript{3}) was condensed (-196°C) on to a solution of [Rh(dpm)(C_{7}H_{12})(C_{4}F_{6})] (0.15 g, 0.28 mmol) in diethyl ether, contained in a Carius tube. The tube was sealed and shaken for 7 days. After opening the tube and removing the volatile material, the
solution was evaporated to give a yellow solid.

Recrystallisation from diethyl ether gave yellow crystals which were identified as \([\text{Rh(dpm}_2\text{C}_4\text{F}_6})(\text{C}_7\text{H}_{12})(\text{C}_4\text{F}_6)_2]\).

Yield = 0.19g, 79%

**M.P.** 234-6°C (decomp)

**Analysis** Calculated for \(\text{C}_{30}\text{H}_{31}\text{O}_2\text{F}_{18}\text{Rh}\): C, 41.49%; H, 3.60%

Found: C, 41.75%; H, 3.80%

**Infra-red.** 1678s, 1649w, 1580m, 1550w, 1291m, 1269s, 1248s, 1230s, 1193s, 1172s, 1150s, 1127s, 1113s, 1081m, 1052m, 1024m, 1011m, 974w, 958w, 941w, 899w, 850w, sh, 843w, 827w, 811w, 776w, 744w, 728m, 712m, 690w, 681m, 669w, 659m, 651w, sh, 638w, 610w, 592w, 540w, 518w, 479w, 452w, 426w.

\(^1\text{H n.m.r.}\) 3.48(s, 1H); 7.35(m, 2H); 7.68-8.40(br, 10H);

8.76(s, 18H).

\(^19\text{F n.m.r.}\) 53.61 (br, 3F); 56.07(br, 12F); 57.54(q, 3F,

\(J_{FF}=15.2\text{Hz})\).

**IV. Treatment of some alkene-alkyne complexes with an excess of the alkene.**

i) **Dipivaloylmethanato(cyclo-octene)(hexafluorobut-2-yne)rhodium(I)**

An excess of cyclo-octene (0.03g, 0.27mmol) was added to a solution of \([\text{Rh(dpm}_2\text{C}_8\text{H}_{14})(\text{C}_4\text{F}_6)]\) (0.10g, 0.18mmol) in diethyl ether, and the mixture was stirred for 2 hours. Evaporation of the solvent and careful addition of methanol gave a yellow powder which was identified as unreacted starting material, by its i.r. and \(^1\text{H n.m.r.}\) spectra.
ii) Dipivaloylmethanato(cycloheptene)(hexafluorobut-2-yne)rhodium(I)

An excess of cycloheptene (0.04g, 0.42mmol) was added to a solution of $[\text{Rh(dpm)}(C_7H_{12})(C_4F_6)]$ (0.10g, 0.18mmol) in diethyl ether, and the mixture was stirred for 5 hours. Evaporation of the solvent gave a yellow solid which was identified as unreacted starting material, by its i.r. and $^1H$ n.m.r. spectra.

iii) Acetylacetonato(cyclo-octene)(hexafluorobut-2-yne)rhodium(I)

An excess of cyclo-octene (0.03g, 0.27mmol) was added to a solution of $[\text{Rh(acac)}(C_8H_{14})(C_4F_6)]$ (0.10g, 0.21mmol) in diethyl ether. The solution was stirred for 2 hours, and the solvent removed. Careful addition of methanol gave a yellow powder which was identified as unreacted starting material, by its i.r. and $^1H$ n.m.r. spectra.

(B) Reactions of alkene-alkyne complexes involving diene formation.

I. Reactions of dipivaloylmethanato(ethene)(hexafluorobut-2-yne)-rhodium(I).

i) With cyclopropane

No reaction occurred when cyclopropane was shaken with $[\text{Rh(dpm)}(C_2H_4)(C_4F_6)]$ in a Carius tube at room temperature for 4 days, so the reaction was repeated at a higher temperature.

An excess of cyclopropane (1.0cm$^3$) was condensed (-196°C) on to a solution of $[\text{Rh(dpm)}(C_2H_4)(C_4F_6)]$ (0.25g, 0.53mmol) in diethyl ether contained in a Carius tube. The tube was sealed and placed in an oven, at 60°C for 20 hours. After opening the tube and removing the
volatile material, the red solution was evaporated to give
a red oil. After pumping dry, this was identified as

\[
[Rh(dpm)(1,2,4,5-\eta-\text{CH}_2=\text{CHCH}_2\text{C}(\text{CF}_3)=\text{C}(\text{H})\text{CF}_3)] \text{ Yield = 0.22g, 85%}.
\]

**Mass spectrum.** m/e = 490(M⁺)

**Analysis.** Calculated for \(\text{C}_{18}\text{H}_{25}\text{O}_6\text{F}_6\text{Rh} \): C, 44.10%; H, 5.14%.

Found:
C, 44.02%; H, 5.28%.

**Infra-red.** 1605m, sh, 1551s, 1538s, 1504s, 1297s, 1278s, 1260s,
1249s, 1226s, 1182s, 1143s, br, 1129s, sh, 1085m, 1042m, 1028w, sh,
965m, 932w, sh, 920m, 893w, 848w, 826w, 804m, 795m, sh, 770m,
750m, 705w, sh, 681m, 668w, 642m, 620w, sh, 596w, 525w, sh, 504w,
494w, 470w, 441w, 382w.

**H n.m.r.** 4.16 (s, 1H); 5.50 (m, H, \(J_{3,1}=8\text{Hz}, J_{3,2}=8\text{Hz}\);
\(J_{3,5}=12\text{Hz}, J_{3,6}=8\text{Hz}\)); 6.38 (dxd, H, \(J_{1,2}=13\text{Hz}, J_{1,3}=8\text{Hz}\));
6.75 (d, H, \(J_{6,5}=8\text{Hz}\)); 6.97 (d, H, \(J_{5,3}=12\text{Hz}\)); 7.49 (q, H, \(J_{4,F}=11\text{Hz}\)); 7.96 (dxd, H, \(J_{2,1}=13\text{Hz}, J_{2,3}=6\text{Hz}\)); 8.87 (s, 18H).

**F n.m.r.** 53.46 ("quin.", 3F, \(J_{FF}=11.0\text{Hz}, J_{HF}=11.0\text{Hz}\));
60.48 (qxd, 3F, \(J_{FF}=11.0\text{Hz}, J_{HF}=1.2\text{Hz}\)).

**Proton-proton decoupling experiments** (see Figure 1.9)

<table>
<thead>
<tr>
<th>Irradiated Signal</th>
<th>Affected Signal</th>
<th>Resultant Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁</td>
<td>H₁ (dxd)</td>
<td>d (J=13Hz)</td>
</tr>
<tr>
<td>H₆</td>
<td>(d)</td>
<td>s</td>
</tr>
<tr>
<td>H₅</td>
<td>(d)</td>
<td>s</td>
</tr>
<tr>
<td>H₆</td>
<td>No obvious change</td>
<td></td>
</tr>
<tr>
<td>H₅</td>
<td>No obvious change</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>H₁ (dxd)</td>
<td>d (J=6Hz)</td>
</tr>
</tbody>
</table>
ii) With propene

An excess of propene (1.0 cm$^3$) was condensed (-196°C) on to a solution of [Rh(dpm)(C$_2$H$_4$)(C$_4$F$_6$)](0.20g, 0.42mmol) in diethyl ether, contained in a Carius tube. The tube was sealed and placed in an oven, at 50°C for 4 days. The tube was opened and the volatile material removed. Evaporation of the solvent gave a red oil, which was pumped dry, and identified as

[\text{[Rh(dpm)(1,2,4,5-\eta^2-\text{CH}_2=\text{CHCH}_2\text{C}(\text{CF}_3)=\text{C}(\text{H})\text{CF}_3)]} by comparing its $^1$H and $^{19}$F n.m.r. spectra with those for the complex prepared in the previous reaction. Yield = 0.19g, 92%.

iii) With tetramethylallene

Tetramethylallene (0.04g, 0.42mmol) was added to a solution of [Rh(dpm)(C$_2$H$_4$)(C$_4$F$_6$)](0.20g, 0.42mmol) in diethyl ether. The solution was stirred for 22 hours, and the solvent slowly removed. Careful addition of methanol gave orange crystals, which were identified as

[\text{[Rh(dpm)(1,2,4,5-\eta^2-\text{CH}_2=\text{C}(\text{CH}_3)\text{C}\{=\text{C}(\text{CH}_3)\}_2\text{C}(\text{CF}_3)=\text{C}(\text{H})\text{CF}_3)]}

Yield = 0.16g, 70%.

M.P. 113-4°C.

Analysis

Calculated for C$_{22}$H$_{31}$O$_2$F$_6$Rh: C, 48.54%; H, 5.74%

Found: C, 50.12%; H, 6.04%

Infra-red 1565m, sh, 1550s, 1536s, 1502s, 1331s, 1281s, 1239m, 1227m, 1186w, 1168m, 1148s, sh, 1140s, 1124m, 1097m, 1077w, sh, 1032m, 1001w, 974w, 962w, 938w, 893w, 829w, 800m, 768m, 761w, 749w, 719m, 705w, 678w, 661w, 648m, 592w, 511w, 450w, 438w, 413w, 386w, 309w.
\[ ^1H \text{n.m.r.} \ 4.19(s, 1H); 6.74(s, 1H); 7.37(d, 1H, J_{RhH}=2.4\text{Hz}); \]
\[ 7.64(qxd, 1H, J_{HF}=9.0\text{Hz}, J_{RhH}=2.4\text{Hz}); 7.85(s, 3H); 8.40(s, 3H); \]
\[ 8.46(s, 3H); 8.89(s, 9H); 8.91(s, 9H). \]
\[ ^{19}F \text{n.m.r.} \ 52.52(q, 3F, J_{FF}=9.0\text{Hz}); 53.86 ("quin"., 3F, \]
\[ J_{FF}=9.0\text{Hz}, J_{HF}=9.0\text{Hz}). \]

II. Reactions of dipivaloylmethanato(cyclo-octene)-(hexafluorobut-2-yn)rhodium(I).

i) With cyclopropane

An excess of cyclopropane (1.0cm\(^3\)) was condensed (-196°C) on to a solution of \([\text{Rh(dpm)}(C_{6}H_{14})(C_{4}F_{6})]\) (0.10g, 0.18mmol) in diethyl ether contained in a Carius tube. The tube was sealed and placed in an oven at 60°C for 3 days. After opening the tube and removing the volatile material, the orange-red solution was evaporated to give a red oil. This was identified as \([\text{Rh(dpm)}(1,2,4,5-\eta\text{-CH}_2=\text{CHCH}_2\text{C(CF}_3)=\text{C(H)CF}_3)]\) by comparing its i.r. and \(^1H \text{n.m.r.} \) spectra with those of the complex prepared in (B)I(i). Yield=0.08g. 97%.

ii) With tetramethylallallene

Tetramethylallallene (0.03g, 0.27mmol) was added to a solution of \([\text{Rh(dpm)}(C_{6}H_{14})(C_{4}F_{6})]\) (0.15g, 0.27mmol) in diethyl ether. The solution was stirred for 3 days, and then evaporated to give a sticky orange-yellow solid. Recrystallisation from diethyl ether/methanol gave orange crystals of \([\text{Rh(dpm)}(1,2,4,5-\eta\text{-CH}_2=\text{C(CH}_3)\text{C}(\text{CH}_3)=\text{C(H)CF}_3]=\text{C(H)CF}_3])\) identified by comparing their \(^1H \text{n.m.r.} \) spectrum with that of the complex prepared in (B)I(iii). Yield = 0.12g, 82%.
III Reactions of dipivaloylmethanato(cycloheptene)-(hexafluorobut-2-yne)rhodium(I).

i) With cyclopropane

An excess of cyclopropane ($1.0\text{cm}^3$) was condensed ($-196^\circ\text{C}$) on to a solution of $[\text{Rh(dpm)}(\text{C}_7\text{H}_{12})(\text{C}_4\text{F}_6)]$ ($0.05\text{g}$, $0.09\text{mmol}$) in diethyl ether, contained in a Carius tube. The tube was sealed and placed in an oven at $60^\circ\text{C}$ for 2 days. The tube was opened, the volatile material was removed, and solution was evaporated to give a red oil. This was identified as $[\text{Rh(dpm)}(1,2,4,5-\eta-\text{CH}_2=\text{CHCH}_2\text{C(CF}_3)\text{=C(H)CF}_3)]$ by comparing its $^1\text{H n.m.r.}$ spectrum with that of the complex prepared in (B)I(i). Yield = $0.04\text{g}$, 95%.

ii) With tetramethylallene

Tetramethylallene ($0.009\text{g}$, $0.09\text{mmol}$) was added to a solution of $[\text{Rh(dpm)}(\text{C}_7\text{H}_{12})(\text{C}_4\text{F}_6)]$ ($0.05\text{g}$, $0.09\text{mmol}$) in diethyl ether, and stirred for 24 hours. Evaporation of the solvent gave an orange-yellow solid which was identified as $[\text{Rh(dpm)}(1,2,4,5-\eta-\text{CH}_2=\text{C(CH}_3)\text{C}^\prime\text{=C(CH}_3)^\prime\text{)}_2\text{C(CF}_3)\text{=C(H)CF}_3)]$ by comparing its $^1\text{H n.m.r.}$ spectrum with that of the complex prepared in (B)I(iii). Yield = $0.04\text{g}$, 80%.

IV Reaction of acetylacetonato(ethene)(hexafluorobut-2-yne)-rhodium(I)

i) With tetramethylallene

Tetramethylallene ($0.05\text{g}$, $0.52\text{mmol}$) was added to a solution of $[\text{Rh(acac(C}_2\text{H}_4)(\text{C}_4\text{F}_6)]$ ($0.20\text{g}$, $0.51\text{mmol}$) in
diethyl ether, and stirred for 24 hours. The solution
turned orange-red, and evaporation of the solvent followed
by careful addition of methanol gave dark yellow crystals
which were identified as
\[
[Rh(acac)(1,2,4,5-\eta-CH_2=CHCH_2C(CF_3)=C(H)CF_3)]
\]
Yield = 0.19g, 81%.

M.P. 130-1°C

Analysis  Calculated for C_{16}H_{19}O_2F_Rh: C, 41.76%; H, 4.16%
Found: C, 43.87%; H, 4.60%

Infra-red. 1581s, 1558s, 1522s, 1500m, 1333s, 1279s, 1238m,
1229s, 1197m, 1163s, 1142s, 1124s, 1100s, 1078m, 1029m, 1005w,
975w, 960w, 949w,br, 894w, 868w, 829w, 785m, 761w, 726w,sh,
719w, 706m, 687w, 661w, 632w, 620w, 593w, 529w, 513w, 499w,
490w,sh, 456w, 441w, 414w, 389w, 306w.

^1_H n.m.r. 4.56(s, 1H); 6.74(s, 1H); 7.35(d, 1H, J_{RHH}=2.3Hz);
7.60(q x d, 1H, J_{HF}=9.0Hz, J_{RHH}=2.7Hz); 7.86(s, 3H);
8.01(s, 3H); 8.04(s, 3H); 8.40(s, 3H); 8.45(s, 3H).

^19_F n.m.r. 53.22(q, 3F, J_{FF}=9.0Hz); 54.51 ("quin", 3F,
J_{FF}=9.0Hz, J_{HF}=9.0Hz).

V Reactions with carbon monoxide and with triphenylphosphine

i) The reaction of [Rh(dpm)(1,2,4,5-\eta-CH_2=CHCH_2C(CF_3)=C(H)CF_3)]
with carbon monoxide.

Carbon monoxide was passed slowly through a solution
of [Rh(dpm)(1,2,4,5-\eta-CH_2=CHCH_2C(CF_3)=C(H)CF_3)] (0.05g,
0.10mmol) in diethyl ether, for 15 minutes. Evaporation
of the solvent gave a red-green solid which was identified
as the known complex [Rh(dpm)(CO)_2], by its i.r. spectrum.
Yield = 0.03g, 88%.
ii) The reaction of \([\text{Rh(dpm)}(1,2,4,5-\eta-\text{CH}_2=\text{CHCH}_2\text{C}(\text{CF}_3)=\text{C}(\text{H})\text{CF}_3)]\) with triphenylphosphine.

Triphenylphosphine (0.05g, 0.20mmol) was added to a solution of \([\text{Rh(dpm)}(1,2,4,5-\eta-\text{CH}_2=\text{CHCH}_2\text{C}(\text{CF}_3)=\text{C}(\text{H})\text{CF}_3)]\) (0.05g, 0.10mmol) in diethyl ether. Stirring for 30 minutes resulted only in complete decomposition to rhodium metal.

iii) The reaction of
\([\text{Rh(dpm)}(1,2,4,3-\eta-\text{CH}_2=\text{C}(\text{CH}_3)\text{C}^|=\text{C}(\text{CH}_3)\text{C}(\text{CF}_3)=\text{C}(\text{H})\text{CF}_3)]\)
with carbon monoxide.

Carbon monoxide was passed slowly through a solution of \([\text{Rh(dpm)}(1,2,4,5-\eta-\text{CH}_2=\text{CHCH}_2\text{C}(\text{CF}_3)=\text{C}(\text{H})\text{CF}_3)]\) (0.10g, 0.18mmol) in diethyl ether, for 20 minutes. Evaporation of the solvent gave a red-green solid which was identified as the known complex \([\text{Rh(dpm)}(\text{CO})_2]\), by its i.r. spectrum. Yield = 0.05g, 82%.

(C) Reactions of phosphines, arsines and stibines with alkene-alkyne complexes.

I Reactions of acetylacetonato(ethene)(hexafluorobut-2-yne)-rhodium(I).

i) With triphenylphosphine

Triphenylphosphine (0.27g, 1.02mmol) was added to a solution of \([\text{Rh(acac)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)]\) (0.20g, 0.51mmol) in diethyl ether, and stirred for 30 minutes. A yellow microcrystalline powder precipitated after about 5 minutes. The powder was filtered, washed with methanol, and identified as \([\text{Rh(acac)}(\text{PPh}_3)_2(\text{C}_4\text{F}_6)]\). Yield = 0.36g, 79%.
M.P. 127-8°C

Analysis Calculated for C_{45}H_{37}O_{2}P_{2}F_{6}Rh: C, 60.82%; H, 4.20%
Found: C, 61.04%; H, 4.45%

Infra-red. 1820m, 1786m, 1585s, 1566m, 1514s, 1252s, 1241s, 1223s, 1203m, 1190m, 1161m, 1136s, 1110s, 1092s, 1030w, 1022w, sh, 1000w, 978w, 933w, 900w, 857w, 851w, 809w, 789w, 773w, 746s, 731w, 725w, 699s, 677m, 642w, 618w, 592m, 538s, 521s, 504s, 459m, 439m, 411w.

^1^H n.m.r. (in CD_{2}Cl_{2}) 2.60(m, 30H); 4.67(s, 1H); 8.27(s, 6H).

^1^9^F n.m.r. (in CD_{2}Cl_{2}) (room temperature) 51.72 (d, J_{RhF}=1.6Hz).
(-32°C) 50.98 (s, 3F); 51.72 (s, 3F).

ii) With triphenylarsine

Triphenylarsine (0.31g, 1.02mmol) was added to a solution of [Rh(acac)(C_{2}H_{4})(C_{4}F_{6})] (0.20g, 0.51mmol) in diethyl ether, and stirred for 30 minutes. The yellow solution turned immediately orange. Addition of methanol followed by slow evaporation of the solvent gave orange crystals of [Rh(acac)(AsPh_{3})_{2}(C_{4}F_{6})]. Yield = 0.39g, 78%.

M.P. 151-2°C

Analysis Calculated for C_{45}H_{37}O_{2}As_{2}F_{6}Rh: C, 55.34%; H, 3.82%
Found: C, 55.29%; H, 4.01%

Infra-red 1829m, 1791m, 1589s, 1569m, 1516s, 1255s, 1243s, 1223s, 1190m, 1161w, 1137m, 1114s, 1081w, 1028w, 1002w, 974w, 934w, 910w, 858w, 806w, 790w, 740s, 697s, 680m, 645w, 600w, 485m, 475m, 463w, 436w, 354w, 331w.

^1^H n.m.r. 2.71 (m, 30H); 4.69 (s, 1H); 8.16 (s, 3H);
8.35(s, 3H).

^1^9^F n.m.r. (in CH_{2}Cl_{2}) (room temperature) 52.50 (d, J_{RhF}=1.8Hz)
(-93°C) 52.01 (d, 3F, J_{RhF}=2.7Hz); 55.54 (d, 3F, J_{RhF}=2.7Hz).
iii) With triphenylstibine

Triphenylstibine (0.09g, 0.26mmol) was added to a solution of [Rh(acac)(C₂H₆)(C₄F₆)] (0.05g, 0.13mmol) in diethyl ether. The solution turned red immediately, and the solvent was quickly evaporated after 5 minutes, to give a red-brown powder. This powder was identified as [Rh(acac)(SbPh₃)₂(C₄F₆)] Yield = 0.11g, 75%.

M.P. 98-100°C (decomp.)

Analysis Calculated for C₆₅H₆₀Sb₂F₁₂Rh: C, 50.48%; H, 3.49%

Found: C, 50.67%; H, 3.80%

Infra-red 1832m, 1790m, 1584s, 1569m,sh, 1511s, 1253s, 1222s, 1189w, 1116s, 1069m, 1022w, 1000w, 934w, 900w, 851w, 803w, 776w, 731s, 697s, 678m, 642w, 600w, 455m, 427w, 271w, 259w.

¹H n.m.r. 2.71 (m, 30H); 4.80(s, 1H); 8.16(s, 3H); 8.49(s, 3H).

¹⁹F n.m.r. (room temperature) 52.57 (d, JRhF=2.0Hz)(-28°C) 52.12(s, 3F); 53.43(s, 3F).

iv) With methyldiphenylphosphine

Methyldiphenylphosphine (0.204g, 1.02mmol) was added to a solution of [Rh(acac)(C₂H₆)(C₄F₆)] (0.20g, 0.51mmol) in diethyl ether, and stirred for 30 minutes. Slow evaporation of the solvent and careful addition of methanol gave yellow microcrystals which were identified as [Rh(acac)(PPh₃Me)₂(C₄F₆)] Yield = 0.38g, 97%.

M.P. 113-4°C.

Analysis Calculated for C₃₅H₃₇O₂P₂F₁₂Rh: C, 54.98%; H, 4.36%

Found: C, 55.03%; H, 4.49%

Infra-red 1815m, 1782m, 1584s, 1574s,sh, 1510s, 1312w, 1289m, 1255s, 1243s, 1223s, 1200m, 1194m, 1161w, 1130s,
1106s, 1075w, 1021w, 1001w, 978w, 930w, 903w, 892w, 886s, 849w, 809w, 768w, 754m, 748m, 738s, 699s, 679m, 643w, 619w, 589w, 511s, 488w, 470w, 450w, 432w, 424w, 401w, 369w.

$^{1}H$ n.m.r. 2.74(m, 20H); 4.96(s, 1H); 8.10(s, 3H); 8.44(s, 3H), 8.46(d, 3H, J$_{PH}$=12Hz); 8.60(d, 3H, J$_{PH}$=12Hz).

$^{19}F$ n.m.r. 51.54(d, 3F, J$_{PF}$=16.4Hz); 51.96(s, 3F).

v) Reaction of acetylacetonebis(triphenylphosphine)-(hexafluorobut-2-yne)rhodium(I) with carbon monoxide.

Carbon monoxide was passed slowly through a solution of [Rh(acac)(PPh$_3$)$_2$(C$_2$H$_4$F$_6$)] (0.11g, 0.12mmol) in benzene, for 30 minutes. The solvent was evaporated, and addition of diethyl ether gave yellow microcrystals. These were identified as the known complex [Rh(acac(CO)(PPh)$_3$)] by their i.r. spectrum and m.p. Yield = 0.05g, 83%.

II Reactions of dipivaloylmethanato(ethene)(hexafluorobut-2-yne)-rhodium(I).

i) With methyldiphenylphosphine

Methyldiphenylphosphine (0.13g, 0.65mmol) was added to a solution of [Rh(dpm)(C$_2$H$_4$)(C$_4$F$_6$)] (0.15g, 0.32mmol) in diethyl ether. After stirring for 45 minutes the solution was evaporated under vacuum, to give yellow microcrystals, which were identified as [Rh(dpm)(PPh$_2$Me)$_2$(C$_4$F$_6$)]. Yield = 0.25g, 92%.

M.p. 126-7°C.

Analysis Calculated for C$_{41}$H$_{45}$O$_2$F$_6$P$_2$Rh: C, 58.02%; H, 5.34%

Found: C, 57.77%; H, 5.67%
Infra-red. 1810m, 1781s, 1581s, 1565s, 1526s, 1296m, 1251s, 1241s, 1223s, 1189s, 1160m, 1125s, 1109s, 1031w, 1001w, 978w, 895m, 889s, 847w, 809m, 785w, 740s, 731m, 699m, 691m, 676m, 643w, 619w, 514m, 502m, 489m, 464w, 450w, 443w, 426w, 414w, 367w.

$^1$H n.m.r. 2.75(m, 20H); 4.51(s, 1H); 8.37(d, 3H, $J_{PH}=9$Hz); 8.46(d, 3H, $J_{PH}=9$Hz); 8.84(s, 9H); 9.23(s, 9H).

$^{19}$F n.m.r. 51.13(d x d, 3F, $J_{PF}=16.3$Hz; $J_{RhF}=3.6$Hz); 51.91(d, 3F, $J_{RhF}=2.2$Hz).

ii) With ethyldiphenylphosphine

Ethyldiphenylphosphine (0.09g, 0.42mmol) was added to a solution of [Rh(dpm)(C$_2$H$_4$)(C$_4$F$_6$)] (0.10g, 0.21mmol) in diethyl ether. After stirring for 3 hours, the solution was slowly evaporated under vacuum, giving a sticky yellow solid, which was purified on an alumina chromatography column, using diethyl ether/methanol (50:50) as eluant. Yellow crystals were obtained from the diethyl ether/methanol solution, and identified as[Rh(dpm)(PPh$_2$Et)$_2$(C$_4$F$_6$)].

Yield = 0.14g, 76%.

M.P. 98-99°C.

Analysis Calculated for C$_{43}$H$_{49}$O$_2$F$_6$P$_2$Rh: C, 58.91%; H, 5.63%

Found: C, 58.05%; H, 5.74%

Infra-red. 1829m, 1790m, 1581s, 1565s, 1546m, 1528s, 1497s, 1256s, 1245s, 1221s, 1191m, 1136s, sh, 1119s, 1107s, sh, 1033w, 1009w, 1000w, 974w, 902w, 851w, 802w, 789w, 756m, 743s, 726m, 708m, sh, 699s, 679m, 668w, sh, 647w, 621w, 540m, 521m, 491m, 462w, 442w, 430w.
\[^{1}\text{H n.m.r.}\] 2.72(m, 20H); 4.37(s, 1H); 7.77(m, 4H); 8.90(s, 9H); 9.08(s, 9H); 9.40(m, 6H).
\[^{19}\text{F n.m.r.}\] 50.66(d, br, 3F, \(J_{\text{PF}}=11\text{Hz}\)); 53.01(s, 3F).

iii) With tricyclohexylphosphine

Tricyclohexylphosphine (0.12g, 0.42mmol) was added to a solution of \([\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)]\) (0.10g, 0.21mmol) in diethyl ether. After stirring for 4 hours, the solution was slowly evaporated under vacuum, to leave a bright yellow microcrystalline solid. This was recrystallised from diethyl ether/methanol, and identified as \([\text{Rh}(\text{dpm})\{\text{P}(\text{C}_6\text{H}_{11})_3\}\{(\text{C}_4\text{F}_6)\}]\). Yield = 0.14g, 91%.

M.P. 184-6°C.

Analysis  Calculated for \(\text{C}_{33}\text{H}_{52}\text{O}_2\text{F}_6\text{Prh}: \text{C}, 54.39\%; \text{H}, 7.19\%\)
Found:

\(\text{C}, 54.23\%; \text{H}, 7.28\%\)

Infra-red. 1924m, 1570m,sh, 1559s, 1531m, 1499s, 1309m,sh, 1294m, 1285m, 1257s, 1222s, 1200m, 1186m, 1179m, 1150s,sh, 1137s, 1125s,sh, 1078w, 1050w, 1031w, 1004w, 957w, 938w, 918w, 899w, 893w,sh, 850w, 827w, 803w, 794w, 770w, 741w, 726w, 718w, 680m, 647w, 626w, 568w, 535w, 520w, 495w, 448w, 432w, 405w.

\[^{1}\text{H n.m.r.}\] 4.21(s, 1H); 8.15(m, 33H); 8.87(s, 18H).
\[^{19}\text{F n.m.r.}\] 52.34(d, \(J_{\text{RhF}}=2.1\text{Hz}\)).

The same complex was subsequently prepared by the reaction of one molar equivalent of tricyclohexylphosphine with \([\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)]\), giving a similar yield.
iv) With triphenylphosphine

Triphenylphosphine (0.055g, 0.21mmol) was added to a solution of \( \text{[Rh(dpm)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)] \)(0.10g, 0.21mmol) in diethyl ether. After stirring for 4 hours, the solution was evaporated under vacuum, leaving yellow microcrystals which were identified as \( \text{[Rh(dpm)}(\text{PPh}_3)(\text{C}_4\text{F}_6)] \).

Yield = 0.14g, 90%.

M.P. 166-7°C.

Analysis Calculated for \( \text{C}_{32}\text{H}_{34}\text{O}_{2}\text{F}_6\text{PRh} \): C, 55.78%; H, 4.82%

Found: C, 55.41%; H, 4.80%

Infra-red. 1940s, 1570m,sh, 1554s, 1532s, 1501s, 1288m,sh, 1263s, 1223s, 1187m, 1162m, 1137s, 1100m, 1076w, 1029w, 1001w, 972w, 958w, 938w, 919w, 900w, 852w, 847w, 803w, 790w, 771w, 751m, 728w, 712m, 700m, 679m, 669w,sh, 645w, 629w, 538m, 533m,sh, 513m, 504w, 490w, 456w, 431w, 424w,sh.

\(^1\text{H n.m.r.} \) 2.46(m, 15H); 4.17(s, 1H); 8.92(s, 9H); 9.22(s, 9H).

\(^{19}\text{F n.m.r.} 53.40(d, J_{\text{RhF}}=2.1Hz).\)

v) With triphenylarsine

Triphenylarsine (0.04g, 0.21mmol) was added to a solution of \( \text{[Rh(dpm)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)] \)(0.10g, 0.21mmol) in diethyl ether. After stirring for 3 hours, the solution was evaporated under vacuum to give a yellow microcrystalline solid, which was identified as \( \text{[Rh(dpm)}(\text{AsPh}_3)(\text{C}_4\text{F}_6)] \).

Yield = 0.13g, 82%.

M.P. 139-41°C.

Analysis Calculated for \( \text{C}_{33}\text{H}_{34}\text{O}_{2}\text{AsF}_6\text{Rh} \): C, 52.54%; H, 4.54%

Found: C, 52.23%; H, 4.75%
Infra-red. 1934s, 1551s, 1534s, 1502s, 1260s, 1223s, 1186m, 1161s, sh, 1156s, 1140s, 1122m, sh, 1083w, 1030w, 1001w, 960w, br, 939w, 921w, 900w, 851w, 809w, 790w, 773w, 741m, 726w, sh, 711w, 695m, 678w, 646w, 635w, sh, 536w, 509w, 481w, 474w, 351w, 339w, 382w.

\[ ^1\text{H n.m.r.} \ 2.64(m, 15H); \ 4.24(s, 1H); \ 8.96(s, 9H); \ 9.18(s, 9H). \]
\[ ^19\text{F n.m.r.} \ 54.03(d, J_{\text{RhF}}=1.6\text{Hz}). \]

vi) With triphenylstibine

Triphenylstibine (0.12g, 0.32mmol) was added to a solution of \([\text{Rh(dpm)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)]\) (0.15g, 0.32mmol) in diethyl ether. The yellow solution turned orange-red immediately, and the solvent was removed under vacuum. Careful addition of methanol gave an orange powder, which was identified as the known complex \([\text{Rh(dpm)}(\text{SbPh}_3)_2(\text{C}_4\text{F}_6)]\) by its i.r. spectrum and m.p.

The i.r. spectrum also showed evidence of the unreacted starting material \(\nu(\text{C}≡\text{C})=1976\text{s}, 1962\text{m}, \text{sh}\). Subsequent reactions of less than one molar equivalent of triphenylstibine, with \([\text{Rh(dpm)}(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)]\) gave only the bis(triphenylstibine) complex, identified by i.r. spectra.

III Reaction of dipivaloylmethanato(cyclo-octene)-(hexafluorobut-2-yn)e)rhodium(I).

i) With triphenylphosphine

Triphenylphosphine (0.047g, 0.18mmol) was added to a solution of \([\text{Rh(dpm)}(\text{C}_8\text{H}_{14})(\text{C}_4\text{F}_6)]\) (0.10g, 0.18mmol) in diethyl ether and stirred for 18 hours. Evaporation of the
solvent, and careful addition of methanol gave yellow microcrystals of \([\text{Rh}(\text{dpm})\text{PPh}_3(C_4F_6)]\), identified by comparing their i.r. spectrum with that of the complex prepared in (C)II(iv). Yield = 0.09g, 70%.

IV Reactions of dipivaloylmethanato(cycloheptene)-(hexafluorobut-2-yne)rhodium(I).

i) With triphenylphosphine

Triphenylphosphine (0.024g, 0.09mmol) was added to a solution of \([\text{Rh}(\text{dpm})(C_7H_{12})(C_4F_6)]\) (0.05g, 0.09mmol) in diethyl ether. After stirring for 18 hours, the solvent was evaporated, and methanol was added, giving a yellow powder. This was identified as \([\text{Rh}(\text{dpm})(\text{PPh}_3)(C_4F_6)]\) by comparing its i.r. spectrum with that of the previously prepared samples. Yield = 0.055g, 86%.

ii) With triphenylarsine

Triphenylarsine (0.133g, 0.43mmol) was added to a solution of \([\text{Rh}(\text{dpm})(C_7H_{12})(C_4F_6)]\) (0.24g, 0.43mmol) in diethyl ether, and stirred for 3 hours. Evaporation of the solvent gave a sticky solid which was recrystallised from diethyl ether/methanol, and identified as \([\text{Rh}(\text{dpm})(\text{AsPh}_3)(C_4F_6)]\) by comparing its i.r. spectrum with that of the complex prepared in (C)II(v). Yield = 0.28g, 86%.
Reactions of dipivaloylmethanato(triphenylarsine)-(hexafluorobut-2-yne)rhodium(I)

i) With tetrafluoroethene

An excess of tetrafluoroethene (1.0 cm$^3$) was condensed (-196°C) on to a solution of [Rh(dpm)(AsPh$_3$)(C$_4$F$_6$)] (0.20 g, 0.27 mmol) in diethyl ether contained in a 50 cm$^3$ "Quickfit" flask. The solution was allowed to warm up to -95°C, and stirred for 1 hour at this temperature. The solvent was then rapidly removed, and careful addition of ethanol gave pale yellow crystals, which were identified as the known complex [Rh(dpm)(AsPh$_3$)(C$_2$F$_4$)] by their i.r. spectrum and m.p. Yield = 0.15 g, 80%.

ii) With hexafluorobut-2-yne

An excess of hexafluorobut-2-yne (1.0 cm$^3$) was condensed (-196°C) on to a solution of [Rh(dpm)(AsPh$_3$)(C$_4$F$_6$)] (0.10 g, 0.13 mmol) in diethyl ether, contained in a Carius tube. The tube was sealed and shaken for 23 hours. After opening the tube and removing the volatile material, the solvent was evaporated to give a dark yellow solid. Crystals were obtained from diethyl ether/methanol solution, and identified as the known complex

\[ [\text{Rh}\{\text{C(CF}_3)\text{=C(CF}_3)\text{=C(CF}_3)\text{=C(CF}_3)\}]\text{(dpm)(AsPh}_3\text{)} \]

by its i.r. spectrum and m.p. Yield = 0.09 g, 76%. 
VI Reaction of dipivaloylmethanatobis(triphenylstibine) - (hexafluorobut-2-ylene)rhodium(I)

i) With hexafluorobut-2-ylene

An excess of hexafluorobut-2-ylene (1.0cm\(^3\)) was condensed (-196\(^\circ\)C) on to a solution of

\[ [\text{Rh}(\text{dpm})(\text{SbPh}_3)_2(\text{C}_4\text{F}_6)] (0.30\text{g}, 0.26\text{mmol}) \]

in diethyl ether, contained in a Carius tube. The tube was sealed and shaken for 23 hours. The red solution had turned yellow and contained a suspended yellow solid. These microcrystals were filtered and washed with methanol and identified as the known complex

\[ [\text{Rh} \{ \text{C}(\text{CF}_3) = \text{C}(\text{CF}_3) \} \text{C}(\text{CF}_3) \} \{ \text{dpm}(\text{SbPh}_3) \}] \]

by their i.r. spectrum and m.p. Yield = 0.22g, 88%.

(D) Reactions of pyridines with [Rh(dpm)(C\(_2\text{H}_6\))(C\(_4\text{F}_6\))]
and with [Rh(dpm)(C\(_2\text{F}_4\))(C\(_2\text{F}_4\))]

I Reactions of dipivaloylmethanato(ethene)(hexafluorobut-2-ylene)rhodium(I)

i) With pyridine

Pyridine (0.05g, 0.64mmol) was added to a solution of [Rh(dpm)(C\(_2\text{H}_6\))(C\(_4\text{F}_6\))] (0.15g, 0.31mmol) in diethyl ether. The solution was slowly evaporated after stirring for 2 hours, to give a pale yellow-green oil. Careful addition of ethanol gave pale green crystals, which were identified as [Rh\{CH\(_2\text{CH}_2\text{C}(\text{CF}_3)\} \text{C}(\text{CF}_3) \} \{ \text{dpm}(\text{C}_5\text{H}_5\text{N}) \}].

Yield = 0.08g, 40%.
M.P. 48-9°C

Analysis Calculated for C_{27}H_{35}N_{2}O_{6}F_{6}Rh:
C, 51.11%; H, 5.25%; N, 4.41%

Found: C, 51.22%; H, 5.40%; N, 4.71%

Infra-red. 1603m, 1582s, 1567s, 1548m, 1531s,sh, 1528s, 1498s,
1484s, 1410s, 1326m, 1276s, 1242s, 1223s, 1196m, 1148s, 1138s,
1123s, 1095s, 1071m, 1061m, 1044w, 1015w, 974w, 956w, 933m,
901w, 822w, 789m, 769m, 758m, 722w, 700s, 671w, 648w, 636w,
610w, 562w, 538w, 504w, 496w, 446w, 427w, 399w.

{^1}H n.m.r. (20°C to 60°C) 1.14(d, 1H); 1.35(d, 1H); 1.86(d, 1H);
1.99(d, 1H); 2.26(quin, 2H); 2.73(m, 4H); 4.49(s) and
4.56(s)(1H); 6.80-7.87(br, 4H); 8.90(s, 9H); 9.01(s, 9H).

{^{19}}F n.m.r. (20°C to 60°C) 52.83(q) and 54.72(q)(3F, J_{FF}=14.0Hz);
57.93(q, 3F, J_{FF}=14.0Hz).

The same complex was also prepared in an analogous
reaction, using one molar equivalent of pyridine. The
complexes could not be purified by column chromatography,
using alumina with 40-60 petrol/diethyl ether (2:1) as eluant.

ii) With 3-methylpyridine

3-Methylpyridine (0.04g, 0.42mmol) was added to a
solution of [Rh(dpm)(C_2H_4)(C_4F_6)](0.10g, 0.21mmol) in
diethyl ether and stirred for 2 hours. Evaporation of
the solvent gave a pale yellow oil from which pale yellow-
green crystals were obtained by careful addition of 40-60
petrol. These crystals were identified as

[Rh\{CH_2CH_2C(CF_3)-C(CF_3)\}(dpm)(3-CH_3C_5H_4N)_2]. Yield =0.09g, 65%.
M.P. 112-4°C.

Analysis Calculated for $C_{29}H_{37}N_{2}O_{2}F_{6}$Rh:

- C, 52.58%; H, 5.63%; N, 4.23%
- Found: C, 52.86%; H, 5.84%; N, 4.36%

Infra-red. 1608w, 1588s, 1570s, 1548m, 1532m, sh, 1526s, 1498s, 1411s, 1280s, 1245s, 1226s, 1187m, 1161s, 1151s, 1134s, 1121s, 1096s, 1061m, 975w, 932m, 900w, 826w, 792m, 724m, 702m, 671w, 650w, 610w, 506w, 490w.

$^1$H n.m.r. 1.45(m), 2.12(m), 2.48(m) and 2.88(m (6H);
4.49(s) and 4.57(s) (1H); 6.78~7.68(br, 4H); 7.64(s),
7.71(s) and 7.77(s) (6H); 8.87(s, 9H), 8.98(s, 9H).

$^{19}$F n.m.r. 53.87(q) and 55.94(q) (3F, $J_{FF}$=15.3Hz);
59.19(5 lines, 3F, $J_{FF}$=15.3Hz).

iii) With 3,5-dimethylpyridine

3,5-Dimethylpyridine (0.09g, 0.84mmol) was added to
a solution of $[\text{Rh(dpm)}(C_{2}H_{4})(C_{4}F_{6})]$(0.20g, 0.42mmol) in
diethyl ether, and stirred for 2 hours. The solvent was
evaporated to give a pale yellow oil, and careful addition
of methanol gave cream coloured crystals which were
identified as $[\text{Rh}\{\text{CH}_{2}\text{CH}_{2}\text{C(CF}_{3})\}^{2-}\text{C(CF}_{3})]$(dpm)(3,5-(CH$_{3}$)$_{2}$C$_{5}$H$_{3}$N)$_{2}$]
Yield = 0.23g, 79%.

M.P. 131-2°C.

Analysis: Calculated for $C_{31}H_{41}N_{2}O_{2}F_{6}$Rh:

- C, 53.92%; H, 5.98%; 4.05%
- Found: C, 53.75%; H, 5.76%; 4.06%
I n f r a - r e d. 1601 m, 1589 s, 1568 s, 1554 m, 1532 s, 1500 s, 1413 s,
1327 m, 1278 s, 1243 s, 1222 s, 1196 m, 1155 s, 1146 s, 1137 s, 1120 s,
1095 s, 1062 w, 1046 w, 974 w, 955 w, 933 w, 901 w, 867 w, 861 w,
825 w, 792 w, 766 w, 755 w, 724 m, 705 m, 675 w, 650 w, 609 w, 561 w,
540 w, 500 w, 489 w, 425 w.

$^{1}H$ n.m.r. 1.51 (m), 1.70 (m), 2.16 (m), 2.37 (m) and 2.68 (m) (6H);
4.51 (s) and 4.61 (s) (1H); 6.81-7.74 (br, 4H); 7.69 (s), 7.76 (s)
and 7.83 (s) (12H); 8.88 (s, 9H); 8.99 (s, 9H).

$^{19}F$ n.m.r. 53.15 (q) and 55.26 (q) (3F, $J_{FF}=12.7$Hz); 58.26
(7 lines, 3F, $J_{FF}=12.7$Hz).

II Reactions of dipivaloylmethanato(ethene)(tetrafluoroethene)-
rhodium(I)

i) With pyridine

Pyridine (0.076 g, 0.96 mmol) was added to a solution of
[Rh(dpm)(C$_{2}$H$_{4}$)(C$_{2}$F$_{4}$)] (0.20 g, 0.48 mmol) in diethyl ether.
After stirring for 1 hour the solvent was evaporated to
give a pale yellow oil. Careful addition of methanol gave
a cream coloured microcrystalline powder which was identified
as [Rh(dpm)(py)$_{2}$(C$_{2}$F$_{4}$)], by analogy with the known complex.

$\text{[Rh(acac)(py)$_{2}$(C$_{2}$F$_{4}$)]. Yield = 0.20 g, 77%.}$

M.P. 122-40°C (decomp.)

Analysis Calculated for C$_{23}$H$_{29}$N$_{2}$O$_{2}$F$_{4}$Rh: C, 50.75%; H, 5.37%.
Found: C, 50.98%; H, 5.41%.

Infra-red. 1609 w, 1601 w, 1587 s, 1568 s, 1550 s, 1529 s, 1500 s,
1410 s, 1249 w, 1229 m, 1220 m, 1196 m, 1155 w, 1140 w, 1092 s, 1070 m, sh,
1061 s, 1042 s, sh, 1039 s, 1013 w, 1002 w, 980 w, 936 w, 829 s, 791 w,
782 w, 764 m, 759 m, sh, 725 w, 701 m, 693 m, 679 w, 669 w, 653 w, br,
630 w, 610 w, 503 w, 487 w, 424 w, 375 w.
III  Reactions with triphenylphosphine and with carbon monoxide.

i) Reaction of \(\text{[Rh}\{\text{CH}_2\text{CH}=\text{C(CF)\_3}\}\{\text{dpm}(\text{py})\}_2\) with triphenylphosphine.

Triphenylphosphine (0.06g, 0.23mmol) was added to a solution of \(\text{[Rh}\{\text{CH}_2\text{CH}=\text{C(CF)\_3}\}\{\text{dpm}(\text{py})\}_2\) (0.15g, 0.23mmol) in diethyl ether. The pale yellow solution was stirred for 1 hour, and then the solvent was evaporated to give an oil. Careful addition of ethanol gave a cream-coloured microcrystalline powder. Pale yellow crystals were obtained from diethyl ether solution, and identified as \(\text{[Rh}\{\text{CH}_2\text{CH}=\text{C(CF)\_3}\}\{\text{dpm}(\text{py})(\text{PPh})\}_2\)].

Yield = 0.12g, 64%.

M.P.  136-8°C.

Analysis  Calculated for \(\text{C}_{40}\text{H}_{43}\text{NO}_2\text{F}_6\text{PRh}\):

\[
\begin{align*}
\text{C} & : 58.76\% \\
\text{H} & : 5.30\% \\
\text{N} & : 1.71\%
\end{align*}
\]

Found:  \[
\begin{align*}
\text{C} & : 58.65\% \\
\text{H} & : 5.45\% \\
\text{N} & : 1.85\%
\end{align*}
\]

Infra-red.  1619m, 1609m, 1592s, 1570s, 1534s,sh, 1530s, 1498s, 1420s, 1414s, 1327m,sh, 1280s, 1241s, 1227s, 1221s, 1190m, 1153s, 1142s,sh, 1136s, 1122s, 1098s, 1075m, 1062m, 1034w, 1004w, 978w, 930m, 894w, 849w, 821w, 792w, 765m, 750s, 726w, 699s, 670w, 639w, 605w,545w, 525s, 502m, 472w, 448w, 430w, 401w.
\[ \text{H n.m.r. 1.39(d) and 2.73(m)(20H); 4.62(s, 1H); 6.50-7.94 (br, 4H); 8.90(s, 9H); 9.00(s, 9H).} \]

\[ {19}F \text{n.m.r. 53.85(m, } 3F); 60.46(q, 3F, J_{HF}=13.1\text{Hz).} \]

\[ {31}P \text{n.m.r. } -14.6 (d x q, J_{\text{RhP}}=82\text{Hz}; J_{PF}=11\text{Hz).} \]

ii) Treatment of [Rh(CH\text{pCHpC(CF)})=C(CF)(dpm)(py)\text{2}] with carbon monoxide.

Carbon monoxide was passed slowly through a solution of [Rh(CH\text{pCHpC(CF)})=C(CF)(dpm)(py)\text{2}] (0.10g, 0.16mmol) in benzene, for 30 minutes. There was no apparent change, and on evaporating the solvent the starting material was recovered unchanged and identified by its i.r. spectrum and m.p.

(E) Attempted preparations of alkene-alkyne complexes from hexafluoroacetylacetonatobis(ethene)rhodium(I).

i) With 3-bromophenyltrimethylsilylethyne

An excess of 3-bromophenyltrimethylsilylethyne (0.20g, 0.79mmol) was added to a solution of [Rh(hfacac)(C\text{2H})\text{2}] (0.20g, 0.55mmol) in diethyl ether. After stirring for 4 days the solvent was removed, leaving a solid which was identified as unreacted starting materials, by its i.r. spectrum.

ii) With but-2-yne

An excess of but-2-yne (1.0cm\text{3}) was condensed (-196°C) on to a solution of [Rh(hfacac)(C\text{2H})\text{2}] (0.20g,0.55mmol) in diethyl ether, contained in a Carius tube. The tube was sealed, and shaken for 24 hours. After opening the tube,
and removing the volatile material, the solvent was evaporated to give a solid which was identified as unreacted starting material by its i.r. spectrum.

iii) With hex-3-yne

An excess of hex-3-yne (0.10 g, 1.22 mmol) was added to a solution of \([\text{Rh(hfacac)}(\text{C}_2\text{H}_4)_2]\) (0.20 g, 0.55 mmol) in diethyl ether, and stirred for 24 hours. Evaporation of the solvent gave a solid which was identified as unreacted starting material, by its i.r. spectrum.
CHAPTER TWO
2.1 Introduction

Alkyne complexes of zerovalent platinum

A. Methods of preparation

Platinum forms complexes with unsaturated hydrocarbons, in both the zerovalent and divalent state. The first such complex, $K[PtCl_2(C_2H_4)H_2O]$, was isolated by Zeise, in 1827. Subsequently alkynes, as well as alkenes, were found to form stable organometallic complexes, and two general methods are now commonly used to prepare zerovalent alkyne platinum complexes, of general formula $[Pt(ac)L_2]$ or $[Pt(ac)_2]$, (ac = alkyne):

(i) Reduction of platinum(II) complexes
(ii) Ligand exchange in platinum(0) complexes.

(i) Reduction of platinum(II) complexes

a) Complexes of the type $[Pt(ac)_2]$.

The white air-stable crystalline complexes of general formula $[Pt(R^1R^2C(OH)CC(OH)R^1R^2)_2]$, complexes (I), have been synthesised by treating an aqueous ethanolic solution of potassium tetrachloroplatinite with the appropriate alkyne, as shown in Figure 2.1.
The X-ray crystal structure of complex (Ib) has been determined, showing that the coordination at the platinum atom is essentially tetrahedral, with the two alkyne ligands being mutually perpendicular:

b) Complexes of the type \([\text{Pt(ac)L}_2]\)

Most zerovalent platinum-alkyne complexes are of the general formula \([\text{Pt(ac)L}_2]\), where L is a phosphine ligand. These can be prepared by the reduction of an ethanolic suspension of \(\text{cis-[PtCl}_2(\text{PR}_3)_2}\), usually with hydrazine hydrate, in the presence of the alkyne\(^5\). The first mechanism proposed for this reaction involves the reduction, by
hydrazine, of cis-[PtCl$_2$(PR$_3$)$_2$] initially forming the hydride complex [PtHCl(PR$_3$)$_2$], which is in turn reduced by hydrazine to give the reactive intermediate [Pt(PR$_3$)$_2$]. This scheme is shown in Figure 2.2:

\[
\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2] + H_2\text{NNH}_2 \rightarrow \text{PtHCl(PPh}_3)_2 + \text{Pt}\text{H} \text{Cl(PPh}_3)_2
\]

\[
\text{Pt(ac)(PPh}_3)_2 \rightleftharpoons \text{Pt(PPh}_3)_2
\]

Figure 2.2

However, this reaction now seems unlikely because: firstly, no bands due to Pt-H or Pt-Cl stretching modes are observed in the infra-red spectrum of the compound isolated from the reaction of ethanolic cis-[PtCl$_2$(PPh$_3$)$_2$] with hydrazine hydrate; secondly, in only a very few cases does the reaction of metal hydrides with alkenes or alkynes result in the isolation of alkene or alkyne complexes, and usually vinyl complexes are produced.

The more likely mechanism is shown in Figure 2.3. The X-ray crystal structure of the bridged intermediate showed it to be a mixture of complexes (II) and (III). The fact that hydroxyalkynes do not react with complex III, although the hydroxyalkyne complexes
Figure 2.3

\[ [\text{Pt(ac)}(\text{PPh}_3)_2] \text{can be prepared by this method, suggests that (II) is the reactive species.} \]
The method has been successfully employed in the preparation of a number of alkyne complexes, for example.\textsuperscript{14-19} It did not work, however, for $[\text{PtCl}_2(\text{PBu}_3)_2]$ or $[\text{PtCl}_2(\text{PPh}_2\text{Me})_2]$.$^{16}$

(ii) Ligand exchange in platinum(O) complexes

a) Complexes of the type $[\text{Pt(ac)}_2]$.

The complex $[\text{Pt(PhC}_2\text{Ph})_2]$ has been synthesised from $[\text{Pt(cod)}_2]$ in its room temperature reaction with an excess of diphenylethyne, and its single crystal X-ray structure was determined.$^{20}$ As for complex (Ib), the bis-diphenylethyne complex is essentially tetrahedral, with the angle between the two Pt-C=C planes being 82°.

b) Complexes of the type $[\text{Pt(ac)L}_2]$.

The complexes $[\text{Pt(PR}_3)_4]$\textsuperscript{21} and $[\text{Pt(PR}_3)_3]$\textsuperscript{21,22} are commonly used as starting materials in the preparation of complexes of the type $[\text{Pt(ac)L}_2]$. The exchange of ligands occurs readily due to the dissociation of phosphines, in solution:$^{23,24}$

\[
\begin{align*}
[\text{Pt(PPh}_3)_4] & \overset{K_1}{\longrightarrow} [\text{Pt(PPh}_3)_3] + \text{PPh}_3 & \text{K}_1 \text{ large} \\
[\text{Pt(PPh}_3)_3] & \overset{K_2}{\longrightarrow} [\text{Pt(PPh}_3)_2] + \text{PPh}_3 & \text{K}_2 = (1.5\pm1)\times10^{-4}
\end{align*}
\]

Hydroxyalkynes have been found to react with $[\text{Pt(PPh}_3)_4]$ to give two types of complex,$^{13}$ as shown in Figure 2.4. An excess of a bulky terminal alkyne gave complexes of type (V), while complexes (IV) were isolated from reactions with less bulky alkynes. The reaction with 1-ethynylcyclohexanol gave both complexes (IV) and (V),$^{13}$ and a single crystal X-ray study on the complex (IV)$^{25}$ confirmed that the alkyne is $\eta^2$-bonded.
A single crystal X-ray study of the complex of type (V)\textsuperscript{26} showed it to be a \textit{trans} bis-alkynyl complex,

\[ [\text{PtL}_4] \rightleftharpoons [\text{PtL}_3] + \text{L} \]

but the hydrogen atoms were not located. Evidence for the platinum(IV) dihydride formulation is provided by the $^1H$ n.m.r. spectrum\textsuperscript{13} where a signal is seen at 22.88$\tau$, the region associated with metal hydride species.
Using a similar method, the two cyclo-alkyne complexes (VIa) and (VIb) have been prepared by the reactions of 1,2-dibromocyclohexene and 1,2-dibromocycloheptene respectively, with a sodium amalgam in thf, in the presence of \([\text{Pt}(\text{PPh}_3)_3]\).\(^{27}\) Their single crystal X-ray structures have been determined.\(^{28}\) Although there is some evidence for the existence of cyclohexyne and cycloheptyne as intermediate species, they have never been isolated in the free state. However, cyclo-octyne can be isolated, and the complex (VIc) has been prepared by the hydrazine hydrate reduction of \text{cis-[PtCl}_2(\text{PPh}_3)_2\] in the presence of cyclo-octyne.\(^{29}\)

An alternative ligand exchange method involves platinum(0) complexes of the type \([\text{Pt}(\text{alkene})(\text{PPh}_3)_2]\) or \([\text{Pt}(\text{alkyne})(\text{PPh}_3)_2]\). Such reactions include, for example, the displacement of co-ordinated ethene from \([\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]\): \(^{30}\)

\[
\begin{align*}
\text{[PtO}_2(\text{PPh}_3)_2] + \text{C}_2\text{H}_4 & \xrightarrow{\text{NaBH}_4} \text{[Pt(C}_2\text{H}_4)(\text{PPh}_3)_2] \\
\text{PhC≡CPh} & \\
\text{[Pt(PhC}_2\text{Ph)(PPh}_3)_2] &
\end{align*}
\]

Similarly, alkene\(^{31}\) and alkyne\(^{32}\) complexes of platinum(0) have been prepared by the displacement of \text{trans-stilbene}...
from $[\text{Pt} \text{(trans}-\text{PhC}(\text{H})\text{C}==\text{C}(\text{H})\text{Ph})(\text{PPh}_3)_2]$. Likewise, using an alkyne complex:\(^{33}\)

$$[\text{Pt(PhC}_2\text{H})(\text{PPh}_3)_2] \begin{array}{c} \begin{array}{c} \text{F}_3\text{CC}==\text{CF}_3 \\ 70^\circ \text{C} \end{array} \rightarrow \end{array} [\text{Pt(F}_3\text{CC}==\text{CF}_3)(\text{PPh}_3)_2]$$

In a series of displacement reactions,\(^5\) the stability of the complexes $[\text{Pt(alkyne)(PPh}_3)_2]$ was shown to increase in the order:

$$\text{HC}==\text{CH}<\text{RC}==\text{CH}<\text{RC}==\text{CR}<\text{PhC}==\text{CH}<\text{PhC}==\text{CPh}<\text{C}_2\text{C}_6\text{H}_4\text{NO}_2^-\text{P}$$

($R = \text{alkyl}$)

Usually, co-ordinated alkynes cannot be displaced by alkenes, but exceptions to this behaviour arise with electronegative alkenes, for example, with tetracyanoethene (TCNE)\(^{34}\):

$$[\text{Pt(PhC}_2\text{Ph})(\text{PPh}_3)_2] \begin{array}{c} \begin{array}{c} \text{TCNE} \end{array} \rightarrow \end{array} [\text{Pt(TCNE)(PPh}_3)_2]$$

and with tetrafluoroethene (see Section 2 of this chapter):

$$[\text{Pt(H}_2\text{C(OH)}\text{C}==\text{CH}_2\text{OH})(\text{PPh}_3)_2] \begin{array}{c} \begin{array}{c} \text{C}_2\text{F}_4 \end{array} \rightarrow \end{array} [\text{Pt(C}_2\text{F}_4)(\text{PPh}_3)_2]$$

The mechanism first proposed\(^1\)\(^4\) for these displacement reactions involves the formation of bis(triphenylphosphine)platinum(0) as an intermediate, as shown in Figure 2.5. This dissociative mechanism is supported by the isolation of $[\text{Pt(PPh}_3)_2]$\(^{35}\) and its
reaction with alkynes to give the complexes

$[\text{Pt} \text{alkyne}(\text{PPh}_3)_2]^+$

However, $^1\text{H}$ n.m.r. studies on $[\text{Pt}(\text{PhC}_2\text{Me})(\text{PPh}_3)_2]^2$ and later, on $[\text{Pt}(\text{D}_{5}\text{C}_6\text{CH})\{\text{P}((\text{C}_{6}\text{D}_{5})_3\}^2]$ showed no indication of rotation or dissociation of the co-ordinated alkyne, in solution. An alternative mechanism for ligand exchange was therefore proposed, as shown in Figure 2.6, where the rate determining step involves a change in the stereochemistry of the original square planar alkyne complex, to give a pseudotetrahedral transition state, by rotation of the alkyne through $90^\circ$ about the platinum-alkyne bond. The incoming alkyne can then be accommodated in a
Figure 2.6

six co-ordinate species, followed by loss of the original alkyne, and rotation back to a square planar complex.

The stability of the complexes has been shown to increase as the electronegativity of the alkyne increases. This observation can be explained by a consideration of the bonding scheme proposed for these complexes.
B. Bonding in alkyne complexes

The bonding scheme which best fits the observed behaviour of these complexes is the $\sigma$-$\pi$ scheme first proposed by Dewar for silver(I) alkene complexes, and later extended by Chatt and Duncanson for platinum(II) alkene complexes. This model was originally designed for square planar complexes, but has since been applied successfully to alkene complexes with other co-ordination geometries, as well as in the description of the bonding between alkynes and metals.

The theory involves a $\sigma$-type bond formed from the overlap of a filled $\pi$ bonding orbital of the alkyne with a vacant hybrid orbital on the metal which enables electron density to be transferred to the metal from the alkyne. This $\sigma$ bond is supplemented by $\pi$ back-donation of charge from a filled non-bonding metal d-orbital to an empty $\pi^*$ antibonding orbital on the alkyne. Figure 2.7(A) illustrates this synergic bonding and shows (B) how $\pi$-type bonding is also possible out of the xy plane, for alkynes, due to their having two orthogonal $\pi$ orbitals. The strength of metal-alkyne bonds is attributed to this synergic bonding.

This bonding scheme adequately allows for theoretical explanations of the physico-chemical properties which are generally observed for metal-alkyne complexes, i.e.:

(i) A weakening, and lengthening, of the triple bond on co-ordination (measured by X-ray diffraction studies, and by the change in the $\text{C}=$C$\text{C}$ stretching frequency observed in the infra-red spectrum).
Figure 2.7

TOP VIEW

SIDE VIEW

$\pi_{xy}$

$\pi_{xy}^*$

$\sigma$

$\pi_{xy}^*$

$d_{x^2-y^2}$

$d_{xz}, d_{yz}$

$-P_{t}$

$P_{t}$

$\pi_{z}$
(ii) The substituents on the alkyne become bent away from the metal, in the plane of the complex (observed by X-ray diffraction studies).

(iii) The change in multiplicity of the alkyne bond, together with the observed change in geometry suggests a change in orbital hybridisation from sp towards sp$^2$ at the alkyne carbon atoms (observed by $^1$H n.m.r. studies on co-ordinated terminal alkynes; for example$^{13,18}$).

C. Physico-chemical properties of platinum-alkyne complexes

The Dewar-Chatt-Duncanson model for bonding can therefore be invoked for alkyne complexes, but the relative contributions of the $\sigma$ and $\pi$ components to the overall bond vary with complexes of different metals, their oxidation states and substituents, and with different alkynes. A closer examination of observed physical and spectroscopic data is now presented, for platinum-alkyne complexes, and rationalised in terms of this bonding model.

(i) Infra-red spectroscopy

Evidence for the weakening of the alkyne triple bond is provided by infra-red spectroscopy. The stretching frequency of this bond is lowered considerably on co-ordination, which supports the proposal that back-donation of electron density to the alkyne $\pi^*$ antibonding orbital, together with the donation of electrons from its $\pi$ bonding orbital, reduces the bond order.

For unco-ordinated alkynes, the stretching frequency occurs in the region 2000-2400cm$^{-1}$, and can be lowered by as much as 600cm$^{-1}$ on co-ordination.
For platinum(II) complexes of the type 
\[ \text{[PtCl}_2\text{X(RC=CR')]} \], (X=Cl, amine, for example), the 
C=C stretch appears as a weak band, lowered by up 
to 200\text{cm}^{-1} from that of the free alkyne. For these 
complexes, it is proposed that the \( \sigma \) component of the 
bonding model is important, but that \( \pi \) back-bonding is 
minimal, due to the high oxidation state of, and 
consequent low electron density on the metal. The 
transfer of electron density from the alkyne to the 
metal is therefore relatively small, and the consequent 
change in geometry is only slight. However, the slight 
bending induced in the alkyne molecule allows the 
obervation of \( \nu(\text{C=C}) \) in the infra-red spectrum.

In platinum(0) complexes of the type \[ \text{[Pt(RC≡CR')L}_2\text{]} \], 
(\( L=\text{phosphine, for example}\)), the stretching frequency can 
be lowered by up to 600\text{cm}^{-1}, due to a much higher 
degree of back-bonding to the \( \pi^* \) antibonding orbitals, 
which contributes to a decrease in the bond order 
almost to two. This is as expected for a zerovalent 
metal, with much electron density available for back-
donation. These two extreme cases, for platinum(II) 
and platinum(0), are illustrated in Figure 2.8. It

![Figure 2.8](image-url)
can be seen that in case B, the most extreme representation of the bonding is a platinacyclopentene system.

Table 2.1 presents the infra-red C≡C stretching frequencies for some alkyne complexes of platinum, together with the values of \( \Delta \nu(C≡C) = \nu(C≡C)(\text{free alkyne}) - \nu(C≡C)(\text{co-ordinated alkyne}) \). As indicated above, the change in stretching frequency, \( \Delta \nu(C≡C) \), is often taken as an approximate quantitative indication of the metal-alkyne bond strength.

### Table 2.1

<table>
<thead>
<tr>
<th>Alkyne stretching frequencies for platinum-alkyne complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu(C≡C)(\text{cm}^{-1}) )</td>
</tr>
<tr>
<td>--------------------------------</td>
</tr>
<tr>
<td>( [\text{PtCl}_3(\text{ac})] ); ac =</td>
</tr>
<tr>
<td>( \text{tBuC≡CC(Me)}_2\text{OH} )</td>
</tr>
<tr>
<td>( [\text{Pt}(\text{ac})(\text{PPh}_2)_2] ); ac=</td>
</tr>
<tr>
<td>( \text{HC≡CC(Me)(Et)OH} )</td>
</tr>
<tr>
<td>( \text{HC≡CPh} )</td>
</tr>
<tr>
<td>( \text{PhC≡CPh} )</td>
</tr>
<tr>
<td>( \text{F}_2\text{CC≡CCF}_3 )</td>
</tr>
<tr>
<td>( \text{NCC≡CCN} )</td>
</tr>
</tbody>
</table>

\(^a\) \( \nu(C≡C) \) taken as the mean of the two observed values.
The metal-alkyne bond is stabilised, therefore, by strongly $\sigma$-donating ligands, which facilitate back-donation from the metal to the alkyne, and likewise, electronegative alkynes encourage greater $\pi$-type back-donation. This explains the stability series for $[\text{Pt}(\text{ac})L_2]$ complexes, mentioned earlier.

(ii) X-ray diffraction studies

The predictions made by the Dewar-Chatt-Duncanson model are again supported by the structural features observed in a number of X-ray diffraction studies. All $[\text{Pt}(\text{alkyne})L_2]$ complexes have approximately planar geometry and the triple bond is lengthened from that of unco-ordinated alkynes (1.204Å, on average). The geometry of the distorted alkynes is cis, as suggested by theoretical considerations.

Table 2.2 gives the triple bond lengths for a number of platinum-alkyne complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Bond length (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Pt}(\text{ac})(\text{PPh}_3)_2]$; ac=</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NCC≡CCN</td>
<td>1.40</td>
<td>49</td>
</tr>
<tr>
<td>$F_2\text{CC≡CCF}_3$</td>
<td>1.255</td>
<td>45</td>
</tr>
<tr>
<td>PhC≡CPh</td>
<td>1.32</td>
<td>50</td>
</tr>
<tr>
<td>K$[\text{PtCl}_3(\text{ac})]$; ac=</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Et}_2\text{C(OH)C≡CCEt}_2\text{OH}$</td>
<td>1.18</td>
<td>51</td>
</tr>
<tr>
<td>$[\text{Pt}(\text{ac})_2]$; ac=</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Et}_2\text{C(OH)C≡CCEt}_2\text{OH}$</td>
<td>1.35</td>
<td>4</td>
</tr>
<tr>
<td>PhC≡CPh</td>
<td>1.28</td>
<td>20</td>
</tr>
</tbody>
</table>
The complexes \([\text{Pt(alkyne)}_2]^{4,20}\) are approximately tetrahedral, with mutually perpendicular alkyne ligands. This again can be explained by the bonding model, because, in order to obtain maximum back-bonding from the available metal orbitals, the two alkynes would be expected to co-ordinate perpendicular to one another. In addition, intramolecular steric interaction is minimised.

(iii) \(\text{N.m.r. spectroscopy}\)

Complexes containing terminal alkynes show a signal in their \(^1\text{H n.m.r. spectra}\) in the range \(-3.2\) to \(3.8\), \(^{13,18,52}\) which is in the region associated with unco-ordinated alkenic protons,\(^{53}\) showing again that some rehybridisation has occurred at the carbon atom.

The possibility of alkyne rotation, about the metal-alkyne bond, can be investigated using \(\text{n.m.r.}\) techniques, but the evidence suggests that for the complexes \([\text{Pt(alkyne)L}_2]\) there is no rotation in solution. For example, complex (VII) shows, in its \(^1\text{H n.m.r. spectrum}\), coupling between the methyl protons and the two inequivalent phosphorus nuclei. This indicates that the alkyne is not rotating.\(^{37,52}\)
Theoretical calculations on platinum(II) and platinum(0) complexes are in accordance with the greater barrier to rotation for platinum(0) systems predicted by the bonding model.

D. Reactions of alkyne complexes of platinum(0)

(i) Ligand displacement reactions

Alkyne exchange reactions have been outlined in Section 2.1A.

(ii) Oxidation reactions

The complexes [Pt(ac)(PPh₃)₂] react with acids, (HX) according to the reaction whose proposed mechanism is shown in Figure 2.9. The proportions of cis- and trans-alkenes formed vary according to both acid and alkene.

Evidence in support of this mechanism is given by the reactions of HCl and F₃CCO₂H with complexes of the type [Pt(ac)(PPh₃)₂], where stable vinyl complexes of platinum(II) were isolated. The reaction of HgX₂ (X=Cl,Br) with [Pt(C₄F₆)(PPh₃)₂] gave the cis-vinyl complex (VIII). The geometry about the double bond is shown to be cis from the ¹⁹F n.m.r. data.
[L = PPh₃;  R = CH₃;  
X = Cl, Br, CH₃CO₂, CF₃CO₂, CH₃COS, picrate.]

Figure 2.9
The platinum(II) complex (IX) was isolated from the oxidative-elimination reaction between tetrachloro-o-benzoquinone and \([\text{Pt}(\text{PhC}_2\text{Ph})(\text{PPh}_3)_2]\)\(^{59,60}\). The alkyne was displaced by the reaction with triphenylphosphine, but the reactions with HCl and HBr give a useful route to the platinum(II)-alkyne complexes (X).

Alkyne-alkynyl isomerisation has been observed for some platinum complexes. The first well defined example was of the photochemical isomerisation of \(\text{[Pt(NCCCN)(PPh}_3)_2]\) to \(\text{cis-}[\text{PtCN(C}_2\text{CN})(\text{PPh}_3)_2]\)\(^{61}\). Recently, the complex \(\text{[Pt(PhC}_2\text{Cl)(PPh}_3)_2]\) was prepared, and shown to isomerise to the trans complex \(\text{[PtCl(C}_2\text{Ph)(PPh}_3)_2]\), via the cis complex, as shown in Figure 2.10.\(^{19}\)
Figure 2.10

i) [L=PPh₃]

ii) [PhC≡CPh]^+

iii) [PhC≡CPh]^-
2.2 Results and discussion

Platinum forms $\eta^2$-alkyne complexes\textsuperscript{13,17,18,53,62} and alkynyl complexes\textsuperscript{63-66} with $\alpha$-hydroxyalkynes. Some interesting dehydration reactions of the alkynyl complexes have been reported.\textsuperscript{65,66} Thus, on refluxing the bis-alkynyl complexes $\text{trans-}[\text{Pt}(\text{C}_2\text{C}(\text{R}_1)(\text{R}_2)\text{OH})_2(\text{PPhMe}_2)_2]$ (XI), in acetic anhydride containing a small amount of pyridine, the bis-enzyme complex (XII)\textsuperscript{65} was formed, as shown in Figure 2.11. The analogous bis-triphenylphosphine complexes

\begin{align*}
\text{HO-C-C=Pt-C=C-C-OH} & \xrightarrow{-2\text{H}_2\text{O}} \text{C-C=Pt-C=C-C} \\
\text{R}_2 & \text{L} & \text{R}_2 & \text{L} & \text{R}_3 & \text{R}_4
\end{align*}

\[(\text{XI}) \quad (\text{XII})\]

$L$=$\text{PPhMe}_2$;

a) $\text{R}_1$=$\text{R}_2$=$\text{Me}$; $\text{R}_3$=$\text{Me}$, $\text{R}_4$=$\text{CH}_2$

b) $\text{R}_1$=$\text{Me}$, $\text{R}_2$=$\text{Et}$; $\text{R}_3$=$\text{Et}$, $\text{R}_4$=$\text{CH}_2$, or $\text{R}_3$=$\text{Me}$, $\text{R}_4$=$\text{C(H)Me}$

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure2.11.png}
\caption{Figure 2.11}
\end{figure}

were prepared by refluxing $\text{cis-}[\text{PtCl}_2(\text{PPh}_3)_2]$ in neat $\alpha$-hydroxyalkyne in the presence of ammonium hydroxide,\textsuperscript{66} as shown in Figure 2.12, for 2-methylbut-3-yne-2-ol.

The mono-enzyme complex (XIII) was prepared by refluxing
cis-[PtCl₂(PPh₃)₂] in chloroform, with an α-hydroxyalkyne, as exemplified in Figure 2.13, for 2-methylbut-3-yne-2-ol.
These reactions show that the presence of the hydroxyl group on the alkyne has an important influence on the reactivity of these complexes.

In the work described here, the $\eta^2$-alkynediol complexes (XIV) were treated with hexafluoropropanone (HFP), to investigate the possibility of dehydration, and ring closure, in these complexes.

A. Reactions of hexafluoropropanone with alkynediolbis-(triphenylphosphine)platinum(0) complexes.

The room temperature reaction of an excess of HFP with but-2-yn-1,4-diolbis(triphenylphosphine)platinum(0) (XIVa) gave a white microcrystalline powder, complex (XV), which from microanalytical data is the product of a 1:1 condensation reaction between the platinum complex and HFP.

The infra-red spectrum of (XV) shows a strong band at 1651 cm$^{-1}$ which is assigned as a carbonyl stretching frequency, and a band of medium intensity at 551 cm$^{-1}$. It has been proposed$^{69}$ that bands at 550-55 cm$^{-1}$ give an indication of the stereochemistry of bis-triphenylphosphine complexes of platinum, and on this evidence, complex (XV) is assigned cis stereochemistry.
The $^1$H n.m.r. spectrum shows, besides a multiplet for the triphenylphosphines, two singlet signals in the alkenic region [4.20(1H) and 4.45(1H)], and a double doublet centred at 7.41 t (2H), which appears as a 1:4:1 triplet, due to platinum coupling ($J_{PtH}=$68Hz). This signal arises from coupling to both the cis and the trans phosphorus ($J_{PcisH}=$6Hz; $J_{PtransH}=$12Hz).

The $^{19}$F n.m.r. spectrum shows one singlet resonance, at 75.94 p.p.m. upfield from external fluorotrichloromethane.

The proton decoupled $^{31}$P n.m.r. spectrum shows the two phosphorus atoms to be inequivalent. There are two doublet resonances ($J_{Pp}$=14.6Hz) at -28.04 p.p.m. (P) and -10.59 p.p.m. (P'), relative to external phosphonium ion, each of which shows coupling to platinum ($J_{PtP}$=2378Hz; $J_{Ptp}$=3975Hz). This data supports the assignment of a cis configuration for the phosphine ligands.

In order to determine the structure of complex (XV), a single crystal X-ray diffraction study has been performed. The crystals of complex (XV), $C_{43}H_{34}O2F6P2Pt$ (molecular weight = 953.95) are monoclinic, with space group $P2_1/n$, and $a = 12.881\AA$, $b = 22.272\AA$, $c = 13.572\AA$, $\beta = 99^\circ$, $U = 3845.67\AA^3$ and $Z = 4$. The result shows that the complex contains a six-membered platinacyclic ring, with a platinum-oxygen and a platinum-carbon bond. The structure, with bond lengths, is shown in Figure 2.14.

The assignment of P and P' is made on the basis of available data. Ligands (L), with a high trans influence cause lower values for $J_{PtP}$ for phosphine ligands trans to (L). The expected value of $J_{Ptp}$ for cis bis-phosphine platinum(II) complexes is greater
[Pt(OCCF₃)₂C(=CH₂)C(=O)CH₂]PP₃₂

(XV)

Figure 2.14
(\textasciitilde3500-3800\text{Hz}) \text{ than that for analogous \textit{trans} complexes (\textasciitilde2200-2400\text{Hz})}. \textsuperscript{70,71} Therefore the signal at \textasciitilde28.04 \text{p.p.m.}, which has the lower value for $J_{\text{pp}}$ (2378Hz) is assigned to the phosphorus (P) which is \textit{trans} to the $\sigma$-bonded carbon, which has a strong \textit{trans} influence.

A possible mechanism for the formation of complex (XV) is shown in Figure 2.15.

The reactions of HFP with 2,5-dimethylhex-3-yne-2,5-diolbis(triphenylphosphine)platinum(0) (XIVb) and with 3,6-dimethyloct-4-yne-3,6-diolbis(triphenylphosphine)-platinum(0) (XIVc), gave the crystalline complexes (XVI) and (XVII), respectively. From microanalytical data, these complexes both appear to be the condensation products of 1:1 reactions, and spectroscopic data suggest that they are similar to each other, but different from complex (XV).

Their infra-red spectra show no evidence for carbonyl groups, or exocyclic double bonds. Both complexes have a band of medium intensity at $548\text{cm}^{-1}$, indicating \textit{cis} configurations.

Besides the aromatic signals, the $^1\text{H n.m.r.}$ spectrum of (XVI) shows a singlet resonance at 8.48\textit{H} (6\textit{H}), and a double doublet centred at 9.04\textit{H} (6\textit{H}) which shows platinum coupling ($J_{\text{ph}}=20\text{Hz}$). This latter signal is assigned to two equivalent methyl groups, which couple to the \textit{cis} and the \textit{trans} phosphorus ($J_{\text{cisph}}=1.5\text{Hz}; J_{\text{transph}}=4\text{Hz}$), in the system:

\begin{center}
\begin{tikzpicture}
\node at (0,0) (Pt) {Pt};
\node at (-1.5,0) (Ph3P1) {Ph$_3$P};
\node at (1.5,0) (Ph3P2) {Ph$_3$P};
\node at (0,-1) (CH3) {CH$_3$};
\node at (-1.5,-1) (C) {C};
\node at (1.5,-1) (C) {C};
\node at (0,-3) (Ph3P1) {Ph$_3$P};
\node at (-1.5,-3) (CH3) {CH$_3$};
\node at (1.5,-3) (CH3) {CH$_3$};
\draw (Pt) -- (C);
\draw (Pt) -- (C);
\draw (Pt) -- (Ph3P1);
\draw (Pt) -- (Ph3P2);
\end{tikzpicture}
\end{center}
\[ \text{[P=Ph}_3\text{P; R=CF}_3.\text{]} \]

Figure 2.15
Complex (XVII) shows singlet resonances at 8.28\(\tau\)(3H) and 8.42\(\tau\)(3H), and a multiplet centred at 9.09\(\tau\)(10H), as well as the aromatic signals, in its \(^1\)H n.m.r. spectrum.

The \(^{19}\)F n.m.r. spectrum of complex (XVI) shows a singlet resonance at 79.86 p.p.m., relative to external fluorotrichloromethane, while that of complex (XVII) shows one multiplet, centred at 81.41 p.p.m.

The \(^{31}\)P n.m.r. spectra of complexes (XVI) and (XVII) show the two phosphorus atoms to be in different environments, in each complex. The two doublet resonances appear at -26.12 p.p.m. (P) and -14.12 p.p.m. (P'), relative to external phosphonium ion, for complex (XVI), (\(J_{PP} = 14.6\)Hz; \(J_{P^2P} = 1899\)Hz; \(J_{P^2P'} = 4522\)Hz). For complex (XVII), the two doublets are at -25.00 p.p.m. (P), and -13.20 p.p.m. (P'), with \(J_{PP} = 14.6\)Hz, \(J_{P^2P} = 1885\)Hz and \(J_{P^2P'} = 4546\)Hz. These data give good evidence for a cis configuration of the phosphine ligands, with P trans to a \(\sigma\)-bonded carbon, and P' trans to oxygen, as in complex (XV).

A proposed structure for complexes (XVI) and (XVII) is shown in Figure 2.16. This structure is consistent with available data, and with the proposed mechanism for the reaction of HFP (Figure 2.15). The result of a single crystal X-ray diffraction study is awaited, for confirmation of the structure of complex (XVI).

The n.m.r. spectroscopic data for complexes (XV), (XVI) and (XVII) are summarised in Table 2.3.

The oxidative linking of HFP with co-ordinated alkenes has been reported for complexes of iron.
<table>
<thead>
<tr>
<th></th>
<th>( ^1\text{H} \text{n.m.r.} )</th>
<th></th>
<th>( ^{19}\text{F} \text{n.m.r.} )</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical Shift</td>
<td>Coupling Constant</td>
<td>Chemical Shift</td>
<td>Coupling Constant</td>
</tr>
<tr>
<td>(XV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><a href="PPh_3">Pt(OC(\text{CF}_3))_2C(:CH_2)C(:O)CH_2</a>_2]</td>
<td>2.73(m, 30H)</td>
<td>4.20(s, 1H)</td>
<td>7.41(dxd, 2H)</td>
<td>75.94(s)</td>
</tr>
<tr>
<td></td>
<td>4.54(s, 1H)</td>
<td>7.41(dxd, 2H)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(XVI)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pt{OC(\text{CF}_3)_2C(=C)C(Me)_2OC(Me)_2}(PPh_3)_2]</td>
<td>2.74(m, 30H)</td>
<td>8.48(s, 6H)</td>
<td>9.04(dxd, 6H)</td>
<td>79.86(s)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(XVII)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Pt{OC(\text{CF}_3)_2C(=C)C(Me)(Et)OC(Me)(Et)}(PPh_3)_2]</td>
<td>2.78(m, 30H)</td>
<td>8.28(s, 3H)</td>
<td>8.42(s, 3H)</td>
<td>81.41(m)</td>
</tr>
<tr>
<td></td>
<td>9.09(m, 10H)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Measured in CDCl\(_3\) solution.

b) Recorded at 100MHz; chemical shifts (\(\tau\)) relative to internal T. M. S.; coupling constants in Hz.

c) Recorded at 94.1MHz; chemical shifts (p.p.m.) relative to external CFCl\(_3\).

d) Recorded at 24.15MHz with complete \(^1\text{H} \) decoupling; chemical shifts (p.p.m.) relative to external PH\(_4\)\(^+\), downfield shifts regarded as negative; coupling constants in Hz.
Rhodium\textsuperscript{72} and platinum,\textsuperscript{73} and some examples are summarised in Figure 2.17.

\begin{align*}
\text{(XVI)} & \quad R_1 = R_2 = \text{Me} \\
\text{(XVII)} & \quad R_1 = \text{Me}, \quad R_2 = \text{Et}
\end{align*}

Figure 2.16

Ring-expansion reactions of HFP with bis-phosphine complexes of platinum(II) are well characterised.\textsuperscript{74-76} Two examples are shown in Figure 2.18.
An interesting carbonylation reaction has been reported for the but-2-yne-1,4-diol complex (XIVa), from which the platinalactone complex (XVIII) was isolated. No mechanism for this reaction was proposed.

B. Reactions of electrophilic alkenes and alkynes with but-2-yne-1,4-diolbis(triphenylphosphine)platinum(0).

A number of attempted displacement reactions were performed, in order to determine the relative stability of this alkynediol complex.
But-2-yne-1,4-diol was readily displaced by the following alkynes: hexafluorobut-2-yne, dimethylethynedicarboxylate, and 1-phenylbut-1-yne-3-one; it was not displaced by diphenylethyne. It was also displaced by the alkenes tetrafluoroethene and tetracyanoethene, but not by tetraethylethene tetra carboxylate at room temperature. The complex

\[ \text{[Pt}\{\text{C}_2(\text{CO}_2\text{Et})_4\}\{\text{PPh}_3\}_2] \]

could, however, be prepared by the displacement of the alkene from the complex

\[ \text{[Pt(trans-stilbene)(PPh}_3\}_2] \]

at room temperature.

The but-2-yne-1,4-diol was also displaced by N-sulphinylaniline, to give the known complex

\[ \text{[Pt(PhNSO)(PPh}_3\}_2] \]

Acetonedicarboxylic acid dimethyl ester, which is known to displace ethene and trans-stilbene from the complexes \[ \text{[Pt(alkene)(PPh}_3\}_2] \] in the presence of dioxygen (see Chapter 3, and reference 3.39), did not react at room temperature with the alkynediol complex, stirred in an open flask.

Proton decoupled $^{31}\text{P}$ n.m.r. spectra were recorded for the alkene and alkyne complexes of platinum(0) thus obtained, and the chemical shifts and coupling constants are presented in Table 2.4.

For the platinum(II) complexes cis-\[\text{[PtX}_2(\text{PBu}_3\}_2]\], the coupling constants $J_{\text{PtP}}$ decrease, and the $^{31}\text{P}$ chemical shifts move to higher field, with a decrease in the electronegativity of X (Cl-Br-I). However, although for the alkyne complexes the coupling constants decrease in the order $\text{C}_2(\text{CO}_2\text{Me})\text{C}_2(\text{CF}_2)\text{C}_2(\text{CH}_2\text{OH})\text{C}_2\text{Ph}\text{C}_2(\text{CMe}_2\text{OH})_2 \approx \text{C}_2(\text{C(Me})(\text{Et})\text{OH})_2$, no such trend is obvious for the alkene complexes. There is no apparent trend in the chemical shift values for any of these platinum(0) complexes.
<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>( J_{\text{PP}, \text{P}} ) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(CN)}_4 { \text{PPh}_3 }_2 )</td>
<td>-15.53 (s)</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(CO}_2 \text{Et}_4 { \text{PPh}_3 }_2 )</td>
<td>-25.41 (7 lines)</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(CO}_2 \text{Me}_4 { \text{PPh}_3 }_2 )</td>
<td>-29.04 (s)</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(CO}_2 \text{Ph}_4 { \text{PPh}_3 }_2 )</td>
<td>-24.20 (s)</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(C}_2 \text{F}_6 { \text{PPh}_3 }_2 )</td>
<td>-21.38 (s)</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(C}_2 \text{F}_6 { \text{PPh}_3 }_2 )</td>
<td>-21.23 (s)</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(C}_2 \text{H}_2 \text{O}_2 \text{Ph}_2 { \text{PPh}_3 }_2 )</td>
<td>-24.10 (d)</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(C}_2 \text{H}_2 \text{O}_2 \text{Ph}_2 { \text{PPh}_3 }_2 )</td>
<td>3799 (P); 3418 (P')</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(C}_2 \text{H}_2 \text{O}_2 \text{Ph}_2 { \text{PPh}_3 }_2 )</td>
<td>-26.4 (s)</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(C}_2 \text{H}_2 \text{O}_2 \text{Ph}_2 { \text{PPh}_3 }_2 )</td>
<td>-21.8 (s)</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(C}_2 \text{H}_2 \text{O}_2 \text{Ph}_2 { \text{PPh}_3 }_2 )</td>
<td>-23.6 (s)</td>
</tr>
<tr>
<td>( \text{Pt}^4 \text{C}_2 \text{(C}_2 \text{H}_2 \text{O}_2 \text{Ph}_2 { \text{PPh}_3 }_2 )</td>
<td>-13.92 (s)</td>
</tr>
</tbody>
</table>

a. Measured in 

b. Measured in benzenes; in CDCl₃ forms cis-\( \text{Pt}^4 \text{C}_2 \text{(C}_2 \text{H}_2 \text{O}_2 \text{Ph}_2 \{ \text{PPh}_3 \}_2 \)

c. Reference 18.
2.3 Experimental

In this section, the melting points, microanalytical results, and infra-red and n.m.r. spectroscopic data are presented for all newly characterised compounds.

Microanalyses were carried out by D. Butterworth, The Butterworth Microanalytical Consultancy Ltd., 42 High Street, Teddington, Middlesex.

Melting points were recorded on a Reichart hot-stage apparatus, and are uncorrected.

Infra-red spectra were recorded as nujol mulls, using CsI plates, on a Perkin-Elmer 580 spectrophotometer, and were calibrated using a polystyrene film.

$^1$H n.m.r. spectra were recorded in CDCl$_3$ solution, on a Jeol JNM-PS-100 spectrometer, operating at 100MHz. Chemical shifts (r) are reported relative to internal T.M.S.

$^{19}$F n.m.r. spectra were recorded in CDCl$_3$ solution, on a Jeol JNM-PS-100 spectrometer, operating at 94.1MHz. Chemical shifts (p.p.m.) are reported relative to external fluorotrichloromethane.

$^{31}$P n.m.r. spectra were recorded in CDCl$_3$ solution on a Jeol JNM-FX60 spectrometer, operating at 24.15 MHz. Chemical shifts (p.p.m.) are reported relative to external phosphonium ion (PH$_4^+$). The spectra were completely $^1$H decoupled.

Reactions were performed at room temperature, under an atmosphere of dry dinitrogen, unless stated otherwise, using previously dried and degassed solvents.

Reactions carried out in Carius tubes (150cm$^3$) were done in 15cm$^3$ of the stated solvent.
Ligands and reagents

The following materials were purchased:

- 2,5-dimethylhex-3-yne-2,5-diol
- 3,6-dimethyloct-4-yne-3,6-diol
- but-2-yne-1,4-diol
- dimethylethylenedicarboxylate
- diphenylethyne
- trans-stilbene
- acetonedicarboxylic acid dimethyl ester
- tetracyanoethene
- 1-phenylbut-1-yne-3-one
- tetraethylethene tetracarboxylate
- polytetrafluoroethene
- hexafluoropropanone
- hexafluorobut-2-yne

Tetrafluoroethene was prepared by the thermal decomposition of polytetrafluoroethene, in a silica tube, under vacuum. It was trapped out by cooling in liquid dinitrogen.

Potassium tetrachloroplatininate was obtained on loan from Johnson Matthey Ltd.

The following were prepared as described in the literature:

- but-2-yne-1,4-diolbis(triphenylphosphine)platinum(0)
- 2,5-dimethylhex-3-yne-2,5-diolbis(triphenylphosphine)platinum(0)
- 3,6-dimethyloct-4-yne-3,6-diolbis(triphenylphosphine)platinum(0)
- trans-stilbenebis(triphenylphosphine)platinum(0)
- diphenylethynebis(triphenylphosphine)platinum(0)
- cis-dichlorobis(triphenylphosphine)platinum(II)
- N-sulphinylandine
Authentic samples of the following were prepared for comparative purposes:

- hexafluorobut-2-ynebis(triphenylphosphine)platinum(0)\textsuperscript{33}
- dimethylethynedicarboxylatebis(triphenylphosphine)platinum(0)\textsuperscript{16}
- 1-phenylbut-1-yne-3-onebis(triphenylphosphine)platinum(0)\textsuperscript{55}
- tetrafluoroethenebis(triphenylphosphine)platinum(0)\textsuperscript{79}
- tetracyanoethenebis(triphenylphosphine)platinum(0)\textsuperscript{80}
- N-sulphinylanilinebis(triphenylphosphine)platinum(0)\textsuperscript{77}
A. Reactions of hexafluoropropanone

(i) With but-2-yne-1,4-diolbis(triphenylphosphine)platinum(0)

An excess of hexafluoropropanone (1.0 cm$^3$) was condensed (-196°C) on to a suspension of

$[Pt(H_2C(OH)C\equiv CCH_2)SH)(PPh_3)_2](0.18g, 0.22mmol)$ in diethyl ether, contained in a Carius tube. The tube was sealed, and shaken for 24 hours. Initially, a colourless solution formed, but after 24 hours, a white microcrystalline powder had precipitated. After opening the tube and removing the volatile material, the white powder was filtered, and washed quickly with diethyl ether. It was identified as $[Pt(OCCF_3)_2C(CH_2)C(O)CH_2]-(PPh_3)_2]$. Yield = 0.13 g, 61% 

M.P. 221-3°C (decomp)

Analysis: Calculated for $C_{43}H_{34}O_{2}F_6P_2Pt$:

- C, 54.14%; H, 3.59%; F, 11.95%
- Found: C, 53.88%; H, 3.78%; F, 12.37%

Infra-red. 1651s, 1605w, 1590w, 1298m, 1251s, 1207s,
1190s, 1185s, 1144s, 1127w, 1099m, 1029w, 1000m, 954s,
835w, 752w, 744m, 730w, 706m, 692s, 679w, 668w, 551m,
523s, 520m, sh, 510w, 501m, 462w, 421w.

$^1$H n.m.r. 2.73(m,30H); 4.20(s,1H); 4.54(s,1H);
7.41(dxd,2H, $J_{PcisH}=6$Hz, $J_{PtransH}=12$Hz; $J_{PtH}=68$Hz).

$^{19}$F n.m.r. 75.94(s)

$^{31}$P n.m.r. -28.04(d, $J_{PP}=14.6$Hz; $J_{PtP}=2378$Hz);
-10.59(d, $J_{PP}=14.6$Hz; $J_{PtP}=3975$Hz).
(ii) With 2,5-dimethylhex-3-yne-2,5-diolbis(triphenylphosphine)-platinum(0)

An excess of hexafluoropropanone (1.0 cm³) was condensed (-196°C) on to a suspension of
[Pt(Me₂C(OH)C≡CCMe₂OH)(PPh₃)₂] (0.20 g, 0.23 mmol) in diethyl ether, contained in a Carius tube. The tube
was sealed, and shaken for 24 hours. A colourless solution formed, and the tube was opened, and the
volatile material removed. A white microcrystalline powder was isolated by slow evaporation of the solvent,
and careful addition of methanol. The powder was collected, washed with methanol, and postulated to be
[Pt{OC(CF₃)₂C(-C)C(Me)₂OC(Me)₂} (PPh₃)₂]. Yield = 0.18 g 78%
M.P. 212-3°C (decomp)

Analysis Calculated for C₄₇H₄₂O₂P₂F₆Pt
    C, 55.89%; H, 4.19%
    Found: C, 54.76%; H, 4.03%

Infra-red. 1589w, 1576w, 1309m, 1292m, 1281m, 1220s,
1204s, 1186s, 1161m, 1135m, 1101m, 1094m, 1062s, 1029w,
1024w, 1001w, 973w, sh, 956s, 937w, 858w, 845w, 772w,
753m, 744m, 731w, 722m, 701s, 694s, 668w, 645w, 617w,
548m, 525s, 521s, sh, 510m, 499m, 460w, 437w, 422w, 416w,
370w.

¹H n.m.r. 2.74 (m, 30H); 8.48 (s, 6H); 9.04 (dxd, 6H),
J₂H₁₈=1.5 Hz, J₂H₃₄=4 Hz; J₂Pt₃=20 Hz).

¹⁹F n.m.r. 79.86 (s)

³¹P n.m.r. 26.12 (d, J₂₂=14.6 Hz; J₂₃=1899 Hz);
-14.12 (d, J₂₂=14.6 Hz; J₂₃=4522 Hz).
(iii) With 3,6-dimethyl-oct-4-yne-3,6-diols bis (triphenylphosphine)-platinum(0)

An excess of hexafluoropropanone (1.0 cm³) was condensed (-196°C) on to a suspension of

\[ \text{[Pt(EtC(Me)(OH)C}\equiv\text{C(Me)}(Et)OH)(PPh₃)₂] } \] (0.28 g, 0.31 mmol)

in diethyl ether, contained in a Carius tube. The tube was sealed, and shaken for 3 days. A colourless solution formed and the tube was opened. After removing the volatile material, a white microcrystalline powder was isolated by evaporation of the solvent and careful addition of methanol. The powder was collected, washed with methanol and postulated to be

\[ \text{[Pt\{OC(CF₃)₂C(=C)C(Me)(Et)OC(Me)(Et)\}(PPh₃)₂] } \]

Yield = 0.15 g, 47%

M.P. 188-91°C (decomp)

Analysis: Calculated for C₄₉H₄₆O₂P₂F₆Pt:

C, 56.69%; H, 4.45%

Found:

C, 55.77%; H, 4.60%

Infra-red: 1590w, 1574w, 1306m, 1291m, 1279m, sh,

1208s, sh, 1199s, 1187s, 1160m, sh, 1131m, 1100m, 1093m,

1071m, br, 1030w, 1001w, 975w, 951m, 920w, 894w, 850w,

774w, 753m, 742m, 724m, 702m, 694s, 668w, 620w, 548m,

523s, 509s, 498m, 454w, 445w, 423w,

¹H n.m.r. 2.78(m, 30H); 8.28(s, 3H); 8.42(s, 3H); 9.09(M, 10H).

¹⁹F n.m.r. 81.41(m).

³¹P n.m.r. -25.00(d, Jₚₚ = 14.6 Hz; JₚPt = 1885 Hz);

-13.20(d, Jₚₚ = 14.6 Hz; JₚPt = 4546 Hz).
B. Reactions of electrophilic alkenes and alkynes with but-2-yne-1,4-diolbis(triphenylphosphine)platinum(0)

(i) With hexafluorobut-2-yne

An excess of hexafluorobut-2-yne (0.5 cm\(^3\)) was condensed (-196\(^\circ\)C) on to a suspension of 
\([\text{Pt}(\text{H}_2\text{C(OH)}\text{C}≡\text{CCH}_2\text{OH})(\text{PPh}_3)_2]\) (0.05 g, 0.06 mmol), in benzene, contained in a Carius tube. The tube was sealed, and placed in an oven at 60\(^\circ\)C for 24 hours. After opening the tube and removing the volatile material, the solution was evaporated to give an impure solid. Recrystallisation from dichloromethane/methanol gave crystals which were identified as 
\([\text{Pt}(\text{C}_3\text{F}_6)(\text{PPh}_3)]\) by their i.r. and \(^{19}\text{F}\) n.m.r. spectra. Yield = 0.05 g, 94%.

\(^{31}\text{P}\) n.m.r. -21.38 p.p.m. (q, \(J_{\text{PF}} = 9.8\text{Hz}; J_{\text{PtP}} = 3394\text{Hz})

\(\text{(ii) With dimethylethynedicarboxylate}\)

A slight excess of dimethylethynedicarboxylate (0.01 g, 0.07 mmol) was added to a solution of 
\([\text{Pt}(\text{H}_2\text{C(OH)}\text{C}≡\text{CCH}_2\text{OH})(\text{PPh}_3)_2]\) (0.05 g, 0.06 mmol) in dichloromethane, and stirred for 5 hours. The colourless solution was evaporated, and crystals were obtained by careful addition of methanol. These crystals were identified as \([\text{Pt}\{\text{C}_2(\text{CO}_2\text{CH}_3)_2\}(\text{PPh}_3)_2]\), by their i.r. spectrum and m.p. Yield = 0.05 g, 97%.

\(^{31}\text{P}\) n.m.r. -24.20 (s; \(J_{\text{PtP}} = 3726\text{Hz})

(iii) With 1-phenylbut-1-yne-3-one

1-phenylbut-1-yne-3-one (0.009 g, 0.06 mmol) was added to a suspension of \([\text{Pt}(\text{H}_2\text{C(OH)}\text{C}≡\text{CCH}_2\text{OH})(\text{PPh}_3)_2]\)
(0.05g, 0.06mmol) in diethyl ether, and stirred for 24 hours. Initially, a pale yellow solution formed, from which a microcrystalline powder precipitated. This was filtered, and recrystallised from dichloromethane/methanol to give crystals which were identified as \([\text{Pt(PhC≡CC(:O)Me)(PPh}_3]^2\)] by their i.r. spectrum, and m.p. Yield = 0.045g, 87%.

\[31^P \text{n.m.r.} \quad -26.72 \text{ (d, } J_{\text{PP}}=24.4\text{Hz; } J_{\text{PtP}}=3799\text{Hz;}}
-24.10\text{ (d, } J_{\text{PP}}=24.4\text{Hz; } J_{\text{PtP}}=3418\text{Hz).}

(iv) With diphenylethyne

Diphenylethyne, (0.022g, 0.12mmol) was added to a suspension of \([\text{Pt(H}_2\text{C(OH)C≡CCH}_2\text{OH)(PPh}_3]^2\)] (0.10g, 0.12mmol) in diethyl ether, and stirred for 4 hours. The suspended powder was filtered, and washed with diethyl ether. The white microcrystals were identified as unreacted starting material, by their i.r. spectrum.

(v) With tetrafluoroethene

An excess of tetrafluoroethene (0.5cm³) was condensed (-196°C) on to a suspension of \([\text{Pt(H}_2\text{C(OH)C≡CCH}_2\text{OH)(PPh}_3]^2\)] (0.05g, 0.06mmol) in benzene, contained in a Carius tube. The tube was sealed, and placed in an oven at 60°C for 24 hours. After opening the tube and removing the volatile material, the solution was evaporated, giving an impure solid. This was recrystallised from dichloromethane/diethyl ether to give crystals which were identified as \([\text{Pt(C}_2\text{F}_4)(\text{PPh}_3]^2\)] by their i.r. and \(^{19}\text{F n.m.r. spectra. Yield = 0.04g, 82%.

\[31^P \text{n.m.r.} \quad -25.41 \text{ (7 lines; } J_{\text{PtP}}=2539\text{Hz).}


(vi) With tetracyanoethene

Tetracyanoethene (0.16 g, 0.12 mmol) was added to \([\text{Pt(H}_{2}\text{C(OH)}\text{C}═\text{CH}_{2}\text{OH})(\text{PPh}_{3})_{2}]\) (0.10 g, 0.12 mmol) suspended in diethyl ether, and stirred for 4 hours. A white microcrystalline solid was filtered, washed with diethyl ether, and identified as \([\text{Pt(C}₂\text{(CN)}₄)(\text{PPh}_₃)₂]\) by its i.r. spectrum and m.p. Yield = 0.07 g, 69%.

\(^{31}P\text{n.m.r.} -15.53 (s; J_{\text{Pt-P}}=3745\text{Hz}).\)

(vii) With tetraethylenetetracarboxylate

Tetraethylenetetracarboxylate (0.02 g, 0.06 mmol) was added to a suspension of \([\text{Pt(H}_{2}\text{C(OH)}\text{C}═\text{CH}_{2}\text{OH})(\text{PPh}_{3})_{2}]\) (0.05 g, 0.06 mmol) in diethyl ether. The mixture was stirred for 24 hours, and a white powder was filtered off. This was identified as unreacted starting material by its i.r. spectrum.

(viii) With N-sulphinylaniline

An excess of N-sulphinylaniline (0.05 g, 0.36 mmol) was added to a suspension of \([\text{Pt(H}_{2}\text{C(OH)}\text{C}═\text{CH}_{2}\text{OH})(\text{PPh}_{3})_{2}]\) (0.10 g, 0.12 mmol) in diethyl ether. After stirring for about 2 minutes, the suspended white powder turned pale yellow. This powder was stirred for 1 hour, and filtered. The pale yellow microcrystalline solid was washed with diethyl ether, and identified as \([\text{Pt(PhNSO)(PPh}_₃)₂]\) by its i.r. spectrum and m.p. Yield = 0.09 g, 87%. 
(ix) With acetonedicarboxylic acid dimethyl ester

An excess of acetonedicarboxylic acid dimethyl ester (0.05g, 0.28mmol) was added to a suspension of $[\text{Pt}(\text{H}_2\text{C(OH)C\equiv\text{CCH}_2\text{OH}})(\text{PPh}_3)_2]$ (0.05g, 0.06mmol), in diethyl ether. The mixture was stirred in an open flask for 24 hours. The white powder which was filtered, and washed with diethyl ether, was identified as unreacted starting material, by its i.r. spectrum.

C. Preparation of tetraethylethenetetracarboxylatebis-(triphenylphosphine)platinum(0)

Tetraethylethenetetracarboxylate (0.20g, 0.63mmol) was added to a suspension of $[\text{Pt}$(trans-stilbene)$(\text{PPh}_3)_2]$ (0.10g, 0.11mmol) in diethyl ether. The mixture was stirred for 24 hours, and the cream coloured powder was filtered. This was recrystallised from dichloromethane/methanol, and identified as $[\text{Pt}$(C$_2$(CO$_2$Et)$_4$)(PPh)$_3$)$_2]$. Yield = 0.07g, 61%.

M.P. 130-32°C (decomp)

Analysis: Calculated for C$_{50}$H$_{50}$O$_{8}$P$_2$Pt:
   C, 57.96%; H, 4.86%

   Found:
   C, 57.49%; H, 4.78%

Infra-red: 1725s, 1701s, 1588w, 1569w, 1310m, 1300m, 1240s, 1208s, 1182m, 1159m, 1100s, 1094s, 1058s, 1028w, 1000w, 973w, 829m,sh, 821m,770w, 750s,sh, 744s, 706s, 693s, 619w, 585w,br, 551m, 539m, 520s, 498s, 472w, 461w, 420w, 350w.

$^1$H n.m.r.  2.73(m,30H); 6.30(q,8H,$J_{\text{HH}}=7$Hz); 9.04(t,12H,$J_{\text{HH}}=7$Hz).

$^{31}$P n.m.r.  -6.45(s; $J_{\text{PtP}}=370$Hz).
CHAPTER THREE
THE PREPARATION OF SOME NOVEL METALLACYCLOBUTANONE COMPLEXES

3.1 Introduction

The preparation and reactions of metallacyclobutane complexes of palladium and platinum.

The first example of a platinacyclobutane complex was reported by Tipper, who found that chloroplatinic acid reacted with cyclopropane to give $\left[\text{PtCl}_2(\text{C}_3\text{H}_6)\right]_n^-$ (I). Treatment with pyridine gave $\left[\text{PtCl}_2(\text{C}_3\text{H}_6)(\text{py})_2\right]^-$ (II), and cyclopropane was evolved from (I) and from (II) on treating with aqueous cyanide. Tipper therefore suggested that the cyclopropane ring was intact in these molecules and that each carbon atom was bonded equally to the platinum atom to form an "edge complex" (IA), with $n=2$.

Spectroscopic, chemical and X-ray data showed the complex (I) to be polymeric and to contain the trimethylene-platinum moiety (IB). The X-ray analysis of complex (II) showed a similar structure, with the $C_1-C_3$ distance of 2.55 Å being too long for there to be significant bonding between these two atoms. N.m.r. studies on

\[ \begin{align*}
\text{(IA)} & \quad & \begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{Cl}
\end{array} \\
2
\end{align*} \\
\begin{align*}
\text{(IB)} & \quad & \begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{Cl}
\end{array} \\
\text{C} \\
\text{C}
\end{align*} \\
\begin{align*}
\text{(II)} & \quad & \begin{array}{c}
\text{Cl} \\
\text{Pt} \\
\text{Py}
\end{array} \\
\text{Py} \\
\text{Cl}
\end{align*}
\]
complex (II), together with $^1$H n.m.r. and X-ray data for the substituted cyclopropane derivatives (III) confirmed the platinum(IV)—trimethylene formulation, and also suggested some Pt-C$_2$ interaction across the four-membered ring.

These platinum(IV) complexes were synthesised according to the following reaction (Figure 3.1)

\[
\begin{align*}
\text{Cl} & \quad \text{Pt} & \quad \text{Cl} \\
\text{Py} & \quad \text{Pt} & \quad \text{Py}
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{Pt} & \quad \text{Cl} \quad + \quad \Delta R \rightarrow \text{C}_2\text{H}_4 \\
\text{Cl} & \quad \text{Pt} & \quad \text{Cl}
\end{align*}
\]

\[
\begin{align*}
\text{Cl} & \quad \text{Pt} & \quad \text{R'} \\
\text{Py} & \quad \text{Pt} & \quad \text{Cl}
\end{align*}
\]

(III)

\[
\begin{align*}
R=n\text{-C}_6\text{H}_{13}; \text{ PhCH}_2; \text{ Ph}, \text{ o-NO}_2\text{C}_6\text{H}_4; R'=\text{H} \\
R=\text{Ph}; \quad R'=p\text{-MeC}_6\text{H}_4. \\
R=R'=\text{Ph(trans)}; R=\text{n-C}_4\text{H}_9; R'=\text{Me(trans)} \\
R=\text{CO}_2\text{Me, COMe, CN}; R'=\text{H}: \text{no reaction}
\end{align*}
\]

Figure 3.1
The proposed mechanism involves electrophilic attack by PtCl₂ on the cyclopropane ring, and the position of the insertion of the PtCl₂ moiety into the ring was studied, using a series of monosubstituted cyclopropanes, by recording the \(^1\)H n.m.r. spectra of the bis-pyridine adducts (III). It was found that, with the exception of R=2-HeC₆H₄, insertion occurred preferentially into the less substituted cyclopropane bond (R=n-C₆H₁₃, PhCH₂, Ph, O-NO₂C₆H₄).

However, the assumption that isomerisation of complexes of type (IB) would not readily occur in the mild reaction with pyridine has been shown to be incorrect, so that characterisation of the complexes (III) does not necessarily show the initial position of ring opening. It was found that the phenylcyclopropane complex (IV) readily isomerised to complex (V), and the mechanism shown in Figure 3.2 was proposed.

![Figure 3.2](image-url)
Complex (IB) was not obtained when cyclopropane was reacted with \([\text{PtCl}_2(\text{C}_2\text{H}_4)]_2\) or with \(\text{H}_{\text{aq}}[\text{PtCl}_3(\text{C}_2\text{H}_4)]\). Instead, \([\text{PtCl}_2(\text{CH} = \text{CH} = \text{CH}_2)]_2\)\(^\text{(VI)}\) was formed\(^\text{12}\). The two isomeric complexes (IB) and (VI) could be readily interconverted by bubbling either cyclopropane or propene through solutions of (VI) or (IB) respectively (Figure 3.3).

\[\text{Figure 3.3}\]

A series of studies on the thermal decomposition of,\(^\text{13,14}\) and the chemical displacement of cyclopropane from \[^\text{15}\]
\([\text{PtX}_2(\text{C}_2\text{H}_6)]\), \([\text{PtX}_2(\text{C}_2\text{H}_6)L_2]\), \((\text{X}=\text{Cl}, \text{Br}; \text{L}=\text{C}_2\text{H}_5\text{N}, \text{4-CH}_2\text{C}_2\text{H}_4\text{N})\) and \([\text{PtX}_2(\text{C}_2\text{H}_6)(\text{L-L})]\)\((\text{X}=\text{Cl}, \text{Br}, \text{L-L}=\text{ethylenediamine}, \text{2,2'-bipyridyl})\) has been reported, and an estimate was made of 113-124 kJ mol\(^{-1}\) for the Pt-C bond strength in these metallacyclobutane systems.

Complex (II) has been found to isomerise\(^2\) in hot benzene to give a yellow ylide complex, \(\text{trans-[PtCl}_2(\text{C}_5\text{H}_4\text{NCHEt})(\text{py})]\) (VII).

\[\text{VII}\]
The crystal structure of this platinum(II) complex has been reported\textsuperscript{4,16}, together with that of the platinum(IV) analogue [PtCl\textsubscript{4}(C\textsubscript{5}H\textsubscript{5}NCHEt)(py)]. The mechanism of this isomerisation has been studied\textsuperscript{17}, and it was suggested that the process is dissociative.

Analogous palladium(II) and platinum(II) metallacyclobutane complexes(VIII) have been prepared (Figure 3.4) using electronegatively substituted cyclopropanes with zerovalent metal complexes acting as nucleophiles\textsuperscript{18,19,20}.

\[
\text{ML}_n + \text{R}^\text{R''} \rightarrow \text{L}_2\text{M} \text{R}^\text{R''}
\]

\[\text{M} = \text{Pt, Pd}, \quad \text{L} = \text{PPh}_3, \text{AsPh}_3, \text{PPh}_2\text{Me}, \quad n = 3, 4.\]

\[\text{R}'' = \text{CN: R=R'=H; R=R'=CH}_3; \quad \text{R}=\text{CH}_3, \text{R'=C}_2\text{H}_5; \quad \text{R+R'}=(\text{CH}_2)_5.\]

\[\text{R}'' = \text{CO}_2\text{C}_2\text{H}_5; \quad \text{R=H, R'=Ph.}\]

\textbf{Figure 3.4}

[Pt(C\textsubscript{5}H\textsubscript{5})(PPh\textsubscript{3})\textsubscript{2}] also gave complexes (VIII), and in some cases, the ligands L in (VIII) could be exchanged\textsuperscript{19}.

These complexes were characterised by their i.r. and \textsuperscript{1}H n.m.r. spectra\textsuperscript{19}, and later by X-ray crystallography\textsuperscript{20,21}. The X-ray data showed that whereas in the octahedral platinum(IV) complexes (II) and (III) the equatorial donor ligand atoms are essentially coplanar about the platinum\textsuperscript{5,8}, in the platinum(II) complexes (VIII) there is some distortion about the platinum from square planar geometry. The suggested mechanism for the reactions (Figure 3.4) of zerovalent palladium or platinum with electronegatively substituted
cyclopropanes is considered to involve nucleophilic attack at a highly electron deficient carbon atom. This mechanism is supported by the fact that $[\text{Pt}(\text{PPh}_3)_4]$ does not react with 1,2-dicyanocyclopropane\textsuperscript{19}.

The platinum(II) and palladium(II) complexes (IX) have been synthesised from the reaction of tetracyano-oxyacyclopropane\textsuperscript{22,23} (TCNEO), with zerovalent palladium or platinum. The structure of the triphenylarsine complex of platinum (IX) has been confirmed by X-ray crystallography. The four equatorial atoms are essentially coplanar about the platinum in this complex. It is noteworthy that there is greater puckering in cyclobutanes than in oxacyclobutanes\textsuperscript{24}. The complexes (IX) were not thermally stable\textsuperscript{23}, and in particular where M=palladium or L=triethylphosphine, only the tricyanoethenolate complexes (X) were isolated. Treatment of (IX) with aqueous cyanide did not liberate TCNEO from the complex\textsuperscript{22}. The reaction of $[\text{Pt}(\text{C}_6\text{H}_4)(\text{PPh}_3)_2]$ with 2,2,3-tricyano-oxacyclopropane gave the expected complex (XI), with metal insertion occurring between the oxygen atom and the most electronegatively substituted carbon atom\textsuperscript{25}. 

\[
\begin{align*}
\text{ML}_4 + & \quad \text{NC}\text{C} \quad \text{C} \quad \text{CN} \\
& \quad \text{NC} \text{CN} \\
\text{L}_2\text{M} & \quad \text{O} \quad \text{C} \quad \text{C} \quad \text{CN} \\
& \quad \text{CN} \quad \text{CN} \\
\text{(X)} & \quad \text{Heat} \\
\text{(IX)}
\end{align*}
\]

$L=\text{PPh}_3, \text{PPh}_2\text{Me}, \text{PET}_3, \text{P}(\text{p-MeC}_6\text{H}_4)_3, \text{AsPh}_3$,

$M=\text{Pt, Pd}$. 

Reactions of cyclopropene derivatives with 
\([\text{Pt(C}_2\text{H}_4)(\text{PPh}_3)_2]\) yielded only alkenic complexes\(^{26,27}\), and 
the structure of the complexes was confirmed by X-ray 
crystallography\(^{26,28}\). The cyclopropenes could be displaced 
from the platinum by treating the complexes with carbon 
disulphide\(^{27}\). This type of complex was shown to be 
intermediate in the ring-opening of cyclopropenone derivatives 
by \([\text{Pt(C}_2\text{H}_4)(\text{PPh}_3)_2]\)\(^{29}\). (Figure 3.5). The reaction of 
diphenylcyclopropenone with \([\text{Pt(PPh}_3)_4]\)\(^{30}\) gave the ring-opened 
complex.

\[
\begin{align*}
\text{(Ph}_3\text{P})_2\text{Pt} & \quad + \quad \text{C}_3\text{H}_3\text{O} \\
\text{(Ph}_3\text{P})_2\text{Pt} & \quad \text{C}_3\text{H}_3\text{O} \\
\text{(Ph}_3\text{P})_2\text{Pt} & \quad \text{C}_3\text{H}_3\text{O}
\end{align*}
\]

**Figure 3.5**
Ring-opening was not observed in the reaction of methylenecyclopropanes with $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$, and only the $\eta^2$-alkene complexes (XII) were isolated. Similarly, only alkene complexes were obtained from the reaction of methylenecyclopropanes with trans-$[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{py})]$. However, the reaction of 1,2-diphenyl-3-dicyanomethylene-cyclopropane with $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ again showed evidence of nucleophilic attack by the Pt(PPh$_3$)$_2$ moiety at the most positively-charged carbon atom, and the two complexes (XIII) and (XIV) were isolated. The structures of (XIII) and (XIV) have been confirmed by single crystal X-ray structure determinations.

\[ \text{R}_1 = \text{R}_2 = \text{R}_3 = \text{H}. \]
\[ \text{R}_1 = \text{R}_3 = \text{CO}_2\text{CH}_3; \text{ R}_2 = \text{H}. \]
\[ \text{R}_1 = \text{R}_2 = \text{CO}_2\text{CH}_3; \text{ R}_3 = \text{H}. \]
Despite much work on the preparation and reactivity of cyclopropanones\textsuperscript{33}, there have been, to date, no reports of platinum or palladium complexes derived from such molecules. In the work presented here, the preparation and characterisation of several metallacyclobutanone complexes is described.
3.2 Results and discussion

The reaction of \([\text{Pt}(\text{PPh}_3)_4]\) in benzene solution, in air, with acetonedicarboxylic acid dimethyl ester, \(\text{MeO}_2\text{CCH}_2\text{COCH}_2\text{CO}_2\text{Me}\), (ACADME) gave a white precipitate, after about 24 hours. The infra-red spectrum of this complex, (XV), had sharp bands in the carbonyl region (1620-1710 cm\(^{-1}\)) and its \(^1\text{H}\) n.m.r. spectrum showed a singlet at \(\tau = 7.00\) (6H), and a doublet at \(\tau = 6.12\) (2H) showing coupling to the trans phosphorus, and with side-bands due to coupling to the platinum. The \(^{31}\text{P}\) n.m.r. showed one signal at -16.74 p.p.m., which was also coupled to the platinum. Complex (XV) was also prepared by the reaction of \([\text{Pt}(\text{trans-stilbene})(\text{PPh}_3)_2]\), in benzene solution with ACADME, in the presence of air.

The reaction of \([\text{PtO}_2(\text{PPh}_3)_2]\) suspended in diethyl ether, with ACADME, again in the air, was found to give complex (XVI), which has a five-membered peroxo-containing ring. This structure was assigned by comparing the i.r. and \(^1\text{H}\) n.m.r.
\[(\text{Ph}_3\text{P})_2\text{PtO}_2 + \text{O=CR} \rightarrow \text{Ph}_3\text{P}\cdot\text{PtO}_2\cdot\text{O=CR} \]

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>R</th>
<th>R'</th>
<th>R</th>
<th>R'</th>
<th>R</th>
<th>R'</th>
<th>R</th>
<th>R'</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>CH₃</td>
<td>C₂H₅</td>
<td>H</td>
<td>CH₃</td>
<td>COCH₃</td>
<td>CF₃</td>
<td>CF₃</td>
<td>CH₃</td>
<td>C(CH₃)₃</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>CH₃</td>
<td>CH₂Cl</td>
<td>CH₃</td>
<td>C₆H₅</td>
<td>COC₆H₅</td>
<td>CF₃</td>
<td>CH₃</td>
<td>CH₃</td>
<td>CH₂CH(CH₃)₂</td>
</tr>
<tr>
<td>H</td>
<td>CH₃</td>
<td>C₆H₅</td>
<td>CH₃</td>
<td>CH₃</td>
<td>COC₂H₅</td>
<td>CH₃</td>
<td>(CH₂)₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>C₆H₅</td>
<td>CH₃</td>
<td>CH₃</td>
<td>C₆H₅</td>
<td>COCH₃</td>
<td>(CH₂)₅</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ref: 34 35 36 37 38

Figure 3.6
spectra of complex (XVI) with those of the complexes formed by the analogous reaction of aldehydes and ketones with $[\text{PtO}_2(P\text{Ph}_3)_2]$ (Figure 3.6). These peroxo-ring complexes can also be prepared by reacting the appropriate aldehyde or ketone with $[\text{Pt}(P\text{Ph}_3)_4]$, in the presence of dioxygen. The five-membered ring peroxo-complexes give a characteristic band in the infra-red spectrum at about $780 \text{ cm}^{-1}$, which has been assigned to $\nu(\text{O-O})$. Complex (XVI) showed a weak band at $776 \text{ cm}^{-1}$ in the infra-red spectrum, together with strong broad bands in the carbonyl region ($1690-1750 \text{ cm}^{-1}$). The $^1\text{H n.m.r.}$ spectrum of (XVI) showed a singlet at $\tau = 6.61(6\text{H})$, and four more peaks at $\tau = 6.66$, $6.80$, $6.93$ and $7.07(4\text{H})$, characteristic of an AB pair. Further evidence for the structure of (XVI) as $[\text{Pt} (\text{OOC(CH}_2\text{CO}_2\text{CH}_3)_2 \text{O}(P\text{Ph}_3)_2]$ was provided by its reaction with hexafluoropropanone (HFP). The product of this reaction was identified as the known complex $[\text{Pt} (\text{OOC(CF}_3)_2 \text{O}(P\text{Ph}_3)_2]$. An analogous reaction in which propanone was replaced by HFP in the complex $[\text{Pt} (\text{OOC(CH}_3)_2 \text{O}(P\text{Ph}_3)_2]$ has been reported.

The reaction of ACADME with $[\text{Pt}(P\text{Ph}_3)_4]$ suspended in diethyl ether was reinvestigated and it was found that the initial product obtained after stirring the reactants in air for 24 hours was a mixture of complexes (XV) and (XVI). From the $^1\text{H n.m.r.}$ spectrum it was clear that the major component of this mixture was complex (XVI). However, it had been found
\[
\text{[Pt\{CH(CO}_2\text{CH}_3\text{)}\text{C(=O)CH(CO}_2\text{CH}_3\text{)}\{PPh}_3\text{)}_2]} \\
\text{(XV)}
\]

\[\text{\(= P, \text{\(= C, \text{\(= O.}
\]

(The phenyl rings have been omitted for clarity.)

Figure 3.7
that on leaving this mixture in dichloromethane solution
for several days, crystals of complex (XV) only were recovered,
and a single crystal X-ray structure determination was carried
out, the result of which is shown in Figure 3.7. It was
therefore apparent that complex (XVI) could react further,
perhaps as a result of being in solution, to give complex (XV),
by losing one molecule each of dihydrogen and dioxygen.

To test the hypothesis, attempts were made to convert a
pure sample of complex (XVI) into pure (XV). Stirring (XVI),
suspended in diethyl ether, in the presence of triphenylphosphine,
or in the presence of ACADME, for 24 hours in an open flask,
resulted in the recovery of unchanged starting material.
Stirring (XVI) in dichloromethane solution, in an open flask
for 4 days, left the complex unchanged, and a further sample
stirred in dichloromethane solution, for 5 days, in the
presence of triphenylphosphine, was also recovered unchanged.
It was found that the conversion, although slow, could be
effected in the presence of both triphenylphosphine and ACADME,
either in diethyl ether or in dichloromethane.

The easiest way to follow this conversion was to record
the changes in the i.r. spectrum, in the 500-560 cm\(^{-1}\) region.
It has been proposed that the band at 550±5 cm\(^{-1}\) is a useful
guide in assigning stereochemistry to [PtXY(PPh\(_3\))\(_2\)] complexes, and that this band is relatively strong in the i.r. spectra of
cis complexes. For complex (XV) this band appears at 541 cm\(^{-1}\),
and for (XVI) it is at 553 cm\(^{-1}\). Thus there is a sufficient
difference between these two bands for mixtures of (XV) and (XVI) to be
easily detected, and the change in this band was used, along
with changes in the carbonyl region, to follow the various
attempted conversions.
Figure 3.9

L = py., P = PPh₃.
It is interesting to compare some of the important features of the crystal structure of complex (XV), which was found (Figure 3.8) to contain a novel metallacyclobutanone ring, with those of the known structures for the metallacyclobutane complexes of platinum(IV), (XVII)\(^5\), (XVIII)\(^8\), (XVIIIb)\(^8\), and of platinum(II), (XIX)\(^21\), (XX)\(^20\) and (XXI)\(^20\), which are shown in Figure 3.9.

![Figure 3.8](image)

The crystals of (XV), \(C_{44}H_{38}O_5P_2Pt\), (molecular weight = 891.88) are triclinic, with space group \(P\overline{1}\), and \(a = 17.591\,\AA\), \(b = 12.736\,\AA\), \(c = 10.272\,\AA\), \(\alpha = 118.19^\circ\), \(\beta = 94.71^\circ\), \(\gamma = 73.98^\circ\), \(U = 1946.44\,\AA^3\) and \(Z = 2\). Table 3.1 compares some of the bond-lengths and angles of these seven complexes. From the table it can be seen that:

i) the dihedral angle between the planes defined by \(C_1\text{-Pt}\text{-C}_3\) and \(C_1\text{-C}_2\text{-C}_3\) is much greater in (XV), that is, the ring is more puckered;

ii) the angle \(C_1\text{-C}_2\text{-C}_3\) is larger in (XV);

iii) the angles Pt-\(C_1\text{-C}_2\) and Pt-\(C_3\text{-C}_2\) are smaller in (XV);

iv) the bond lengths \(C_1\text{-C}_2\) and \(C_2\text{-C}_3\) are considerably shorter in (XV).

As a consequence of these differences observed for (XV),

v) the Pt...C\(_2\) distance is very short, measuring 2.4\(\AA\).
<table>
<thead>
<tr>
<th>Intramolecular distances (Å)</th>
<th>(XVII)$^1$</th>
<th>(XVIII)$^1$</th>
<th>(XVIIIb)$^1$</th>
<th>(XIX)</th>
<th>(XX)</th>
<th>(XXI)</th>
<th>(XV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt - C$_1$</td>
<td>2.04(5)</td>
<td>2.06(3)</td>
<td>2.05(3)</td>
<td>2.137(6)</td>
<td>2.137(6)</td>
<td>2.158(14)</td>
<td>2.149(6)</td>
</tr>
<tr>
<td>Pt - C$_2$</td>
<td>2.69(4)</td>
<td>2.60(4)</td>
<td>2.62(3)</td>
<td>2.712(6)</td>
<td>2.694(6)</td>
<td>2.687(14)</td>
<td>2.420(6)</td>
</tr>
<tr>
<td>Pt - C$_3$</td>
<td>2.19(5)</td>
<td>2.11(5)</td>
<td>2.17(3)</td>
<td>2.139(6)</td>
<td>2.159(6)</td>
<td>2.200(14)</td>
<td>2.128(6)</td>
</tr>
<tr>
<td>C$_2$ - C$_3$</td>
<td>1.82(9)</td>
<td>1.48(5)</td>
<td>1.71(4)</td>
<td>1.584(9)</td>
<td>1.548(10)</td>
<td>1.509(19)</td>
<td>1.457(10)</td>
</tr>
<tr>
<td>C$_2$ - C$_1$</td>
<td>1.48(8)</td>
<td>1.59(7)</td>
<td>1.59(4)</td>
<td>1.545(9)</td>
<td>1.557(9)</td>
<td>1.556(19)</td>
<td>1.497(9)</td>
</tr>
<tr>
<td>C$_1$ - C$_3$</td>
<td>2.55(10)</td>
<td>2.39(7)</td>
<td>2.60(4)</td>
<td>2.404(9)</td>
<td>2.394(9)</td>
<td>2.403(20)</td>
<td>2.397(10)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angles (°)</th>
<th>(XVII)$^1$</th>
<th>(XVIII)$^1$</th>
<th>(XVIIIb)$^1$</th>
<th>(XIX)</th>
<th>(XX)</th>
<th>(XXI)</th>
<th>(XV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt - C$_1$ - C$_2$</td>
<td>99(4)</td>
<td>90(2)</td>
<td>91(2)</td>
<td>93.5(4)</td>
<td>92.3(4)</td>
<td>91.2(8)</td>
<td>81.1(4)</td>
</tr>
<tr>
<td>Pt - C$_3$ - C$_2$</td>
<td>84(3)</td>
<td>91(3)</td>
<td>84(2)</td>
<td>92.3(4)</td>
<td>91.7(4)</td>
<td>90.8(8)</td>
<td>82.6(4)</td>
</tr>
<tr>
<td>C$_1$ - C$_2$ - C$_3$</td>
<td>101(4)</td>
<td>102(3)</td>
<td>104(2)</td>
<td>100.4(5)</td>
<td>100.9(6)</td>
<td>103.2(11)</td>
<td>108.5(5)</td>
</tr>
<tr>
<td>C$_1$ - Pt - C$_3$</td>
<td>74(2)</td>
<td>70(2)</td>
<td>76(1)</td>
<td>68.4(2)</td>
<td>67.7(2)</td>
<td>66.9(5)</td>
<td>68.2(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dihedral Angles (°)</th>
<th>(XVII)$^1$</th>
<th>(XVIII)$^1$</th>
<th>(XVIIIb)$^1$</th>
<th>(XIX)</th>
<th>(XX)</th>
<th>(XXI)</th>
<th>(XV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_3$ - Pt - C$_1$</td>
<td>12(5)</td>
<td>28(3)</td>
<td>22(2)</td>
<td>24.4(4)</td>
<td>28.6(6)</td>
<td>29.7(13)</td>
<td>49.7</td>
</tr>
<tr>
<td>C$_1$ - C$_2$ - C$_3$</td>
<td>12(5)</td>
<td>28(3)</td>
<td>22(2)</td>
<td>24.4(4)</td>
<td>28.6(6)</td>
<td>29.7(13)</td>
<td>49.7</td>
</tr>
</tbody>
</table>

1. The data for these complexes are of limited accuracy because the crystals decomposed during data collection.
Comparing the shapes of the platinacyclobutane ring systems with those of cyclobutanes, it can be seen that the $C_1 \ldots C_3$ distance is greater in the platinacyclobutanes. In contrast to the platinacyclobutanone ring, cis-2,4-dibromo-2,4-di-t-butylcyclobutanone has four internal angles of approximately $90^\circ$, and a fold angle of only $10^\circ$.

The Pt $\ldots C_2$ distance of $2.4^\circ$ in (XV) is interesting. Interaction between these two atoms has been proposed previously, on the basis of theoretical considerations, and supported by $^{13}C$ n.m.r. data. A bonding model was proposed for (XVII) and (XVIII), for which the formulation was an intermediate between a cyclopropane complex and a trimethylene complex. Synergic interaction was envisaged, between available metal orbitals of the correct symmetry and the Walsh molecular orbitals of the cyclopropane moiety (Figure 3.10).

Figure 3.10

1. Electron donation to empty metal $\sigma$-orbital.
2. Back donation from metal $\pi$-orbital to empty cyclopropane orbital.
Relatively large $^{195}\text{Pt}-^{13}\text{C}_2$ coupling constants were recorded for complexes of type (XVII)$^6$, where $^2J_{\text{PtC}}=103-110\text{Hz}$. This was contrasted with $^2J_{\text{PtC}}=0-38\text{Hz}$ for ethylplatinum complexes, and suggested that there may be some bonding interaction between the platinum atom and the carbon atom ($\text{C}_2$). The even shorter $\text{Pt}...\text{C}_2$ distance in complex (XV) therefore suggests that $^{13}\text{C}$ n.m.r. studies of this complex might reveal a Pt-C$_2$ coupling constant of similar magnitude. The results of these studies are awaited.

The dihedral angle in complex (XV), between the planes defined by $\text{C}_1$-$\text{Pt}$-$\text{C}_3$ and $\text{C}_1$-$\text{C}_2$-$\text{C}_3$ is nearly $50^\circ$, and the substituents on $\text{C}_1$ and $\text{C}_3$ are therefore pseudo-axial and pseudo-equatorial. On one carbon atom, the hydrogen atom occupies an "axial" position, and on the other, it occupies an "equatorial" position. The room temperature $^1\text{H}$ n.m.r. spectrum showed these two protons to be equivalent, so the equilibrium shown in Figure 3.11 was proposed, whereby the two protons exchange "equatorial" and "axial" environments. Low temperature $^1\text{H}$ n.m.r. spectra were recorded (-26°C), to endeavour to "freeze out" the two environments by slowing down the

![Figure 3.11](image-url)
equilibrium, if indeed such an equilibrium exists. The fact that the low temperature and room temperature spectra were identical shows either that an even lower temperature is required to slow down the "axial" - "equatorial" exchange, or that the chemical shifts for the two environments are equal.

Complexes (XXII), (XXIII) and (XXIV) were isolated by

\[
\begin{align*}
\text{XXII} & : L = \text{PPh}_2\text{Me}, M = \text{Pt} \\
\text{XXIII} & : L = \text{PPhMe}_2, M = \text{Pt} \\
\text{XXIV} & : L = \text{PPh}_3, M = \text{Pd}
\end{align*}
\]

the reaction of ACADME with \([\text{Pt(PPh}_2\text{Me})_4]\), \([\text{Pt(PPhMe}_2\text{)}_4]\) and \([\text{Pd(PPh}_3\text{)}_4]\) respectively. The \(^1\text{H n.m.r.}\) spectra of these complexes were similar to that obtained for complex (XV) (see Table 3.2), and this, together with i.r. and microanalytical data, suggested the metallacyclobutanone formulation for (XXII), (XXIII) and (XXIV).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
M & L & CH\_3 & CH & \(3J_{\text{Pt-H}}\) (Hz) & \(2J_{\text{Pt-H}}\) (Hz) \\
\hline
Pt & PPh\_2 & 7.00(s) & 6.12(d) & 6 & 52 \\
Pt & PPh\_2 Me & 6.98(s) & 6.00(d) & 5.3 & 55.8 \\
Pt & PPhMe\_2 & 6.50(s) & 5.91(d) & 5.7 & 57.3 \\
Pd & PPh\_3 & 7.03(s) & 5.86(d) & 3.3 &  \text{data, suggested the metallacyclobutanone formulation for (XXII), (XXIII) and (XXIV).}
\end{tabular}
\caption{\(^1\text{H n.m.r.}\) data for complexes \([M\{\text{CH(CH=CHC(O)CH}_2\text{CH\_3)}\} L_2]\)}
\end{table}
None of the zerovalent $[ML_4]$ complexes react with ACADME in the absence of dioxygen. This observation, together with the isolation of the five-membered ring peroxo complex (XVI), and its subsequent conversion to the platinacyclobutanone complex (XV), suggests that all of these reactions might proceed via an intermediate peroxo ring complex analogous to (XVI).

Preliminary investigations into the reactivity of the platinacyclobutanone complex (XV) have shown that the two platinum-carbon bonds can be cleaved with concentrated hydrochloric acid, or with trifluoroethanoic acid, to give cis-$[\text{PtCl}_2(\text{PPh}_3)_2]$ and cis-$[\text{Pt(OOCF}_3)_2(\text{PPh}_3)_2]$, respectively. Treatment of complex (XV) with t-butyl isocyanide resulted only in the recovery of unchanged starting material. The complex (XV) was also recovered unchanged after treatment with N-sulphinylaniline.

An attempt to make the triphenylarsine analogue of complex (XV), by treating $[\text{Pt(AsPh}_3)_4]$ with ACADME was unsuccessful, as were attempts to displace triphenylphosphine from complex (XVI), with either methyldiphenylphosphine or 1,2-bis(diphenylphosphino)ethane.
3.3 Experimental

In this section, the melting points, microanalytical results, and infra-red and n.m.r. spectroscopic data are presented for all newly characterised compounds.

Microanalyses were carried out by D. Butterworth, The Butterworth Microanalytical Consultancy Ltd., 41 High Street, Teddington, Middlesex.

Melting points were recorded on a Reichart hot-stage apparatus, and are uncorrected.

Infra-red spectra were recorded as nujol mulls, using CsI plates, on a Perkin-Elmer 580 spectrophotometer, and were calibrated using a polystyrene film.

$^1$H n.m.r. spectra were recorded in CDCl$_3$ solution, on a Jeol JNM-PS-100 spectrometer, operating at 100MHz. Chemical shifts (δ) are reported relative to internal T.M.S.

$^{31}$P n.m.r. spectra were recorded in CDCl$_3$ solution on a Jeol JNM-FX60 spectrometer, operating at 24.15 MHz. Chemical shifts (p.p.m.) are reported relative to external phosphonium ion (PH$_4^+$). The spectra were completely $^1$H decoupled.

Reactions were performed at room temperature under an atmosphere of dry dinitrogen, using previously dried and degassed solvents, except where it is stated that the reaction had to be performed in the air.

Ligands and Reagents

The following materials were purchased:

- acetonedicarboxylic acid dimethyl ester  Koch Light Labs.Ltd.
- trifluoroethanoic acid  Aldrich Chemical Co.Ltd.
- methyldiphenylphosphine  Maybridge Chemical Co.Ltd.
- 1,2-bis(diphenylphosphino)ethane  Maybridge Chemical Co.Ltd.
- Potassium tetrachloroplatinite was obtained on loan from Johnson Matthey Ltd.
The following were prepared as described in the literature:

- tetrakis(triphenylphosphine)platinum(O)\textsuperscript{44}
- tetrakis(triphenylarsine)platinum(O)\textsuperscript{44}
- peroxobis(triphenylphosphine)platinum(II)\textsuperscript{45}
- trans-stilbenebis(triphenylphosphine)platinum(O)\textsuperscript{46}
- N-sulphinylaniline\textsuperscript{47}
- t-butylisocyanide\textsuperscript{48}
A. Reactions of acetonedicarboxylic acid dimethyl ester

i) With tetrakis(triphenylphosphine)platinum(O) in benzene solution

An excess of acetonedicarboxylic acid dimethyl ester (0.10g, 0.57mmol) was added to a yellow solution of [Pt(PPh₃)₄] (0.32g, 0.26mmol) in benzene, and stirred in an open flask for 24 hours. A white microcrystalline powder was filtered off, washed with diethyl ether, and identified as [Pt{CH(CO₂CH₃)C(=O)CH(CO₂CH₃)}(PPh₃)₂].

Yield = 0.14g, 60%

M.P. 212-3°C (decomp.)

Analysis. Calculated for C₄₃H₃₈O₃P₂Pt:

C, 57.90%; H, 4.29%; O, 8.96%

Found: C, 57.77%; H, 4.40%; O, 8.35%

Infra-red. 1710s, 1695s, 1676m, 1620s, 1584w, 1570w, 1316m, 1298m, sh, 1236m, 1191w, 1180w, 1161m, sh, 1148s, 1135s, 1106m, 1095m, 1090m, 1073m, 1037m, 1028m, 999w, 961w, 912w, 890w, 864w, 845w, 800w, 770w, 756m, 743m, 704s, sh, 696s, 685m, 602w, 541m, 526s, 510s, 495m, 461w, 423w, 385w, 360w.

¹H n.m.r. (-26°C to +20°C) 2.76(m, 30H); 6.12(d, 2H, J_H₂=6Hz; J_PtH=52Hz); 7.00(s, 6H).

³¹P n.m.r. -16.74(s, J_PtP=3066Hz).

ii) With trans-stilbenebis(triphenylphosphine)platinum(O)

An excess of acetonedicarboxylic acid dimethyl ester (0.20g, 1.15mmol) was added to a pale yellow solution of [Pt(trans-stilbene)(PPh₃)₂] (0.31g, 0.34mmol) in benzene, and stirred in an open flask for 4 days. The white
microcrystalline powder which was filtered off and washed with diethyl ether was identified as

\[ \text{[Pt\{CH(CO₂CH₃)C(CH₃)CH(CO₂CH₃)\}{PPh₃}₂]} \]

by its i.r. and \(^1\)H n.m.r. spectra. Yield = 0.16g, 52%.

iii) With peroxobis(triphenylphosphine)platinum(II)

An excess of acetonedicarboxylic acid dimethyl ester (0.20g, 1.15mmol) was added to \([\text{PtO₂}{(\text{PPh₃})₂}]\)(0.30g, 0.40mmol) suspended in diethyl ether, and the mixture was stirred in an open flask for 1 hour. The cream-coloured suspension had turned white, and these white microcrystals were filtered, washed with diethyl ether, and identified as

\[ \text{[Pt\{OOC(CH₂CO₂CH₃)₂\}{PPh₃}₂]} \]

Yield = 0.25g, 68%.

M.P. 158-9°C (decomp.)

Analysis. Calculated for C\(_{43}\)H\(_{40}\)O\(_7\)P\(_2\)Pt:

\[
\text{C, 55.78%; H, 4.35%; O, 12.10%}
\]

Found:

\[
\text{C, 55.12%; H, 4.40%; O, 11.91%}
\]

Infra-red. 1742s, 1725s,sh, 1696m, 1589w, 1573w, 1316m,sh, 1298s, 1223m, 1215m,sh, 1186m, 1170s, 1149m, 1114m, 1100s, 1074m, 1046w, 1030w, 1020w, 1000m, 979w, 938w, 850w, 776w,sh, 758m, 747s, 726w, 706s,sh, 699s, 621w, 574m, 553s, 530s, 523s, 518s, 504s, 468w, 452w, 424w, 361s, 320w.

\(^1\)H n.m.r. 2.80(m, 30H); 6.61(s, 6H); 6.66, 6.80, 6.93. 7.07

(AB pattern, \(^4\)H, \(J_{HH}=14\)Hz, \(\Delta v=23.1\)Hz).
iv) With tetakis(triphenylphosphine)platinum(0), suspended in diethyl ether.

An excess of acetonedicarboxylic acid dimethyl ester (0.20g, 1.15mmol) was added to a suspension of [Pt(PPh$_3$)$_4$] (0.50g, 0.40mmol) in diethyl ether, and stirred in an open flask for 24 hours. A sample of the white powder was filtered from the reaction, and shown to be a mixture of complexes (XV) and (XVI) by its i.r. and $^1$H n.m.r. spectra, with complex (XVI) as the major component.

The remainder of the mixture was left stirring for a total of 12 days, in diethyl ether. The suspended white powder was filtered and shown to be complex (XV), by its i.r. and $^1$H n.m.r. spectra. Final yield = 0.32g, 89%.

Alternatively, the mixture of complexes could be converted into pure complex (XV) by stirring the mixture in dichloromethane solution, for 4 days, in an open flask. Overall yield = 87%.

B. Attempted conversions of $\left[\text{Pt}\{\text{OOC(CH$_2$CO$_2$CH$_2$)$_2$O}\right\}_2\text{(PPh$_3$)$_2$}\}$ (XVI) into $\left[\text{Pt}\{\text{CH(CO$_2$CH$_2$)}\text{C(O)}\text{CH(CO$_2$CH$_2$)}\}_2\text{(PPh$_3$)$_2$}\}$ (XV).

1. In suspension

i) Complex (XVI) (0.10g, 0.11mmol) was stirred in diethyl ether with acetonedicarboxylic acid dimethyl ester (0.02g, 0.11mmol) in an open flask for 24 hours. The white powder was filtered and washed with diethyl ether, and identified as unchanged (XVI) by its i.r. spectrum and m.p.
ii) Complex (XVI) (0.10g, 0.11mmol) was stirred in diethyl ether with triphenylphosphine (0.01g, 0.04mmol) in an open flask for 24 hours. The white powder was filtered and washed with diethyl ether, and identified as unchanged (XVI) by its i.r. spectrum and m.p.

iii) Complex (XVI) (0.20g, 0.22mmol) was stirred in diethyl ether with acetonedicarboxylic acid dimethyl ester (0.03g, 0.17mmol) and triphenylphosphine (0.02g, 0.08mmol) in an open flask for 6 days. The white powder was filtered and washed with diethyl ether, and identified as pure (XV), by its i.r. and $^1H$ n.m.r. spectra, and its m.p.

2. In solution

i) Complex (XVI) (0.10g, 0.11mmol) was stirred in dichloromethane with triphenylphosphine (0.01g, 0.04mmol) in an open flask for 5 days. The white powder, which was recovered by slow evaporation of the solvent, was washed with diethyl ether, and identified as unchanged (XVI), by its i.r. spectrum and m.p.

ii) Complex (XVI), (0.10g, 0.11mmol) was stirred in dichloromethane in an open flask for 4 days. Evaporation of the solvent, and careful addition of diethyl ether produced a white powder which was identified as unchanged (XVI), by its i.r. spectrum and m.p.
Complex (XVI), (0.10g, 0.11mmol) was stirred in dichloromethane with triphenylphosphine (0.01g, 0.04mmol) and acetonedicarboxylic acid dimethyl ester (0.02g, 0.11mmol) in an open flask for 4 days. Evaporation of the solvent, followed by careful addition of diethyl ether produced a white powder which, after thorough washing with diethyl ether, was shown to be pure (XV), by its i.r. and $^1$H n.m.r. spectra, and its m.p.

**C. Reactions of $\left[\text{Pt}\left(\text{CH}(\text{CO}_2\text{CH}_3)\text{C(=O)}\text{CH}(\text{CO}_2\text{CH}_3)\right)\right]_2(P\text{Ph}_3)$ (XV)**

1) **With concentrated hydrochloric acid**

An excess of concentrated hydrochloric acid (36% w/w, 0.1 cm$^3$) was added to $\left[\text{Pt}\left(\text{CH}(\text{CO}_2\text{CH}_3)\text{C(=O)}\text{CH}(\text{CO}_2\text{CH}_3)\right)\right]_2(P\text{Ph}_3)$ (0.25g, 0.28mmol) in dichloromethane solution, and stirred for 3 days. Evaporation of the solvent gave a white powder which was collected and washed quickly with chloroform. The powder was identified as cis-$\left[\text{PtCl}_2(P\text{Ph}_3)_2\right]$ by its i.r. spectrum ($\nu$(Pt-Cl)=319, 293 cm$^{-1}$; (Lit. 316, 297 cm$^{-1}$) and its m.p. [310°C; (Lit. = 310-312°C)]

Yield = 0.19g, 86%.

2) **With trifluoroethanoic acid**

Trifluoroethanoic acid (0.026g, 0.228mmol) was added to $\left[\text{Pt}\left(\text{CH}(\text{CO}_2\text{CH}_3)\text{C(=O)}\text{CH}(\text{CO}_2\text{CH}_3)\right)\right]_2(P\text{Ph}_3)$ (0.20g, 0.22mmol) in dichloromethane solution, and stirred for 3 hours. A white solid was isolated by slow evaporation of the solvent, and recrystallised from dichloromethane/40-60 petrol. The white crystals were identified as cis-$\left[\text{Pt}(\text{OCOCF}_3)_2(P\text{Ph}_3)_2\right]$, by their
i.r. spectrum $[\nu(\text{CO})=1727, \, 1700 \, \text{cm}^{-1}; \, (\text{Lit.} \, 1727, \, 1700, \, 1400 \, \text{cm}^{-1})^{50}]$ and their m.p. $[223^\circ\text{C}; \, (\text{Lit.} \, 220-250^\circ\text{C})^{50}]$.

Yield = 0.18 g, 87%.

### iii) With t-butylisocyanide

T-Butylisocyanide (0.037 g, 0.44 mmol) was added to $[\text{Pt}\left\{\text{CH(}\text{CO}_2\text{CH}_3\right)\text{C(:}0\text{)CH(}\text{CO}_2\text{CH}_3\}\right\} \text{(PPh}_3\text{)}^2]$ (0.20 g, 0.22 mmol) in diethyl ether, and stirred for 3 days. The white powder which was filtered was identified as unreacted (XV) by its i.r. spectrum.

### iv) With N-sulphinylaniline

A slight excess of freshly prepared N-sulphinylaniline (0.04 g, 0.28 mmol) was added to $[\text{Pt}\left\{\text{CH(}\text{CO}_2\text{CH}_3\right)\text{C(:}0\text{)CH(}\text{CO}_2\text{CH}_3\}\right\} \text{(PPh}_3\text{)}^2]$ (0.20 g, 0.22 mmol) in diethyl ether and stirred for 8 hours. There was no apparent change, and the powder which was filtered was identified as unreacted (XV), by its i.r. spectrum.

### D. An attempt to prepare $[\text{Pt}\left\{\text{CH(}\text{CO}_2\text{CH}_3\right)\text{C(:}0\text{)CH(}\text{CO}_2\text{CH}_3\}\right\} \text{(AsPh}_3\text{)}^2]$  

An excess of acetonedicarboxylic acid dimethyl ester (0.08 g, 0.46 mmol) was added to a suspension of $[\text{Pt(AsPh}_3\text{)}^4]$ (0.32 g, 0.23 mmol) in diethyl ether, and stirred in an open flask overnight. The cream powder was filtered and washed with diethyl ether and identified as unreacted $[\text{Pt(AsPh}_3\text{)}^4]$ by its i.r. spectrum.
Attempts to displace PPh₃ from \( \text{[Pt\{OOC(CH₂CO₂CH₃)₂\} (PPh₃)₂]} \) (XVI)

i) With 1,2-bis(diphenylphosphino)ethane

1,2-Bis(diphenylphosphino)ethane (0.043g, 0.16mmol) was added to \( \text{[Pt\{OOC(CH₂CO₂CH₃)₂\} (PPh₃)₂]} \) (0.10g, 0.11mmol) in diethyl ether and stirred for 3 days in an open flask. The white powder was filtered and identified as unreacted starting material, by its i.r. spectrum.

ii) With methyldiphenylphosphine

Methyldiphenylphosphine (0.043g, 0.22mmol) was added to \( \text{[Pt\{OOC(CH₂CO₂CH₃)₂\} (PPh₃)₂]} \) (0.10g, 0.11mmol) in diethyl ether and stirred for 4 hours. The white powder which was filtered was identified as unreacted starting material, by its i.r. spectrum.


1.40 D. R. Russell, Personal communication.


1.77 M.E. Howden, Personal Communication.

REFERENCES FOR CHAPTER TWO


REFERENCES

FOR

CHAPTER THREE


