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

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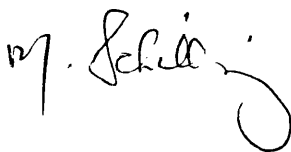
STATEMENT

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

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CONTENTS

CHAPTER 3 THE PREPARATION OF SOME NOVEL METALLACYCLOBUTANONE

COMPLEXES

SUMMARY

In chapter one, the series of complexes of the type

[Rh(dpm)(alkene)(C_4F_6)] is extended by alkene displacement

reactions of [Rh(dpm)(C_2H_4)(C_4F_6)]. The reaction of some of

these alkene-alkyne complexes with cyclopropane, propene and

tetramethylallene, to give 1,4-diene complexes of rhodium is

described, together with the X-ray crystal structure of the

tetramethylallene derivative. Complexes of the type

[Rh(acac)(L)$_2$(C_4F_6)] (L=PPh_3, PPh_2Me, $AsPh_3$, $SbPh_3$) and

[Rh(dpm)(L)(C_4F_6)] (L=PPh_3, $P(C_6H_{11})_3$, $AsPh_3$) are characterised,

and rhodacyclopentene complexes [Rh$\{\overline{CH_2CH_2C(CF_3)=\overset{\frown}{C}(CF_3)}\}$(dpm)(L)$_2$]

are isolated from the reaction of pyridine derivatives

(L=C_5H_5N, 3-MeC_5H_4N,3,5-Me$_2C_5H_3N$) with [Rh(dpm)(C_2H_4)(C_4F_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(O)-alkyne

complexes. This is followed by a description of the

characterisation of some platinacyclic complexes which are

isolated from the reactions of hexafluoropropanone with

alkynediolbis(triphenylphosphine)platinum(O) 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 [Pt(H_2C(OH)C≡CCH$_2$OH)(PPh_3)$_2$],

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 ML_4 (M=Pt, L=PPh$_3$, PPh$_2$Me, PPhMe$_2$; M=Pd, L=PPh$_3$).

ABBREVIATIONS

General

Å	Angström unit
ac	alkyne
acac	anion of acetylacetone
ACADME	acetonedicarboxylic acid dimethyl ester
apemino	anion of 4-aminopent-3-ene-2-imine
cod	cis-cis-cyclo-octa-1,5-diene
cp	anion of cyclopentadiene
diphos	1,2-bis(diphenylphosphino)ethane
dpm	anion of dipivaloylmethane(2,2,6,6-tetramethyl-3,5-heptanedione)
Et	ethyl
hfacac	anion of hexafluoroacetylacetone
HFP	hexafluoropropanone
Me	methyl
Ph	phenyl
py	pyridine
^{t}Bu	tertiary butyl
thf	tetrahydrofuran
TMA	tetramethylallene

Experimental data

br	broad
d	doublet
eV	electron volt
i.r.	infra-red
m	multiplet (n.m.r.); medium (i.r.)
M^+	molecular ion
MHz	mega-hertz

mmol	millimole
M.P.	melting point
n.m.r.	nuclear magnetic resonance
p.p.m.	parts per million
q	quartet
quin	quintet
s	singlet (n.m.r.); strong (i.r.)
sh	shoulder
t	triplet
T.M.S.	tetramethylsilane
w	weak

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 $[Rh(\beta$-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-β -ketoenolate ring. In complexes (I)

cyclocotrimerisation 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

CH$_2$ CH$_2$
‖   ‖
CH$_2$ CH$_2$
   \   /
    Rh
   /   \
  X   Y
  ‖   ‖
  C   C
 /   \
R   C   R'
     ‖
     H

H$_2$ H$_2$
C   C
CH   /   \   CH
 ‖   C   C   ‖
CH H$_2$ H$_2$ CH
   \   /
      Rh
     /   \
    X   Y
    ‖   ‖
    C   C
   /   \
  R   C   R'
       ‖
       H

X=Y=NH; R=R'=CH$_3$

X=Y=O; R=CH$_3$, R'=NHPh

X=O, Y=NH;
R=R'=CH$_3$

X=Y=O;R=R'=CH$_3$

X=Y=O;R=R'=C(CH$_3$)$_3$

X=Y=O; R=R'=CH$_3$

X=Y=O; R=R'=C(CH$_3$)$_3$

X=Y=O; R=CH$_3$, R'=NHPh

X=Y=O; R=R'=Ph

X=NH, Y=O; R=R'=CH$_3$

X=Y=NH; R=R'=CH$_3$

+C$_4$F$_6$ +C$_4$F$_6$ +C$_4$F$_6$

H H
H   H
F$_3$C   CF$_3$
F$_3$C   CF$_3$
      Rh
    X C(CF$_3$) Y
    ‖   C(CF$_3$)   ‖
    C   C
   R   C   R'
          ‖
          H

F$_3$C   CF$_3$
F$_3$C   CF$_3$
F$_3$C   CF$_3$
      Rh
    X C(CF$_3$) Y
    ‖   C(CF$_3$)   ‖
    C   C
   R   C   R'
          ‖
          H

(I)   Figure 1.1   (II)
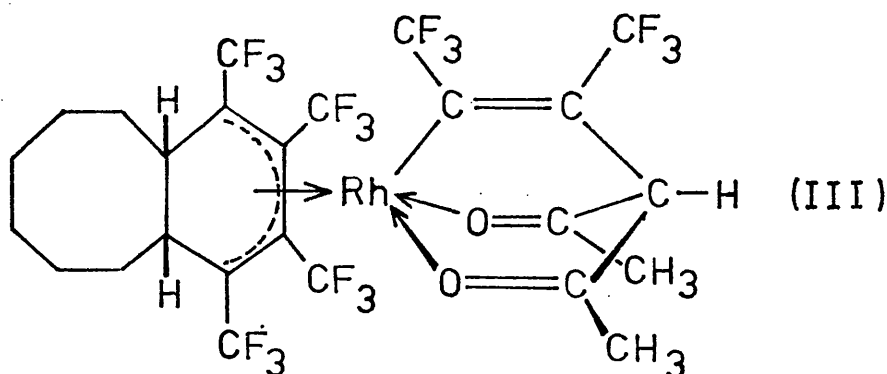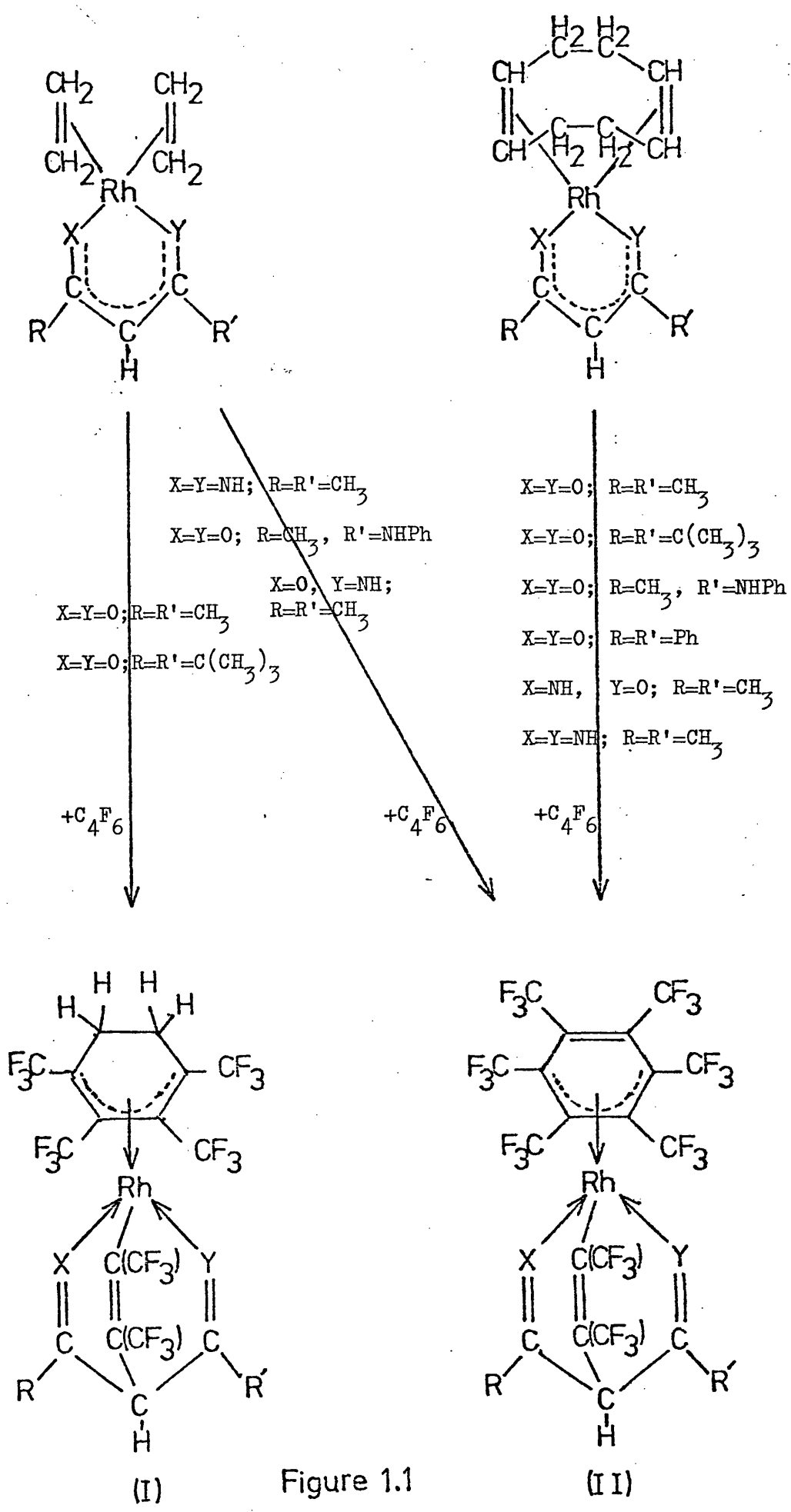
$[Rh(acac)(\underline{cis}-C_8H_{14})_2]$ at room temperature to give complex (III).[4] One molecule of cyclo-octene has been incorporated in the bicyclo [6.4.0] dodeca-9,11-diene ring.

The metal catalysed cyclocotrimerisation 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.[5-14] The intermediacy of metallacyclopentadienes has been shown,[5,8,10,11] as exemplified in Figure 1.2 for cobalt[8], and in Figure 1.3 for palladium[10].

A metallacyclopentene intermediate has been shown for cobalt[9] (Figure 1.4).
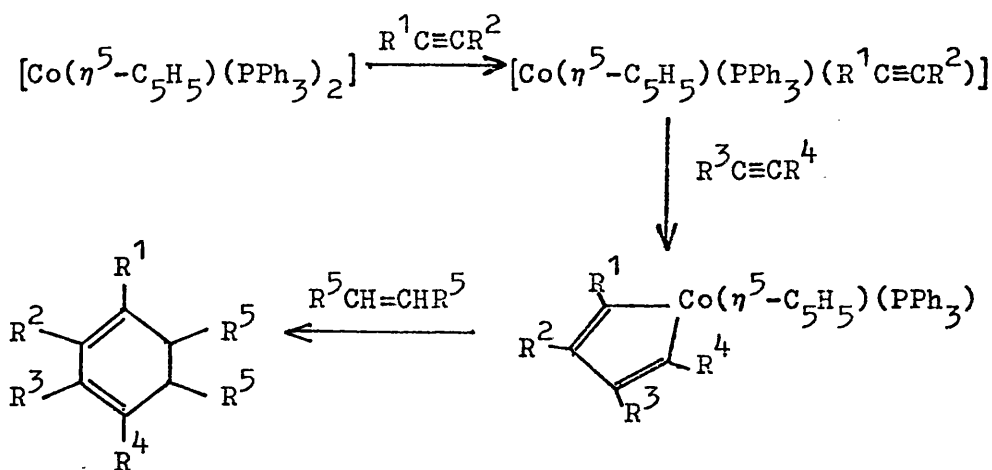
Figure 1.2   [R=H, Ph, CO_2Me.]
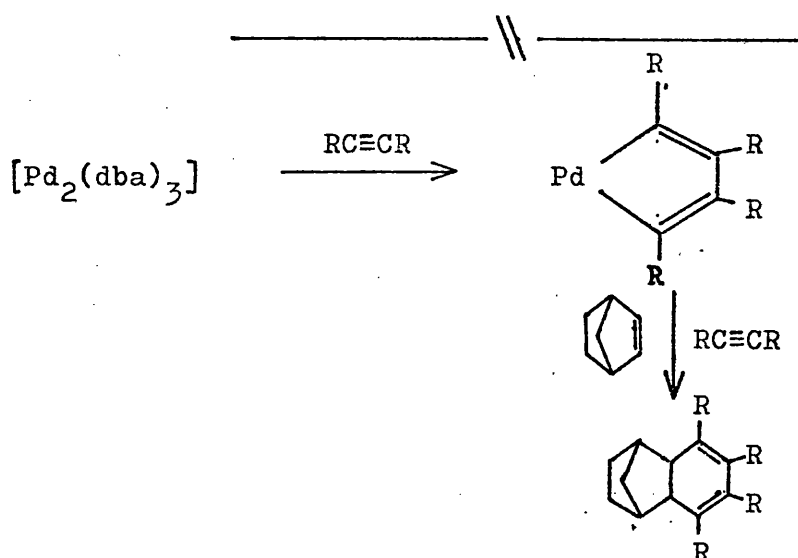
Figure 1.3   [dba = dibenzylidene acetone;   R = CO_2Me.]

$$[Co(\eta^5\text{-}C_5H_5)(PPh_3)(RC{\equiv}CR')] \xrightarrow{RCH=CHR}$$

$$\xrightarrow{R'C{\equiv}CR'}$$
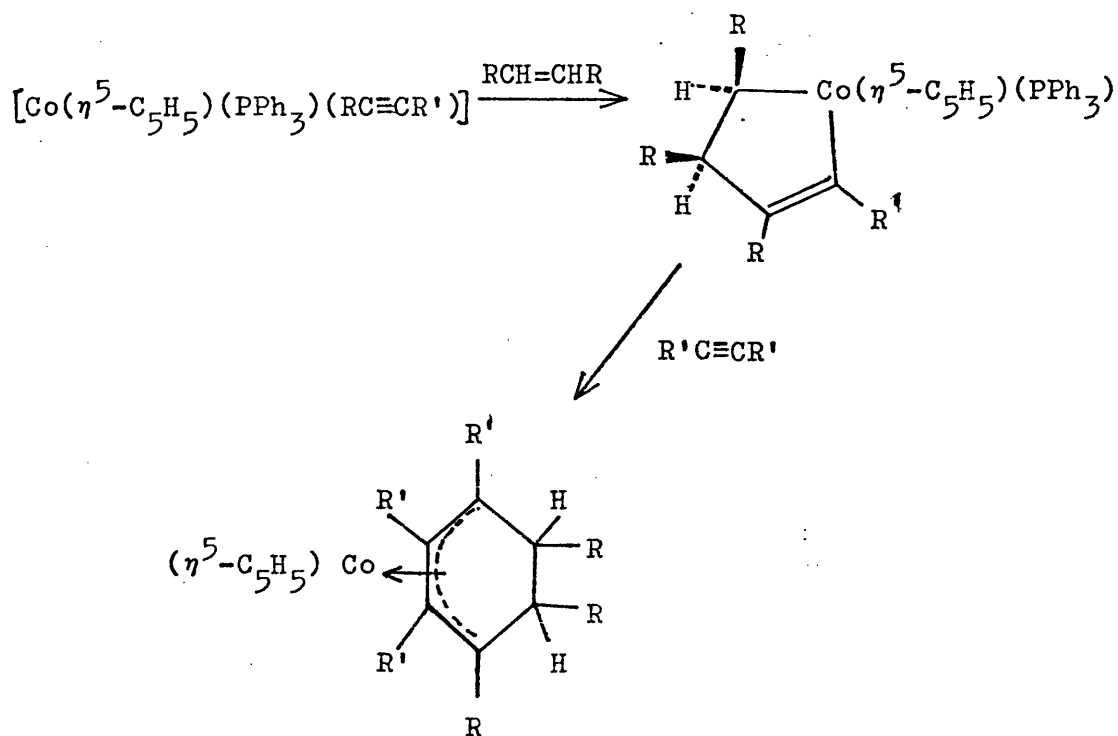
Figure 1.4 [$R=CO_2Me$; $R'=Ph$.]

Recently, mono-alkene-alkyne complexes of rhodium(I) were isolated[13], and shown to be intermediates in the formation of the cyclohexadiene systems (I) and (III), (Figure 1.5):

$$[Rh(dpm)(C_2H_4)_2] \xrightarrow[-78°C]{C_4F_6} [Rh(dpm)(C_2H_4)(C_4F_6)]$$

$$C_4F_6 \quad \Big| \quad \text{Room temperature}$$

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

a) $R_2C:CR_2 = C_2H_4$; $R'=CH_3$
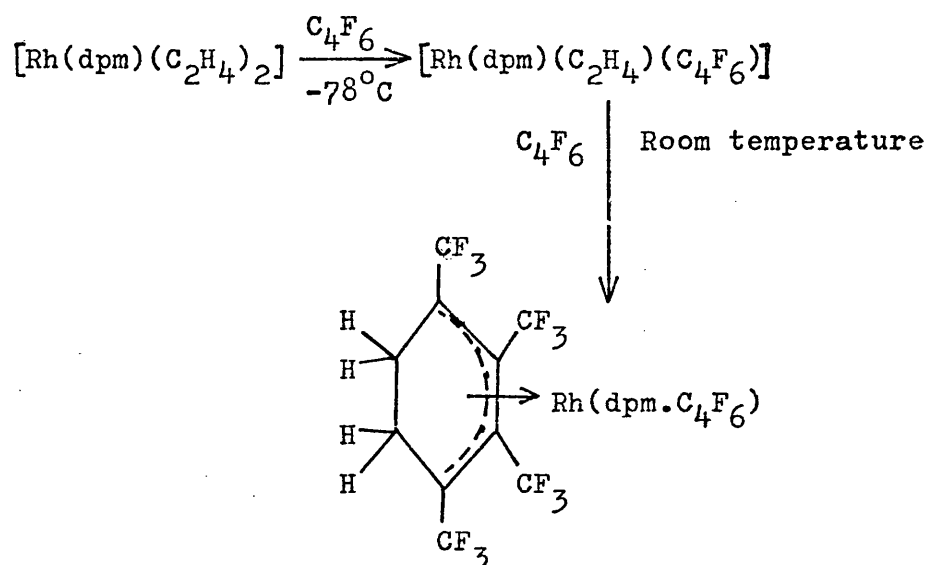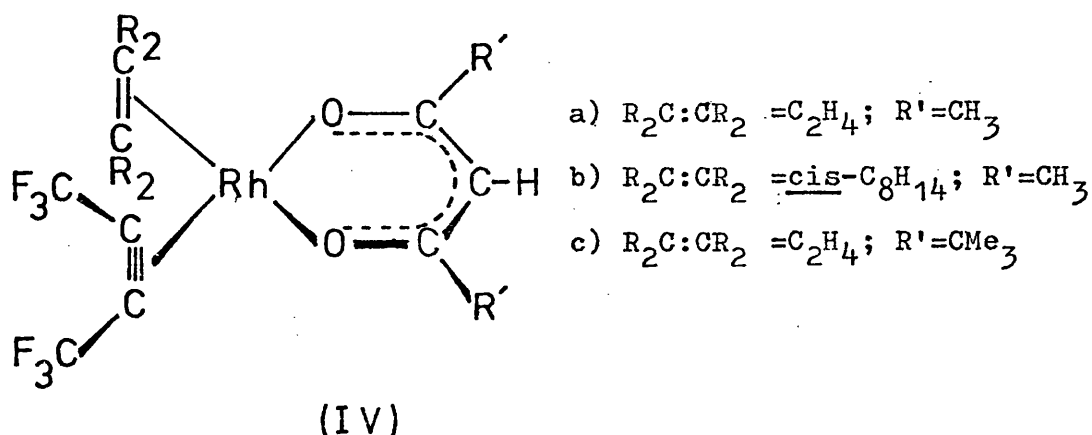
b) $R_2C:CR_2 = cis-C_8H_{14}$; $R'=CH_3$

c) $R_2C:CR_2 = C_2H_4$; $R'=CMe_3$

(IV)

$[Rh(\beta\text{-ketoenolate})(\text{alkene})_2].$[13] The crystal structures of the complexes (IVa) and (IVb) showed[13] 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 $[Rh(acac)(C_2H_4)_2]$[14] and $[Rh(acac)(C_2H_4)-(C_2F_4)]$[14], and later of $[Rh(cp)(C_2H_4)(C_2F_4)]$[15], that the π-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[16,17] which had indicated that there is more π-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 $[Rh(L)(alkene)_2]$ and $[Rh(L)(alkene)(alkyne)]$.

	$Rh-C_1$ [a.]	$Rh-C_2$	$Rh-C_3$	$Rh-C_4$	Reference
$[Rh(acac)(C_2H_4)_2]$	2.13(2)	2.14(2)	2.13(2)	2.14(2)	14
$[Rh(acac)(C_2H_4)(C_2F_4)]$	2.19(1)	2.19(1)	2.00(1)	2.02(1)	14
$[Rh(cp)(C_2H_4)(C_2F_4)]$	2.165(6)	2.169(5)	2.022(5)	2.026(5)	15
$[Rh(acac)(C_2H_4)(C_4F_6)]$	2.142(14)	2.171(17)	2.016(10)	2.042(11)	13
$[Rh(acac)(C_8H_{14})(C_4F_6)]$	2.163(13)	2.196(11)	2.034(10)	2.059(10)	13

(a. C_1 and C_2 for C_2H_4 or C_8H_{14}; C_3 and C_4 for C_2F_4 or C_4F_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 $[Rh(dpm)(C_2H_4)_2]$, 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 cis-cyclo-octene, cycloheptene, propene, cis-but-2-ene and trans-but-2-ene all displaced ethene from complex (IVc), to give complexes (IVd-h) respectively.

$$R_2C:CR_2 = \text{cis-}C_8H_{14} \quad (d)$$
$$C_7H_{12} \quad (e)$$
$$C_3H_6 \quad (f)$$
$$\text{cis-}C_4H_8 \quad (g)$$
$$\text{trans-}C_4H_8 \quad (h)$$

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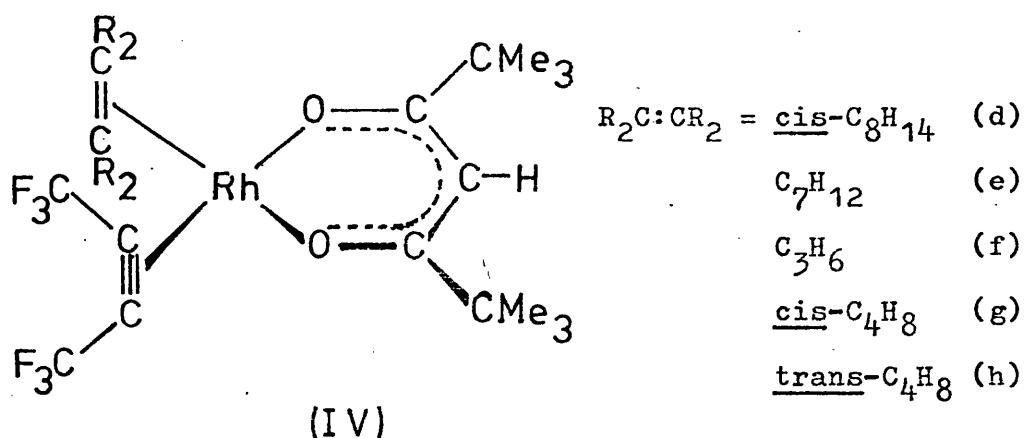
No reaction was observed with the alkenes cyclohexene, bicyclo [2.2.1]hept-2-ene and 2,3-dimethylbut-2-ene.

Complexes (IVd-h) have infra-red spectra which are very similar to that for (IVc); the band for the $C\equiv C$ 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 $(CD_3)_2CO$ or CD_2Cl_2,[10] 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 $[Rh(dpm)(alkene)(C_4F_6)]$.

The ^{1}H n.m.r. spectrum of (IVc), $[Rh(dpm)(C_2H_4)(C_4F_6)]$, was re-run in $CDCl_3$, and showed separate signals for the t-butyl groups, at 8.84 and 8.89τ [lit.value = $8.86\tau(s)$[4]]. The ethene protons were seen as a doublet, with coupling to the rhodium, $(6.33\tau, J_{RhH}=2Hz)$[4] at room temperature. On cooling to $-50°C$, the signal was found to split into two doublets, centred at 5.80 and 7.06τ.

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.
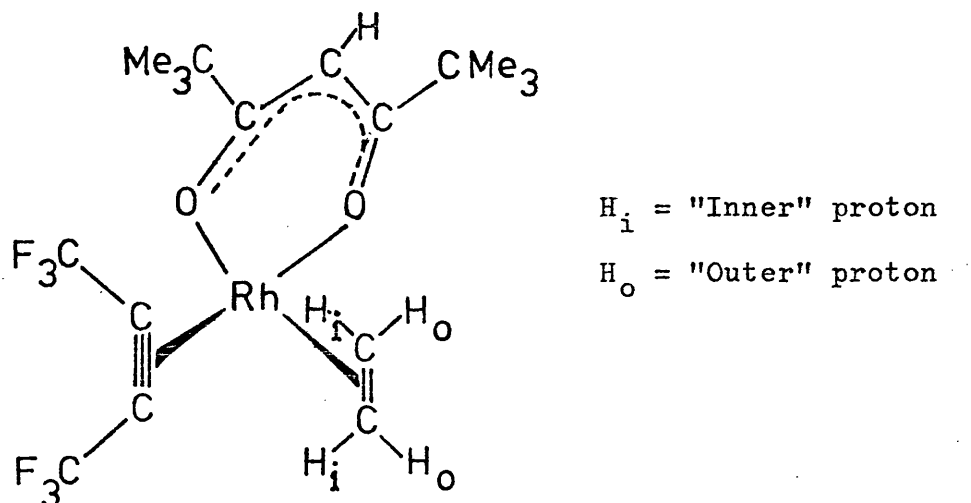

H_i = "Inner" proton

H_o = "Outer" proton

Figure 1.6

Table 1.2

N.m.r. data for some mono-alkene alkyne complexes of rhodium(I)

Complex	^{19}F n.m.r.[a]		^1H n.m.r.[b]			
			dpm		alkene	
	C_4F_6	J_{RhF}(Hz)	CMe_3	-CH	=CH	=CCH₃
$[Rh(dpm)(C_2H_4)(C_4F_6)]$ i) R.T.	55.02	2	8.84(s) 8.89(s)	4.12(s)	6.33(d)	-
ii) -50°C	Not recorded		8.84(s) 8.89(s)	4.12(s)	5.80(d) 7.06(d)	-
$[Rh(dpm)(C_3H_6)(C_4F_6)]$	52.68	-	8.84(s) 8.92(s)	4.17(s)	6.03-6.88(m)	8.27(d)
$[Rh(dpm)(\underline{cis}-C_4H_8)(C_4F_6)]$	52.91	1.6	8.85(s) 8.94(s)	4.20(s)	6.58(m)	8.27(d)
$[Rh(dpm)(\underline{trans}-C_4H_8)(C_4F_6)]$	53.72	-	8.85(s) 8.94(s)	4.22(s)	6.58(m)	7.83(s)
$[Rh(dpm)(C_8H_{14})(C_4F_6)]$	52.66	2	8.83(s) 8.95(s)	4.20(s)	6.64(quin x d)	$-(CH_2)_n-$ 7.67(m) 8.22-8.76(br)
$[Rh(dpm)(C_7H_{12})(C_4F_6)]$	53.33	2	8.82(s) 8.98(s)	4.19(s)	6.36(quin x d)	7.63(m) 7.92-8.68(br)

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)[17-24], five-co-ordinate cyanoalkene complexes of rhodium(I)[25-28], mono-alkene complexes of platinum(II)[29-32] and various alkene complexes of iridium(I)[33-35] have been studied, using variable-temperature ^{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

A   B

Figure 1.7

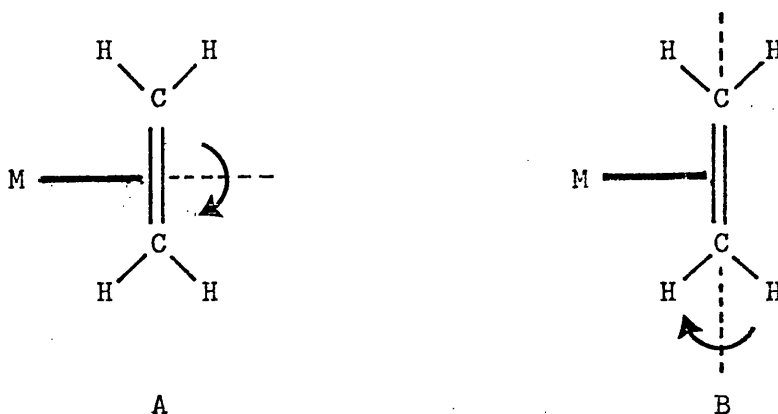these cases, because mechanism B would result in the breaking of both the σ- and π-components of the metal-alkene bond (using the bonding scheme proposed by Dewar[36], and Chatt and Duncanson[37]), causing dissociation of the alkene. Mechanism A always leaves the σ-bond intact, and only the d-π^*-orbital overlap is ruptured, so the "propellor-like" rotation seems more probable.

Direct evidence for this type of rotation has been

shown, using the complex $[Os(CO)(NO)(PPh_3)_2(C_2H_4)][PF_6]$[38],

where each end of the co-ordinated ethene molecule is in

a different chemical environment, by a study of its variable-

temperature ^{13}C n.m.r. spectrum.

The coalescence temperature for complex (IVc) was

found to be $-30°C$, 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:

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

Table 1.3 compares the free energies of activation for

a number of bis-alkene complexes of rhodium(I).

The ^{1}H n.m.r. spectra for complexes (IVf) and (IVg) are

temperature invariant, with a signal for the methyl protons

on the alkenes at 8.27τ (doublet) in both cases. The

spectrum for the propene complexes (IVf) is very similar to

that described for the bis-propene complex $[(Rh(acac)(C_3H_6)_2]$[16],

Table 1.3

Rotational energy barriers for bis-alkene complexes of rhodium(I)

Complex	T_c Coalescence temperature	ΔG Free Energy of Activation (kcal.mol^{-1})	E_a Activation Energy (kcal.mol^{-1})	Reference
$[Rh(dpm)(C_2H_4)(C_4F_6)]$	-30°C	11.4	-	This work
$[Rh(C_5H_5)(C_2H_4)(C_2F_4)]$	-10°C	-	13.6	17
$[Rh(C_5H_4CN)(C_2H_4)_2]$	22°C	14.1	-	21
$[Rh(C_5H_4CO_2Me)(C_2H_4)_2]$	22°C	14.1	-	21
$[Rh(C_5Me_5)(C_2H_4)_2]$	>60°C	>16.9	-	21
$[Rh(C_5H_5)(C_2H_4)_2]$	55°C	15.7	15.0	21
$[Rh(acac)(C_2H_4)_2]$	-23°C	12.26	11.02	24
$[Rh(C_5H_5)(C_2H_3F)_2]$	68°C	16-17	-	22

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.[40] The methyl groups are, as predicted by steric arguments, directed away from the co-ordinated alkyne, as shown in Figure 1.8.
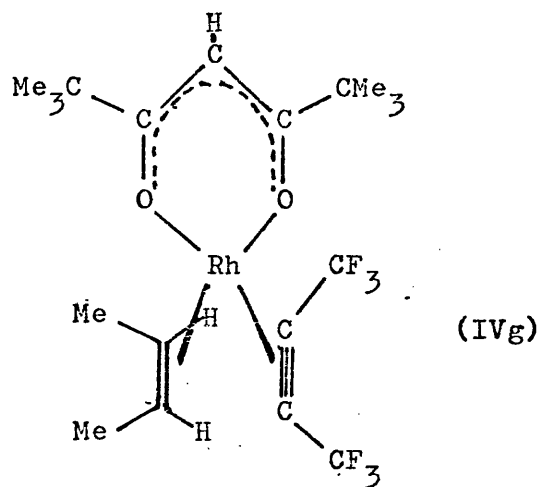

(IVg)

Figure 1.8

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 ^{1}H 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 $CDCl_3$ 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 $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (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,[41-47] and metal hydride,[45,47] ionic[41,42] or dipolar[46] 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 $-C(CF_3)=C(H)CF_3$ group.

It was also possible to prepare the cyclo-octene complex (IVd) by the low temperature (-78°C) reaction of hexafluorobut-2-yne with $[Rh(dpm)(C_8H_{14})_2]$. Cyclocotrimerisation occurred between one molecule of the cyclic alkene and two molecules of hexafluorobut-2-yne in the room temperature reactions of C_4F_6 with complexes (IVd) and (IVe), to give complexes (V) and (VI) respectively. These complexes were shown to be analogous to complex (III)[4]
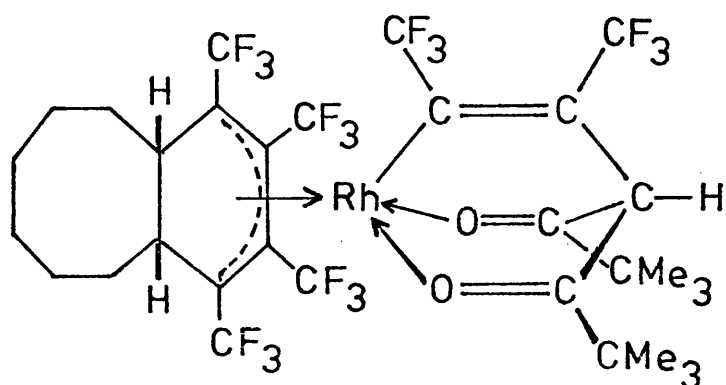
(V)

by their [19]F n.m.r. spectra. The cyclocotrimerised diene

ligands are distinguished from the rigid hexakis(trifluoromethyl)-

benzene ligand by having two,[2,4] instead of three [2,4,48]
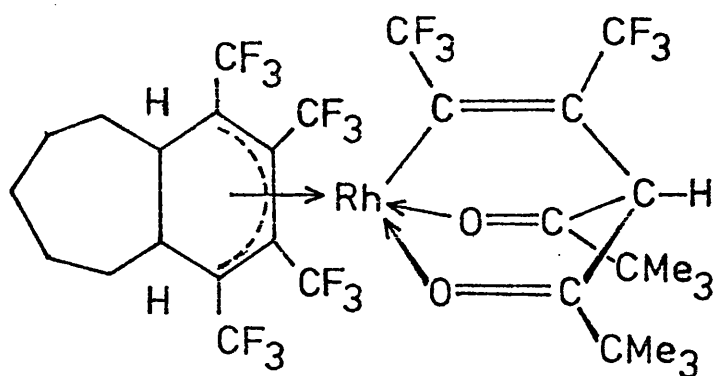
(VI)

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

[Rh(dpm)(C$_2$H$_4$)(C$_2$F$_4$)] at -78°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]

Complex	$RhC(CF_3)^1_3 = C(CF_3)^2_3$		$\{C_6(CF_3)_6\}$	$\{(C_8H_{14})(C_4F_6)_2\}$ or $\{(C_7H_{12})(C_4F_6)_2\}$	Reference
	$(CF_3)^1_3$	$(CF_3)^{2f}_3$			
$[Rh(cp)\{C_6(CF_3)_6\}]$[b]	-	-	54.0, 57.1, 61.1	-	48
$[Rh(apemino.C_4F_6)\{C_6(CF_3)_6\}]$[c]	55.1	64.23(15.6)	54.56, 57.25, 61.62	-	4
$[Rh(acac.C_4F_6)\{C_6(CF_3)_6\}]$[d]	55.7	64.2 (16)	55.7, 57.5, 61.8	-	2
$[Rh(dpm.C_4F_6)\{C_6(CF_3)_6\}]$[d]	55.86	59.17(15.8)	55.86, 57.54, 61.97	-	2
$[Rh(acac.C_4F_6)\{C_8H_{14}(C_4F_6)_2\}]$[c] (III)	56.09	64.67(15.5)	-	58.68, 59.14	4
$[Rh(dpm.C_4F_6)\{C_8H_{14}(C_4F_6)_2\}]$[e] (V)	52.70	56.19(15.9)	-	54.44, 54.92	This work
$[Rh(dpm.C_4F_6)\{C_7H_{12}(C_4F_6)_2\}]$[e] (VI)	53.61	57.54(15.2)	-	56.07[g]	This work

a) Chemical shifts (p.p.m.) are relative to $CFCl_3$.

b) Measured in tetrahydrofuran solution, at 56.4 MHz.

c) Measured in $(CD_3)_2CO$ solution, at 94.1 MHz.

d) Measured in $(CH_3)_2CO$ 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

$[Rh(dpm)(C_2H_4)(C_2F_4)]$ with displacement of the C_4F_6.

The reaction of cis-cis-cyclo-octa-1,5-diene with

complex (IVc), at room temperature, also caused the

C_4F_6 ligand to be displaced, along with C_2H_4, to give

the known complex $[Rh(dpm)(cod)]$.

The co-ordinated hexafluorobut-2-yne was reported

to be displaced from the cyclo-octene complex (IVb),

by cyclo-octene, at room temperature, to give

$[Rh(acac)(C_8H_{14})_2]$.[4] However, it seems likely that

this was unreacted starting material from the reaction:

$$[Rh(acac)(C_8H_{14})_2] \xrightarrow[C_4F_6]{-78^\circ C} [Rh(acac)(C_8H_{14})(C_4F_6)] + C_8H_{14}$$
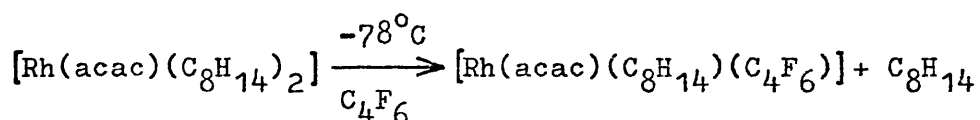
rather than the product of the reverse reaction, because

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 $[Rh(acac)(C_8H_{14})(C_4F_6)]$ (IVb) was then

treated with an excess of C_8H_{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 $[Rh(dpm)(C_2H_4)(C_4F_6)]$

(IVc) at $60^\circ C$ 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-η-penta-1,4-diene structure, on the basis of its

^{1}H and ^{19}F n.m.r. spectra. Microanalytical results and

(VII)
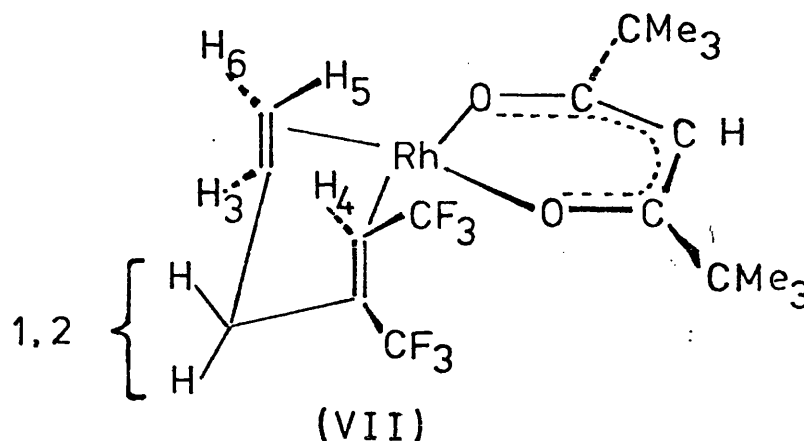
the mass spectrum for complex (VII) indicate that one

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 ^{1}H n.m.r. spectrum of complex (VII) is

temperature invariant, and the six distinct environments

for the six protons of the $CH_2=CHCH_2C(CF_3)=C(H)CF_3$

ligand which appear in the spectrum are reproduced in

Figure 1.9.

The proton resonance at 7.49τ appears as a quartet,

due to geminal coupling to three equivalent fluorines

(J_{HF}=11.0Hz) 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.[18,49] The doublet resonance centred at

6.97τ is assigned to the other "inner" alkenic proton, H$_5$,

A section of the ^{1}H n.m.r. spectrum of complex (VII)
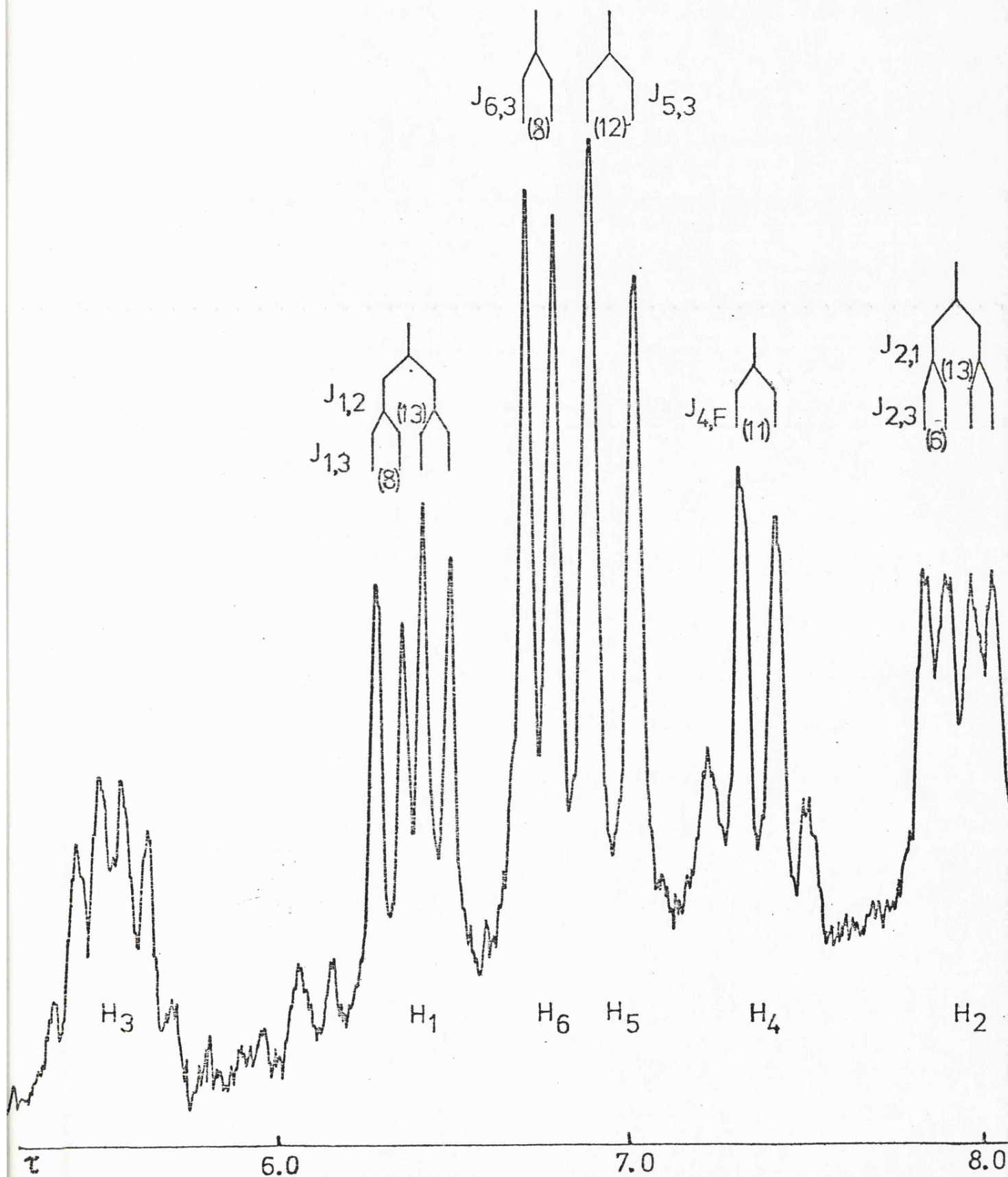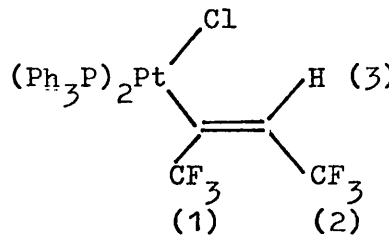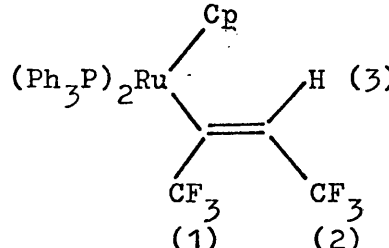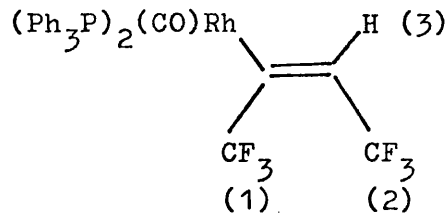
(Coupling constants (Hz) in parentheses)
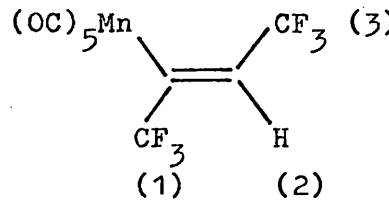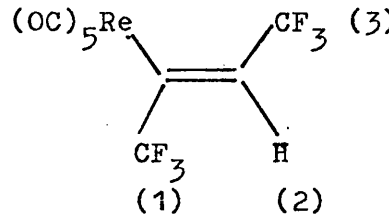
Figure 1.9

and appears as a doublet due to <u>trans</u> coupling to

H_3 (J_{HH}=12Hz). The "outer" proton, H_6, appears at lower

field (6.75τ), as is generally observed[18,49] and shows

<u>cis</u> 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 5.50τ 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 6.38τ and 7.96τ

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)I(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 <u>cis</u> 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 <u>cis</u>[50-52] or <u>trans</u>[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

Complex	J_{12}(Hz)	J_{13}(Hz)	J_{23}(Hz)	Ref.
	12.2 (F,F)	0 (H,F)	9.6 (H,F)	50
	14.4 (F,F)	0 (H,F)	11.0 (H,F)	51
	11.2 (F,F)	2.5 (H,F)	10.7 (H,F)	52
	2.3 (H,F)	2.3 (F,F)	9.6 (H,F)	53
	2.5 (H,F)	2.5 (F,F)	9.1 (H,F)	54

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.
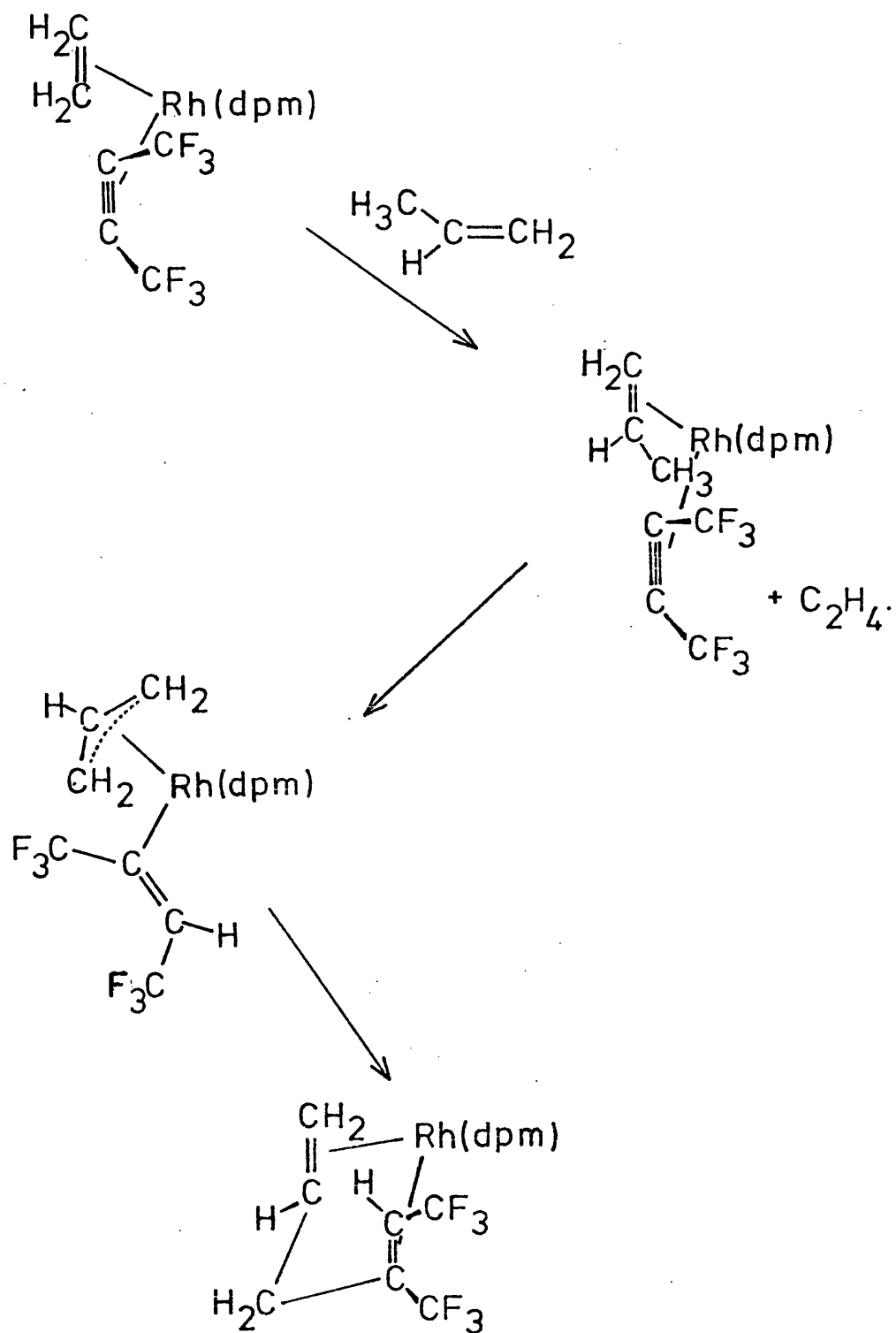
Figure 1.10

Some evidence for the formation of the η^3-allyl

intermediate is given by the preparation of allyl complexes

from the reaction of propene with $[IrH_5(PPh_3)_2]$ [55] and with

$[Ru(PPh_3)_4(\pi\text{-MeCN})].MeCN$, [56] and by the observation of the

temperature dependent equilibrium:[57]
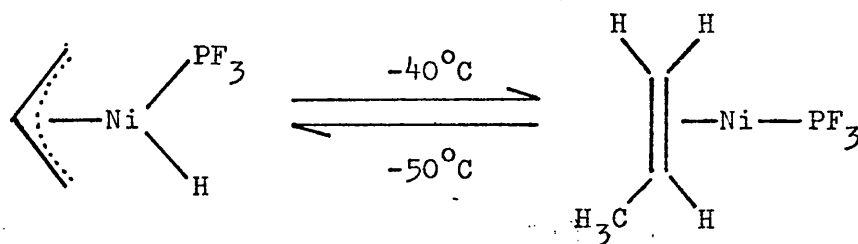
Allyl complexes of rhodium(III) have been prepared from

divinylcyclopropane derivatives[58,59]. Bis-allyl complexes

of rhodium(III) have been shown to give η^4-hexa-1,5-diene

$$[Rh^{III}(\eta^3\text{-allyl})_2Cl]_2 \xrightarrow[\text{thf}]{AgBF_4} [Rh^{III}(\eta^3\text{-allyl})_2(thf)_2].BF_4$$

Arene

Rh^I (Arene)

(VIII)
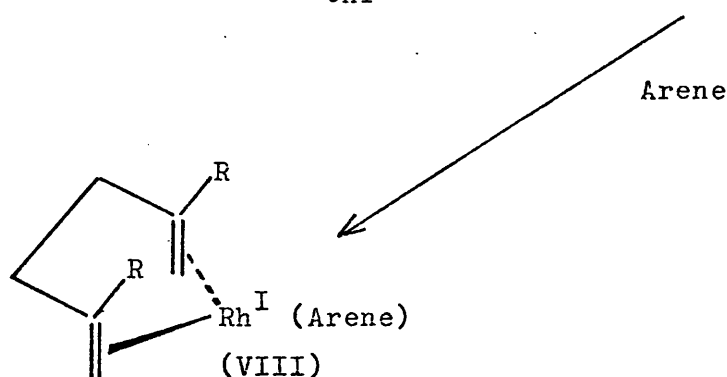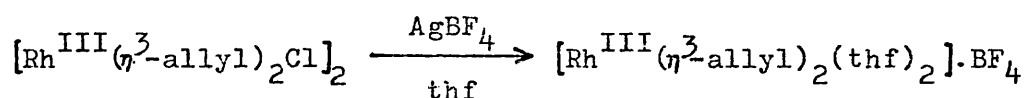
a) R=H, Arene = $1,3,5\text{-}C_6H_3Me_3$ d) R=Me, Arene = $1,3,5\text{-}C_6H_3Me_3$

b) R=H, Arene = C_6Me_6 e) R=Me, Arene = C_6Me_6

c) R=H, Arene = $1,2\text{-}C_6H_4(OMe)_2$ f) R=Me, Arene = $1,2\text{-}C_6H_4(OMe)_2$

Figure 1.11.

complexes, by the reductive dimerisation of the two

η^3-allyl ligands. In this way, the arene rhodium(I) complexes

(VIII) were isolated, as shown in Figure 1.11.[60]

Allyl palladium complexes have been prepared from substituted cyclopropanes,[61-63] and a small amount of cyclopropane was isomerised to propene, in its reaction with $PdCl_2$.[64] 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 η^3-allyl rhodium(III) hydride complex was proposed as an intermediate.[65]

The reaction of cyclopropane with $[Rh(dpm)(C_2H_4)\cdot (C_4F_6)]$ may therefore also involve a rhodium-allyl intermediate (Figure 1.10).

Tetramethylallene (TMA) reacts with $[Rh(dpm)(C_2H_4)-(C_4F_6)]$ (IVc) at room temperature, to form yellow crystals of the substituted $1,2,4,5-\eta$-penta-1,4-diene complex (IXa).

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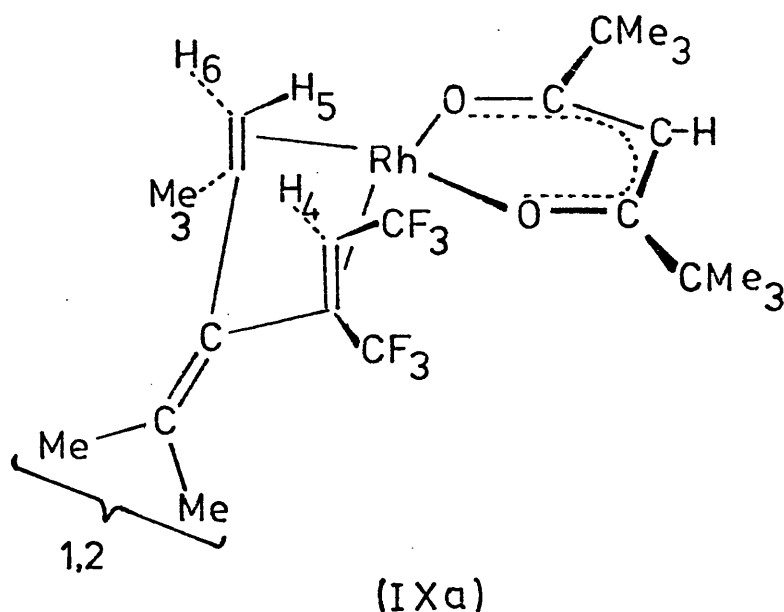
A section of the [1]H n.m.r. spectrum of complex (IXa) is reproduced in Figure 1.12, together with peak assignments

A section of the ^{1}H n.m.r. spectrum of complex (IXa)

(Coupling constants (Hz) in parentheses)

J_{RhH} (24)

J_{HF} (9)

J_{RhH} (24)

H$_6$ H$_5$ H$_4$ Me$_3$ Me$_{1,2}$

τ 7.0   8.0
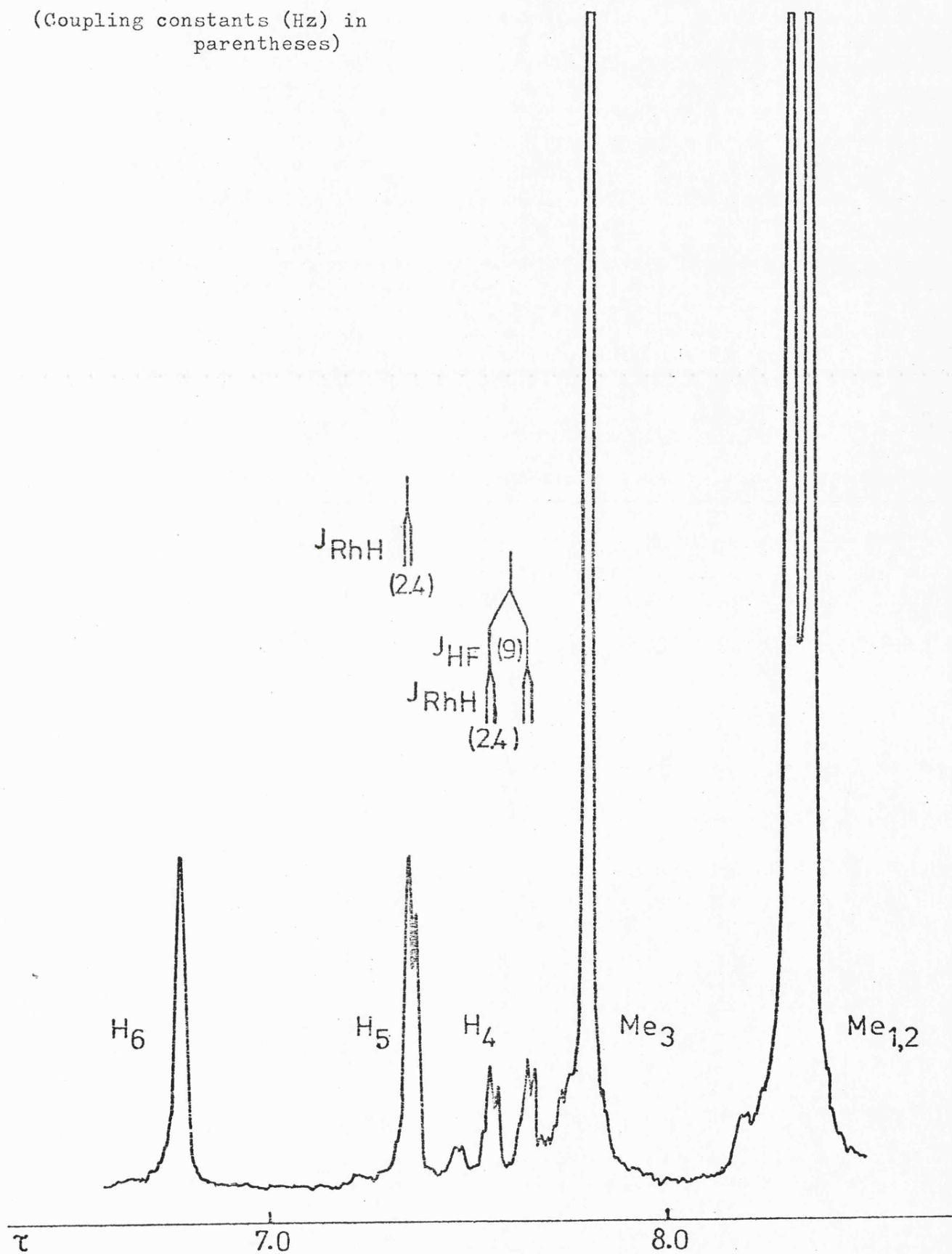
Figure 1.12

and coupling constants. As for complex (VII) the chemical shifts for the alkenic protons are consistent with data for π^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}=9.0Hz), together with an apparent quintet at 53.86 p.p.m. (J_{FF}=J_{HF}=9.0Hz), 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 $\underline{cis}$ 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 $[Rh(dpm)(C_8H_{14})(C_4F_6)]$ (IVd) and with $[Rh(dpm)(C_7H_{12})(C_4F_6)]$ (IVe).

In an identical reaction, the acetylacetonato analogue (IXb) of complex (IXa) was isolated by treating $[Rh(acac)(C_2H_4)(C_4F_6)]$ (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}=9.0Hz) and a "quintet" at 54.51 p.p.m. (J_{FF}=J_{HF}=9.0Hz), 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), $C_{22}H_{31}O_2F_6Rh$, (molecular weight = 544.39) are monoclinic with space group $P2_1/c$, and a = 11.50Å, b = 19.00Å, c= 23.32Å, β= 99.74°, U = 5022.0Å^3 and Z = 8.

Other penta-1,4-diene complexes of rhodium have been reported,[45,66] and it is useful to make a comparison of the results. The crystal structure of the dibenzylideneacetone complex (X) has been reported[67], and a comparison of some

(X)
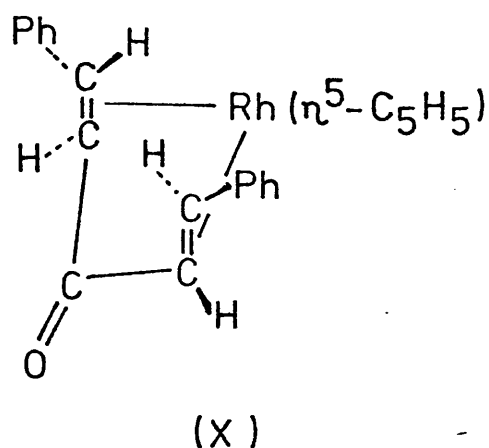
of the bond lengths in the carbon skeletons of the 1,4-dienes in (IXa) and (X) is shown in Table 1.6.

The complexes (XI) were prepared for diene isomerisation studies,[45] and were isolated as red oils.

(XI)

a) R=H; L=η^5-C$_5$H$_5$
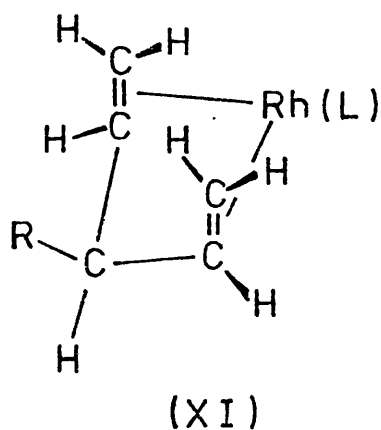
b) R=H, L=η^5-C$_5$H$_4$CO$_2$Me

c) R=Me, L=η^5-C$_5$H$_4$CO$_2$Me.

Table 1.6

Some interatomic distances($\overset{o}{A}$) for complexes (IXa)[a] and (X)

	(IXa)	(X)
$Rh-C_1$	2.185	2.241(6)
$Rh-C_2$	2.171	2.149(6)
$Rh-C_5$	2.155	2.230(6)
$Rh-C_4$	2.089	2.152(6)
C_1-C_2	1.469	1.406(8)
C_5-C_4	1.435	1.416(9)
C_3-C_6	1.380	—
C_3-O	—	1.236(7)
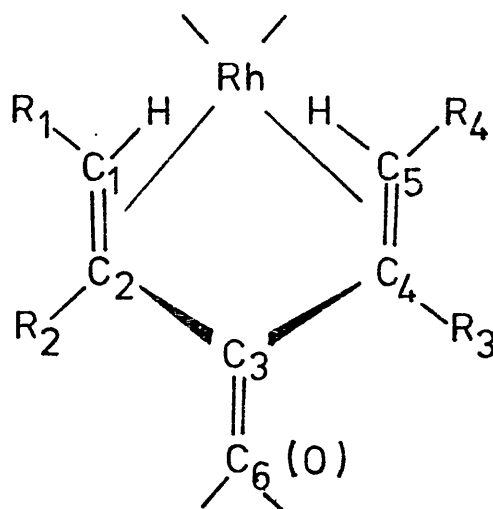
(IXa) $R_1=H$, $R_2=Me$,

$R_3=R_4=CF_3$.

(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.
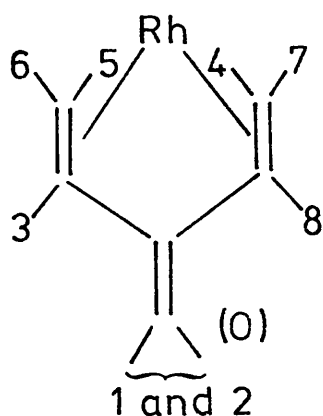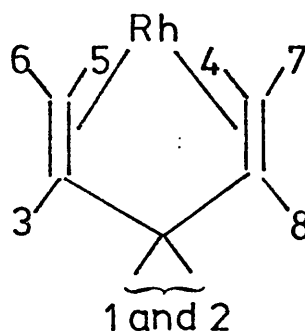
(IXa,b);(X).   (VII);(XIa,b,c).

Figure 1.13

In their reactions with carbon monoxide, complexes

(VII) and (IXa) both gave the known complex $[Rh(dpm)(CO)_2]^{68}$

$[\nu(C=O)=2080, 2011 \text{ cm}^{-1}]$, 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

dipivaloylmethanato(alkene)(alkyne)rhodium(I) complexes

reported here is in complete contrast with the reaction

Table 1.7

¹H n.m.r. chemical shifts for η^4-penta-1,4-diene ligand protons in rhodium(I) complexes [a,b].

Complex	1	2	3	4	5	6	7	8	Reference
(VII)	6.38(dd) 7.96(dd)		5.50(m)	7.49(q)	6.97(d)	6.75(d)	(CF₃)	(CF₃)	This work
(IXa)	8.40(s)[Me] 8.46(s)[Me]		7.85(s)[Me]	7.64(qd)	6.74(s)	7.37(d)	(CF₃)	(CF₃)	This work
(IXb)	8.40(s)[Me] 8.45(s)[Me]		7.86(s)[Me]	7.60(qd)	6.74(s)	7.35(d)	(CF₃)	(CF₃)	This work
(X)	[C=O]		5.17(dd)	6.47(dd)	6.47(dd)	2.80(m)[Ph]	2.80(m)[Ph]	5.17(dd)	66
(XIa)	7.8(m)		6.9(m)	8.92(dd)	8.92(dd)	7.74(dt)	7.74(dt)	6.9(m)	45
(XIb)	7.8(m)		6.9(m)	8.7(dd)	8.7(dd)	7.68(dt)	7.68(dt)	6.9(m)	45
(XIc)	8.3(m)	8.5(d)[Me]	6.9(m)	8.75(dd)	8.75(dd)	7.69(dt)	7.69(dt)	6.9(m)	45

a. See Figure 1.13 for numbering of protons.

b. dd = doublet of doublets; dt = doublet of triplets; qd = quartet of doublets.

31

of allene with acetylacetonatobis(ethene)rhodium(I),

which was performed at low temperature.[69]   A bis-allyl

rhodium(III) complex was isolated, together with a

3,4-dimethylenerhodacyclopentane complex, which was

shown to be an intermediate in the reaction, as shown

in Figure 1.14.

$[Rh(acac)(C_2H_4)_2]$

$H_2C=C=CH_2$

-78°C

-35°C
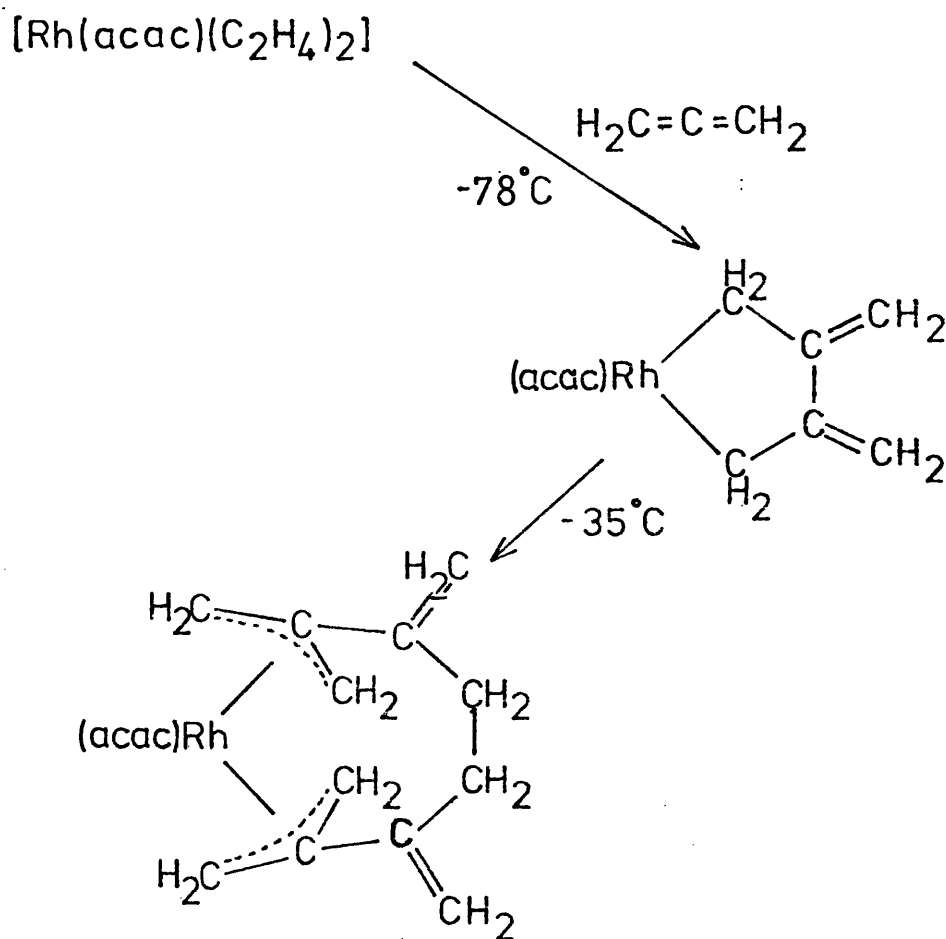
Figure 1.14

The room temperature reaction of hexafluorobut-2-yne

with the bis-alkene complex $[(TMA)_2Rh(acac)]$ has been

reported,[3] and a hexakis(trifluoromethyl)benzene complex

(II) was isolated (cf. Figure 1.1).   The result of a

similar reaction, performed at -78°C is awaited with

interest.

C. **Reactions of phosphines, arsines and stibines with**

   alkene-alkyne complexes.

   Complex (IVc), $[Rh(dpm)(C_2H_4)(C_4F_6)]$, is known to

react with triphenylphosphine, triphenylarsine,

triphenylstibine[13] and 1,2-bis(diphenylphosphino)ethane[4]

to give the complexes (XII).
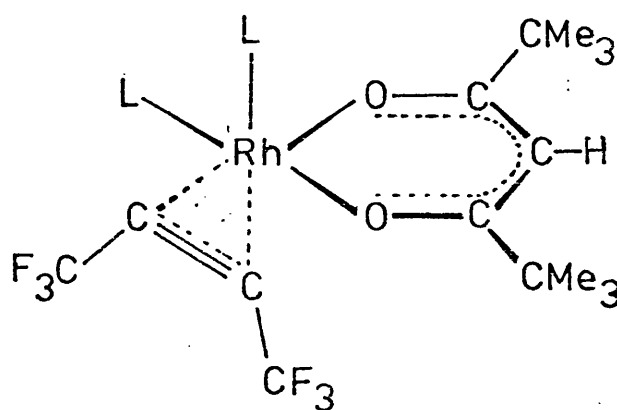
(XII)

a) L = PPh_3

b) L = $AsPh_3$

c) L = $SbPh_3$

d) L-L = $Ph_2PCH_2CH_2PPh_2$

This series of reactions has been extended, and

complexes (XIIe) and (XIIf) have been prepared, where

L = PPh_2Me and PPh_2Et respectively.

In a similar series of reactions, the analogous

acetylacetonato complexes (XIII) were prepared from

$[Rh(acac)(C_2H_4)(C_4F_6)](IVa)$.
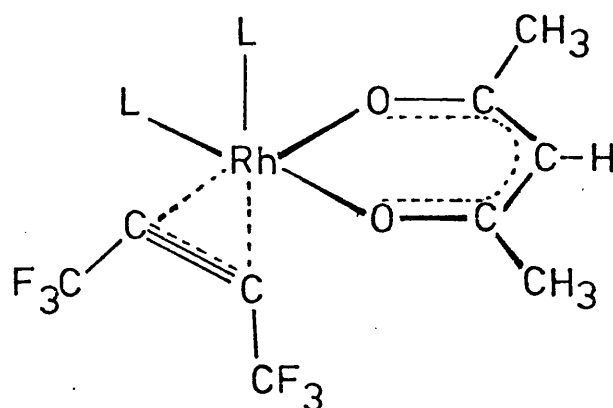
(XIII)

a) L = PPh$_3$

b) L = AsPh$_3$

c) L = SbPh$_3$

d) L = PPh$_2$Me

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]
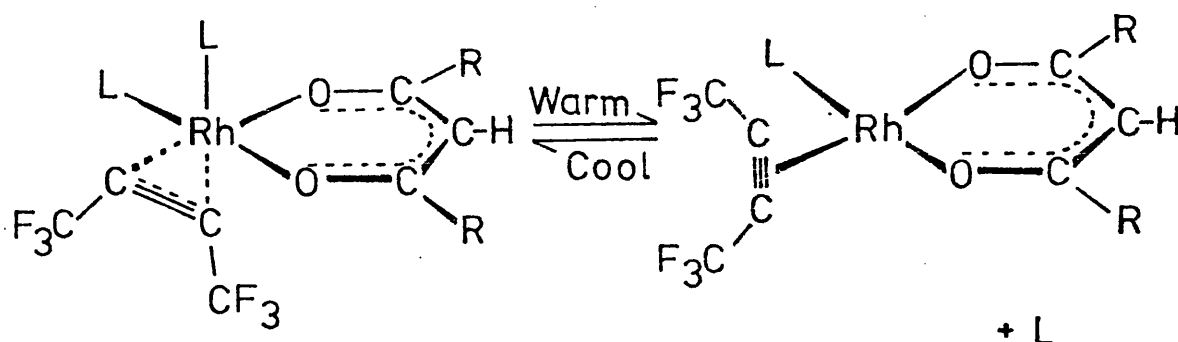
R = CMe$_3$;
L = PPh$_3$, AsPh$_3$, SbPh$_3$

Figure 1.15

The room temperature ^{19}F n.m.r. spectra all showed

one signal, which appeared as a doublet due to coupling

to the rhodium (J_{RhF}=1.5-2Hz). Coupling to phosphorus

was not observed for the triphenylphosphine complex (XIIa).

On cooling the solutions to $-58^{\circ}C$, the spectra then showed

two signals, of equal intensity, and phosphorus coupling

was observed on the low field signal for complex (XIIa),

(J_{PF}=16.8Hz). 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 (XIId) showed two signals in its

^{19}F n.m.r. spectrum at room temperature,[4] showing that the

hexafluorobut-2-yne 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}F n.m.r. spectra similar to that for (XIId), showing

that the phosphines PPh_2Me and PPh_2Et 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]

$$PPh_3 \simeq PPh_2Me > PPhMe_2 > PMe_3$$
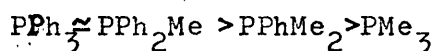
It seems likely that, in these complexes, the smaller phosphines are more easily accommodated than PPh_3, $AsPh_3$ or $SbPh_3$, to give the d^8 rhodium(I) complexes $[Rh(dpm)(L)_2(C_4F_6)]$, ($L=PPh_2Me$, PPh_2Et).

In the acetylacetonatorhodium(I) complexes (XIII), exactly the same situation is observed. One signal is observed in the room temperature ^{19}F n.m.r. spectrum for complexes (XIIIa-c), showing that ligand dissociation is occurring. Rhodium coupling ($J_{RhF}=1.6-2.0Hz$) 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 (XIIId) shows two signals at room temperature, with phosphorus coupling observed on the low field signal ($J_{PF}=12Hz$), as for the dipivaloylmethanato analogue (XIIe), and indicating that the phosphine ligands are not dissociating at room temperature.

The ^{19}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 1.8

^{19}F n.m.r. spectroscopic data for complexes $[Rh(dpm)(L)_2(C_4F_6)]$ and $[Rh(acac)(L)_2(C_4F_6)]$

Complex[d]	Room Temperature	Low Temperature	T_c[e] °C	Ref.
(XIIa) $[Rh(dpm)(PPh_3)_2(C_4F_6)]$[a]	51.66(d, J_{RhF}=2Hz)	51.62(d, 3F, J_{PF}=16.8Hz) 52.41(s, 3F)	-19	13
(XIIb) $[Rh(dpm)(AsPh_3)_2(C_4F_6)]$[a]	52.66(d, J_{RhF}=2Hz)	51.03(s, 3F) 52.48(s, 3F)	-44	13
(XIIc) $[Rh(dpm)(SbPh_3)_2(C_4F_6)]$[a]	52.97(d, J_{RhF}=1.5Hz)	51.62(s, 3F) 54.10(s, 3F)	-21	13
(XIId) $[Rh(dpm)(diphos)(C_4F_6)]$[a]	51.80(dxd, 3F, J_{PF}=17.4Hz, J_{RhF}=4.5Hz) 53.42(d, 3F, J_{RhF}=3Hz)	-	-	4
(XIIe) $[Rh(dpm)(PPh_2Me)_2(C_4F_6)]$[a]	51.13(dxd, 3F, J_{PF}=16.3Hz, J_{RhF}=3.6Hz) 51.91(d, 3F, J_{RhF}=2.2Hz)	-	-	This work
(XIIf) $[Rh(dpm)(PPh_2Et)_2(C_4F_6)]$[a]	50.66(d, 3F, J_{PF}≈11Hz) 53.01(s, 3F)	-	-	"
(XIIIa) $[Rh(acac)(PPh_3)_2(C_4F_6)]$[b]	51.72(d, J_{RhF}=1.6Hz)	50.98(s, 3F) 51.72(s, 3F)	-28	"
(XIIIb) $[Rh(acac)(AsPh_3)_2(C_4F_6)]$[c]	52.50(d, J_{RhF}=1.8Hz)	52.01(d, 3F, J_{RhF}=2.7Hz) 55.54(d, 3F, J_{RhF}=2.7Hz)	-57	"
(XIIIc) $[Rh(acac)(SbPh_3)_2(C_4F_6)]$[a]	52.57(d, J_{RhF}=2.0Hz)	52.12(s, 3F) 53.43(s, 3F)	~ -25	"
(XIIId) $[Rh(acac)(PPh_2Me)_2(C_4F_6)]$[a]	51.54(d, 3F, J_{PF}=12Hz) 51.96(s, 3F)	-	-	"

a. Measured in $CDCl_3$ solution. b. Measured in CD_2Cl_2 solution. c. Measured in CH_2Cl_2 solution. d.p.p.m. rel. to $CFCl_3$.
e. Coalescence temperature(°C).

molar equivalent of triphenylstibine with $[Rh(dpm)(C_2H_4)(C_4F_6)]$

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

$[Rh(dpm)(SbPh_3)(C_4F_6)]$ 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 ($J_{RhF} \approx 2Hz$) in each case.

The infra-red stretching frequencies $\nu(C \equiv C)$ are

shown in Table 1.9, for complexes (XII), (XIII) and (XIV).

The triphenylphosphine complex (XIVb) was also

isolated from the reaction of $[Rh(dpm)(C_8H_{14})(C_4F_6)]$(IVd)

or $[Rh(dpm)(C_7H_{12})(C_4F_6)]$(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)[a]

Complex		ν (C≡C)
(XIIa)	$[Rh(dpm)(PPh_3)_2(C_4F_6)]$	1815s, 1787s
(XIIb)	$[Rh(dpm)(AsPh_3)_2(C_4F_6)]$	1821s, 1790s
(XIIc)	$[Rh(dpm)(SbPh_3)_2(C_4F_6)]$	1829s, 1790m
(XIId)	$[Rh(dpm)(diphos)(C_4F_6)]$	1829s, 1794m
(XIIe)	$[Rh(dpm)(PPh_2Me)_2(C_4F_6)]$	1810m, 1781s
(XIIf)	$[Rh(dpm)(PPh_2Et)_2(C_4F_6)]$	1829m, 1790m
(XIIIa)	$[Rh(acac)(PPh_3)_2(C_4F_6)]$	1820m, 1786m
(XIIIb)	$[Rh(acac)(AsPh_3)_2(C_4F_6)]$	1829m, 1791m
(XIIIc)	$[Rh(acac)(SbPh_3)_2(C_4F_6)]$	1832m, 1790m
(XIIId)	$[Rh(acac)(PPh_2Me)_2(C_4F_6)]$	1815m, 1782m
(XIVa)	$[Rh(dpm)\{P(C_6H_{11})_3\}(C_4F_6)]$	1924s
(XIVb)	$[Rh(dpm)(PPh_3)(C_4F_6)]$	1940s
(XIVc)	$[Rh(dpm)(AsPh_3)(C_4F_6)]$	1934s

a. Recorded as nujol mulls.
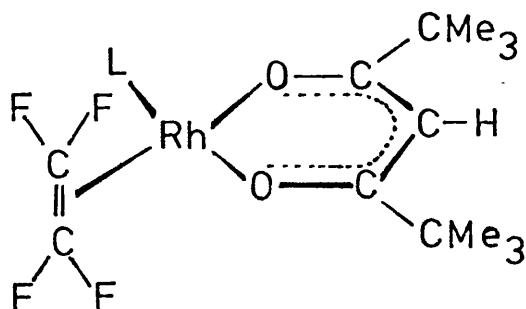
(XV)

a) L = PPh₃

b) L = AsPh₃

c) L = SbPh₃

temperature to give the five co-ordinate rhodacyclopentadiene

complexes (XVIa) and (XVIb) respectively.[3] The reactions of

(XVI)
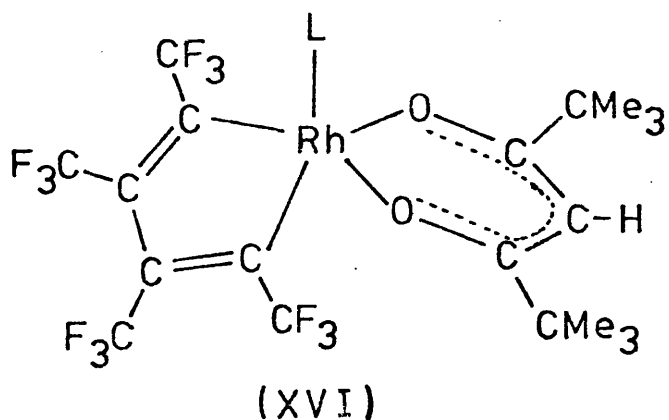
a) L = AsPh₃

b) L = SbPh₃

hexafluorobut-2-yne with [Rh(dpm)(AsPh₃)(C₄F₆)], (XIVc),

and with [Rh(dpm)(SbPh₃)₂(C₄F₆)], (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 -95°C, displaces the co-ordinated hexafluorobut-2-yne, as in the room temperature reaction with $[Rh(dpm)(C_2H_4)(C_4F_6)]$ discussed in Section 1.2A, and $[Rh(dpm)(AsPh_3)(C_2F_4)]$(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 $[Rh(acac)(PPh_3)_2(C_4F_6)]$, (XIIIa), also resulted in the displacement of the co-ordinated alkyne, to give yellow crystals of the known complex $[Rh(acac)(CO)(PPh_3)]$.[72]

D. Reactions of pyridines with alkene-alkyne complexes

In the course of investigating the reactions of σ-donor ligands with $[Rh(dpm)(C_2H_4)(C_4F_6)]$(IVc), the rhodium(III) complexes (XVII) were isolated. These

(XVII)
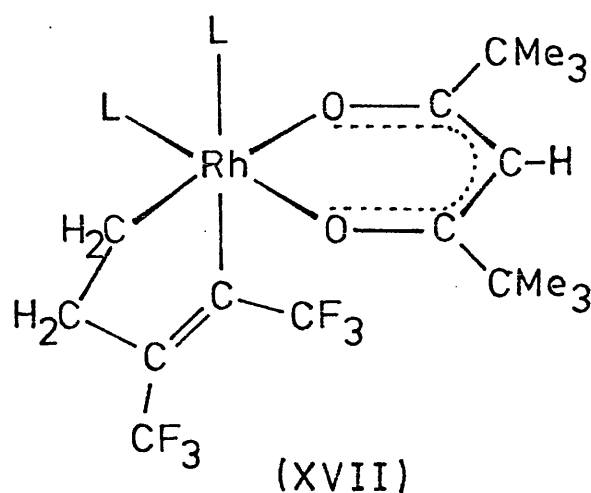
a) L = pyridine
b) L = 3-methylpyridine
c) L = 3,5-dimethylpyridine
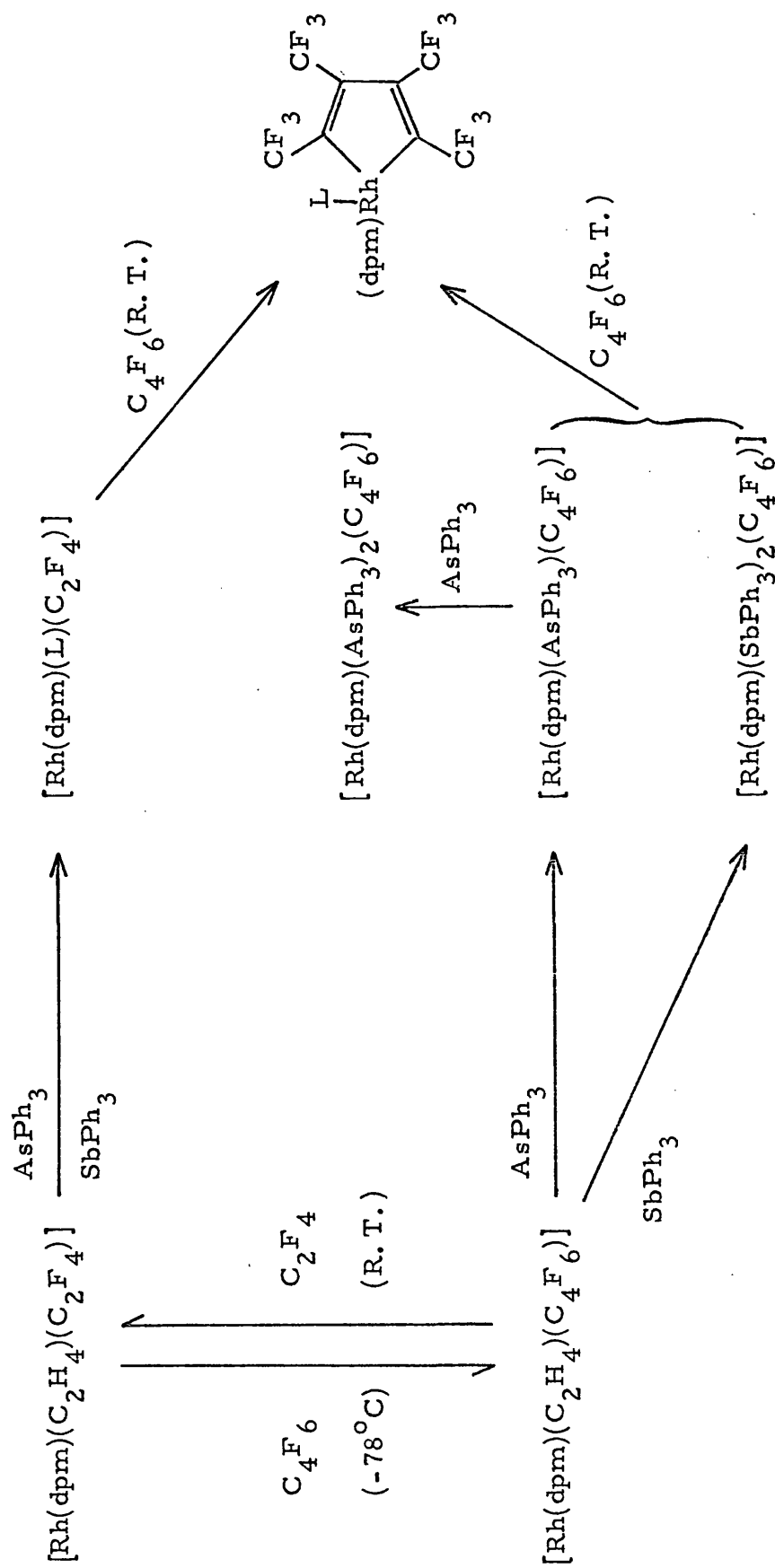
Figure 1.16 [L = AsPh$_3$ or SbPh$_3$]

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_2H_4 protons as a broad signal (6.80-7.87τ, 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
$>C=\overset{|}{C}-CH_2-CH_2-\overset{|}{C}=C<$ moiety,[2,3,18] for example. The spectrum
also shows two singlet signals of unequal intensities
(4.49 and 4.56τ), which are assigned to the γ-CH of the
dpm ligand, and a singlet for each t-butyl group of the
dpm ligand (8.90 and 9.01τ), 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}=14.0Hz) 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 1.10

N.m.r. spectroscopic data for the complexes $[Rh\{CH_2CH_2C(CF_3)=C(CF_3)\}(dpm)(L)_2]$

Complex	L	^{19}F n.m.r. [a]	^1H n.m.r. [b]		
			γ-CH	t-butyl	$-CH_2-CH_2-$
(XVIIa)	C_5H_5N	52.83(q), 54.72(q)(3F); 57.93(q,3F)	4.49(s) (1H) 4.56(s)	8.90(s,9H) 9.01(s,9H)	6.80-7.87(br)
(XVIIb)	$3\text{-}MeC_5H_4N$	53.87(q), 55.94(q)(3F); 59.19(5 lines, 3F)	4.49(s) (1H) 4.57(s)	8.87(s,9H) 8.95(s,9H)	6.78-7.68(br)
(XVIIc)	$3,5\text{-}Me_2C_5H_3N$	53.15(q), 55.26(q)(3F); 58.26(7 lines, 3F)	4.51(s) (1H) 4.61(s)	8.88(s,9H) 8.99(s,9H)	6.81-7.74(br)

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.

Complexes (XVIIb) and (XVIIc) similarly show two

unequal singlets in their ^{1}H n.m.r. spectra, which are

again assigned to the γ-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), $C_{27}H_{33}N_2O_2F_6Rh$, (molecular

weight = 634.46) are monoclinic, with space group $P2_1/n$,

and a=11.561Å, b=16.686Å, c=14.854Å, β=90.2°, U=2865.4Å^3

and Z=4. The results show complex (XVIIa) to be an

octahedral rhodium(III) complex, with the pyridine ligands

in a cis configuration.[40] 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:[69]

(XVIII)

$[Rh\{CH_2CH_2C(CF_3)=C(CF_3)\}(dpm)(py)_2]$

(XVIIa)

2.14Å

2.02Å

2.03Å

1.53Å

Rh

1.54Å

1.33Å
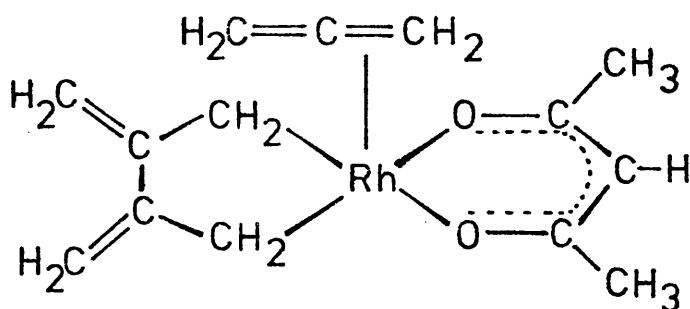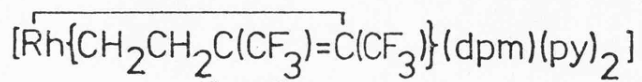
2.01Å
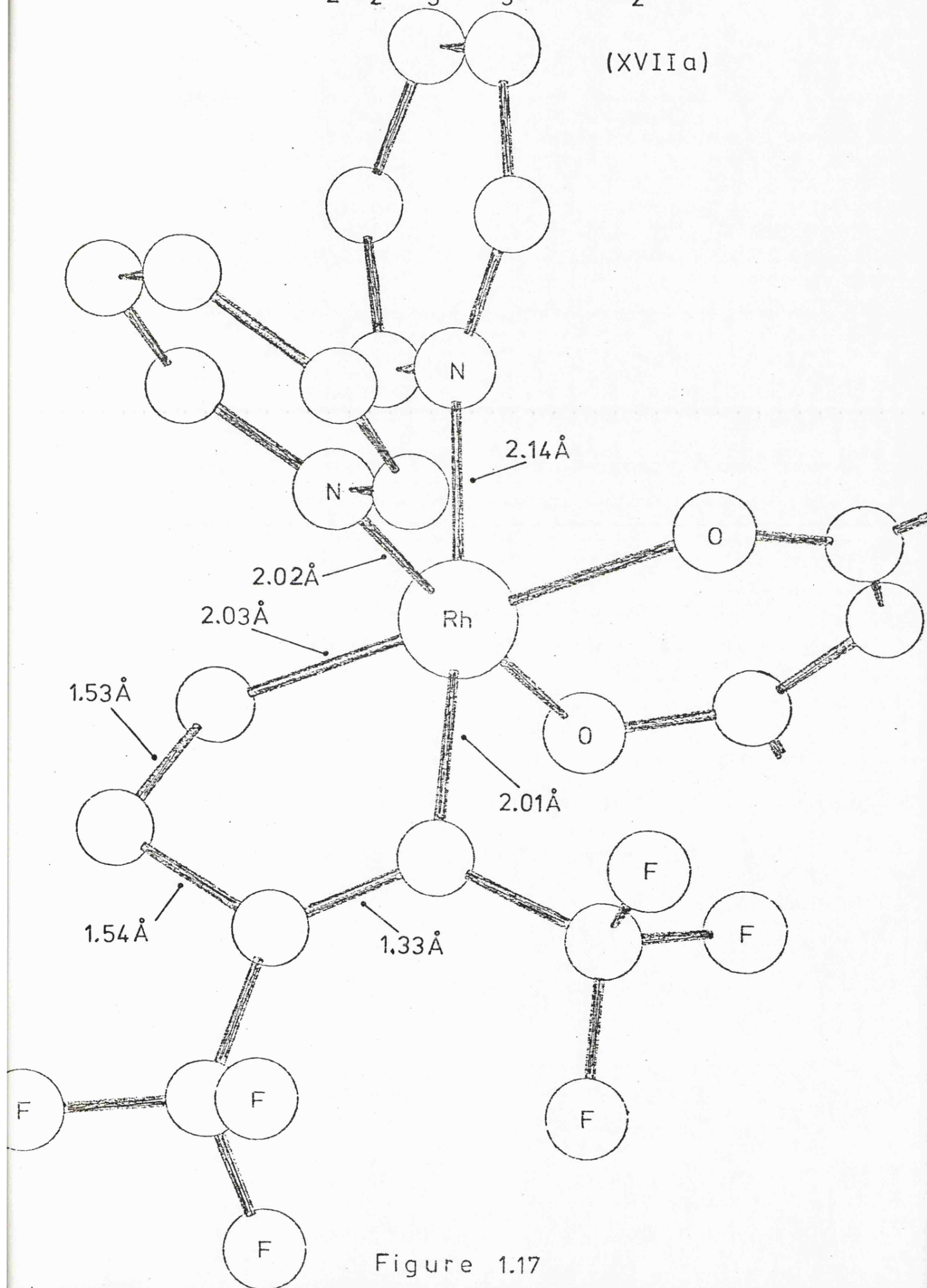
Figure 1.17

This microcrystalline complex was formed by adding

$[Rh(acac)(C_2H_4)_2]$ to liquid allene at $-78^\circ C$, but was

found to be unstable at temperatures higher than $0^\circ C$.

The reactions of complex (XVIII) with pyridine and with

triphenylphosphine are outlined in Figure 1.18.

$$C_5H_5N \nearrow [(Acac)Rh(C_3H_4)_2(C_5H_5N)_2] + C_3H_4$$
$$(XIX)$$

$$[(Acac)Rh(C_3H_4)_3]$$

$$PPh_3 \searrow [(Acac)Rh(C_3H_4)_2(PPh_3)_2] + C_3H_4$$
$$(XX)$$
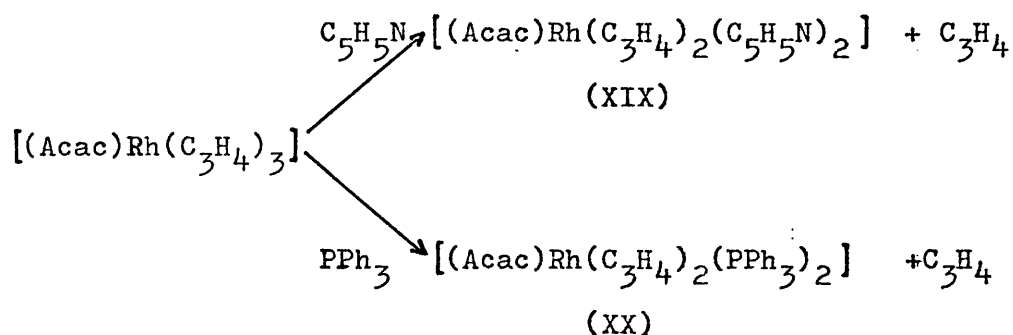
Figure 1.18

The single crystal X-ray structure of complex (XIX) has

been reported,[73] and it was shown to be an octahedral

(XIX)
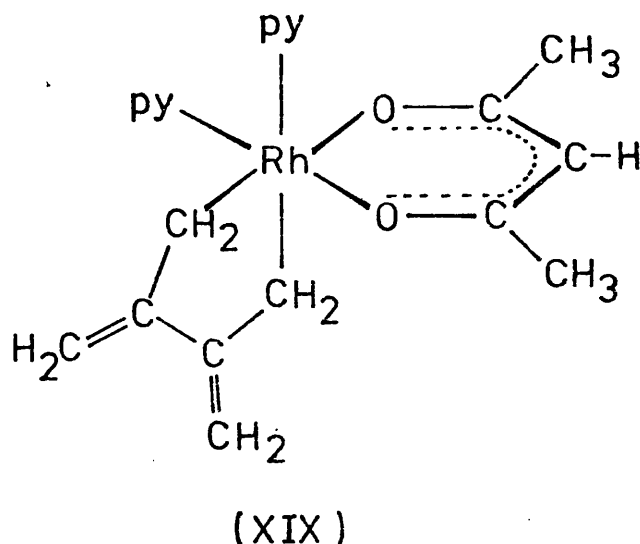
rhodium(III) complex, with cis pyridine ligands. The

structure of complexes (XVII) is therefore very similar

to that of complex (XIX). Complex (XX),however, was
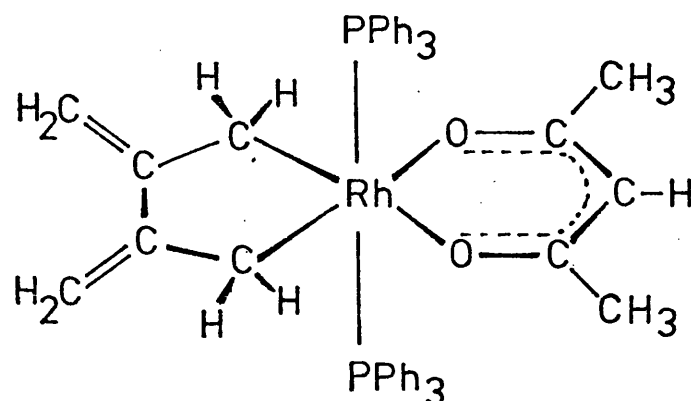
(X X)

assigned a _trans_ configuration, on the basis of
^{1}H 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 γ-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

^{1}H n.m.r. spectrum, which are assigned to the γ-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}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 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 $[\overline{Rh\{CH_2CH_2C(CF_3)=C(CF_3)\}}-$

$(dpm)(py)_2]$ (XVIIa) does not affect the ^{19}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

^1H, ^{19}F and proton decoupled ^{31}P n.m.r. spectra suggest

that complex (XXI) is the pure cis isomer:
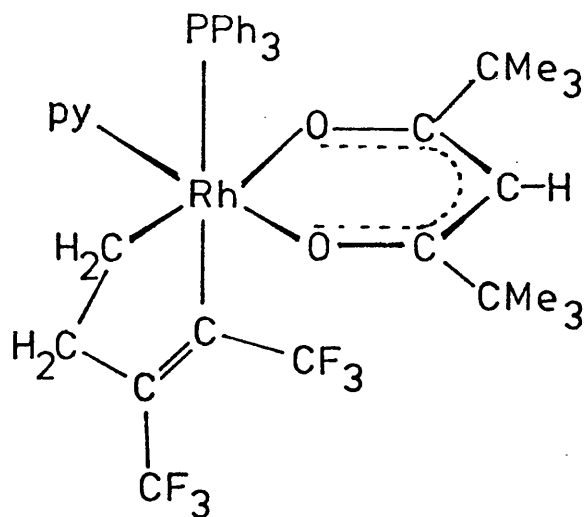
(XXI)

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.

[R = CF₃]

Figure 1.19

The ^{1}H n.m.r. spectrum shows only one singlet

resonance for the γ-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, 3F, J_{FF}=13.1Hz),

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

[A]

[B]

Figure   1.20

which shows one signal centred at -14.6 p.p.m.,relative

to external phosphonium ion, (doublet of quartets,

$J_{RhP}=82Hz$, $J_{FP}=11Hz$). This indicates that the

triphenylphosphine ligand is trans to the carbon atom

carrying a 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,[74,75] and the chemical

shift, too, (-14.6 p.p.m.) is typical for rhodium(III)[75].

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-yne, 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 $[Rh(dpm)(CO)_2]$, (Section 1.2B), the

rhodium(III) complex (XVIIa) showed no reaction, in

solution with carbon monoxide.

The reaction of pyridine with the complex

$[Rh(dpm)(C_2H_4)(C_2F_4)]$ was also investigated. The

crystalline product was identified as

dipivaloylmethanatobis(pyridine)(tetrafluoroethene)rhodium(I),

complex (XXII). The analogous acetylacetonato complex,

$[Rh(acac)(py)_2(C_2F_4)]$[76] is known, and the ^{19}F n.m.r.
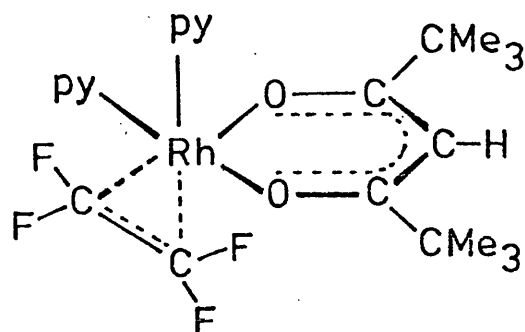
(XXII)

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 $[Rh(dpm)(C_2H_4)_2]$ with electrophilic alkynes, other than hexafluorobut-2-yne, did not result in the isolation of mono-alkene-alkyne complexes,[77] so an alternative approach was tried.

Hexafluoroacetylacetonatobis(ethene)rhodium(I)[69] was treated, at room temperature, with some electron-rich alkynes. However, no reaction occurred with 3-bromophenyltrimethylsilylethyne, 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-PS-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-PS-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 (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 (150cm^3) were done in 15cm^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	Koch Light Labs. Ltd.
cycloheptene bicyclo[2.2.1] heptene 2,3-dimethylbut-2-ene tetramethylallene triphenylphosphine triphenylarsine triphenylstibine dipivalcylmethane	Aldrich Chemical Co. Ltd.
tricyclohexylphosphine methyldiphenylphosphine ethyldiphenylphosphine	Maybridge Chemical Co. Ltd.
pyridine	— May and Baker Ltd.
cyclohexene	— Fisons Ltd.

propene

cis-but-2-ene   } The Matheson Co.

trans-but-2-ene

carbon monoxide   } B.O.C.

ethene

3-methylpyridine

acetylacetone

cyclopropane   } B.D.H. Chemicals Ltd.

polytetrafluoroethene

but-2-yne   —   B.A.S.F.

hexafluorobut-2-yne   —   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:

$[Rh(dpm)(C_2H_4)(C_4F_6)]$, $[Rh(acac)(C_2H_4)(C_4F_6)]$ and
$[Rh(acac)(C_8H_{14})(C_4F_6)]$[13]
$[Rh(dpm)(C_2H_4)(C_2F_4)]$[71]
$[Rh(dpm)(C_8H_{14})_2]$[78]
$[Rh(hfacac)(C_2H_4)_2]$[69]
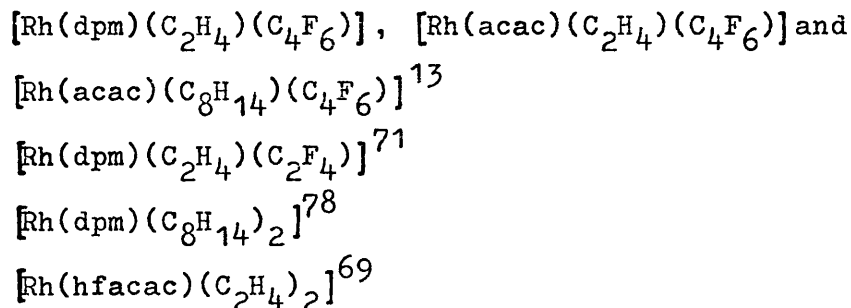
(٭) The preparation of new mono-alkene–alkyne complexes of rhodium(I)

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

i) With cis-cyclo-octene

To a stirred solution of $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (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 $[Rh(dpm)(cis-C_8H_{14})(C_4F_6)]$

Yield = 0.13g, 74%.

M.P. 140-2°C (decomp)

Analysis Calculated for $C_{23}H_{33}O_2F_6Rh$: 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}H n.m.r. 4.20(s, 1H); 6.64 (quin.x d, 2H, J_{HH}=7Hz, J_{RhH}=2Hz); 7.67(m,4H); 8.22-8.76(br,8H); 8.83(s,9H); 8.95(s, 9H).

^{19}F n.m.r. 52.66(d, J_{RhF}=2Hz).

ii) With cycloheptene

Cycloheptene (0.03g, 0.32mmol) was added to a solution of $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (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 $[Rh(dpm)(C_7H_{12})(C_4F_6)]$.

Yield = 0.15g, 87%.

__M.P.__   121-2°C (decomp)

__Analysis__   Calculated for $C_{22}H_{31}O_2F_6Rh$: 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, 809m, 788w, 772w, 751w, 727w, 708w, 672m, 643m, 618w,sh, 534w, 516w, 498w, 468w, 454w, 442w, 431w.

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

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

iii) With propene

An excess of propene (1.0cm^3) was condensed (-196°C) on to a solution of $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (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 $[Rh(dpm)(CH_3C(H)=CH_2)(C_4F_6)]$. Crystals were obtained by recrystallisation from diethyl ether/methanol.

Yield = 0.17g, 83%.

<u>M.P.</u> 61-2°C (decomp)

<u>Analysis</u> Calculated for $C_{18}H_{25}O_2F_6Rh$: C, 44.10%; H, 5.14%

Found: C, 44.34%; H, 5.18%

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

<u>^{1}H n.m.r.</u> 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).

<u>^{19}F n.m.r.</u> 52.68(s).

iv) <u>With cis-but-2-ene</u>

An excess of <u>cis</u>-but-2-ene (1.0cm^3) was condensed (-196°C) on to a solution of $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (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 $[Rh(dpm)(\underline{cis}-CH_3C(H)=C(H)CH_3)(C_4F_6)]$.

Yield = 0.07g, 71%

<u>M.P.</u> 57-58°C

<u>Analysis</u> Calculated for $C_{19}H_{27}O_2F_6Rh$: C, 45.25%; H, 5.40%

Found: C, 45.28%; H, 5.35%

Infra-red   1973s, 1961s, 1555s, 1538s, 1532m,sh, 1506s,

1269s, 1248m, 1226s, 1199m, 1185m, 1164s,sh, 1151s, 1113m,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}=6Hz);

8.85(s,9H); 8.94(s,9H).

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

v)   With trans-but-2-ene

An excess of trans-but-2-ene (1.0cm^3) was condensed

(-196°C) on to a solution of $[Rh(dpm)(C_2H_4)(C_4F_6)]$

(0.20g, 0.42mmol) 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, and careful

addition of methanol, gave a yellow solid, which was

identified as $[Rh(dpm)(\underline{trans}-CH_3C(H)=C(H)CH_3)(C_4F_6)]$

Yield = 0.16g, 76%.

M.P.   102-3°C

Analysis   Calculated for $C_{19}H_{27}O_2F_6$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, 752w, 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)

vi)   With cyclohexene

Cyclohexene (0.03g, 0.32mmol) was added to a solution

of $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (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 [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.

vii) With bicyclo[2.2.1]heptene

Bicyclo[2.2.1]heptene (0.03g, 0.32mmol) was added

to a solution of $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (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

[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.

viii) With 2,3-dimethylbut-2-ene

2,3-dimethylbut-2-ene (0.03g, 0.32mmol) was added to

a solution of $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (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 [1]H n.m.r. spectra.

ix) **With tetrafluoroethene**

An excess of tetrafluoroethene (1.0cm^3) was condensed (-196°C) on to a solution of [Rh(dpm)(C$_2$H$_4$)(C$_4$F$_6$)] (0.15g, 0.32mmol) 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 [Rh(dpm)(C$_2$H$_4$)(C$_2$F$_4$)] by its i.r. and ^{19}F n.m.r. spectra. Yield = 0.10g, 75%.

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

To a solution of [Rh(dpm)(C$_2$H$_4$)(C$_4$F$_6$)] (0.05g, 0.11mmol) in diethyl ether, cis-cis-cyclo-octa-1,5-diene (0.012g, 0.11mmol) 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 [Rh(dpm)(cod)], by their i.r. and ^{1}H n.m.r. spectra. Yield = 0.04g, 92%.

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

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

An excess of hexafluorobut-2-yne (1.0cm^3) was condensed (-196°C) on to a solution of [Rh(dpm)(C$_8$H$_{14}$)$_2$] (0.56g, 1.11mmol) 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 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 $[Rh(dpm)(C_8H_{14})(C_4F_6)]$,
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 $[Rh(dpm)(C_2H_4)(C_2F_4)]$
(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
$[Rh(dpm)(C_2H_4)(C_4F_6)]$, 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 $[Rh(dpm)(C_8H_{14})_2]$
(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
$[Rh(dpm·C_4F_6)\{(C_8H_{14})(C_4F_6)_2\}]$ Yield = 0.15g. 42%

<u>M.P.</u>   197-8°C (decomp)

<u>Analysis</u>   Calculated for $C_{31}H_{33}O_2F_{18}Rh$: C, 42.19%; H, 3.77%

                 Found: C, 42.13%; H, 4.06%

<u>Infra-red.</u> 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.

^1H n.m.r. 3.55(s, 1H); 7.54(m, 2H); 7.88-8.66(br, 12H);

8.77(s, 18H).

^{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) <u>Dipivaloylmethanato(cyclo-octene)(hexafluorobut-2-yne)rhodium(I)</u>

       An excess of hexafluorobut-2-yne (1.0cm^3) was condensed

(-196°C) on to a solution of $[Rh(dpm)(C_8H_{14})(C_4F_6)]$

(0.15g, 0.27mmol) 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 $[Rh(dpm.C_4F_6)\{(C_8H_{14})(C_4F_6)_2\}]$,

by comparing their ^{19}F n.m.r. and i.r. spectra with those

from the previous experiment.   Yield = 0.16g, 67%.

iii) <u>Dipivaloylmethanato(cycloheptene)(hexafluorobut-2-yne)rhodium(I)</u>

       An excess of hexafluorobut-2-yne (1.0cm^3) was

condensed (-196°C) on to a solution of $[Rh(dpm)(C_7H_{12})(C_4F_6)]$

(0.15g, 0.28mmol) 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 $[Rh(dpm.C_4F_6)\{(C_7H_{12})(C_4F_6)_2\}]$.

Yield = 0.19g, 79%

<u>M.P.</u>   234-6°C (decomp)

<u>Analysis</u>   Calculated for $C_{30}H_{31}O_2F_{18}Rh$: C, 41.49%; H, 3.60%

                 Found: C, 41.75%; H, 3.80%

<u>Infra-red.</u> 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}<u>H n.m.r.</u> 3.48(s, 1H); 7.35(m, 2H); 7.68-8.40(br, 10H);

8.76(s, 18H).

^{19}<u>F n.m.r.</u> 53.61 (br, 3F); 56.07(br, 12F); 57.54(q, 3F,

$J_{FF}=15.2Hz$).

IV. <u>Treatment of some alkene-alkyne complexes with an excess</u>
     <u>of the alkene.</u>

i) <u>Dipivaloylmethanato(cyclo-octene)(hexafluorobut-2-yne)rhodium(I)</u>

        An excess of cyclo-octene (0.03g, 0.27mmol) was added

to a solution of $[Rh(dpm)(C_8H_{14})(C_4F_6)]$ (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}H n.m.r. spectra.

ii) <u>Dipivaloylmethanato(cycloheptene)(hexafluorobut-2-yne)rhodium(I)</u>

An excess of cycloheptene (0.04g, 0.42mmol) was added

to a solution of $[Rh(dpm)(C_7H_{12})(C_4F_6)]$ (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) <u>Acetylacetonato(cyclo-octene)(hexafluorobut-2-yne)rhodium(I)</u>

An excess of cyclo-octene (0.03g, 0.27mmol) was added

to a solution of $[Rh(acac)(C_8H_{14})(C_4F_6)]$(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) <u>Reactions of alkene-alkyne complexes involving diene formation.</u>

I. <u>Reactions of dipivaloylmethanato(ethene)(hexafluorobut-2-yne)-rhodium(I).</u>

i) <u>With cyclopropane</u>

No reaction occurred when cyclopropane was shaken with

$[Rh(dpm)(C_2H_4)(C_4F_6)]$ 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 $[Rh(dpm)(C_2H_4)(C_4F_6)]$

(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-η-CH$_2$=CHCH$_2$C(CF$_3$)=C(H)CF$_3$)] Yield = 0.22g,85%.

Mass spectrum. m/e = 490(M$^+$)

Analysis. Calculated for C$_{18}$H$_{25}$O$_2$F$_6$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.

^{1}H n.m.r. 4.16(s, 1H); 5.50(m, H$_3$, J$_{3,1}$=8Hz, J$_{3,2}$=6Hz,

J$_{3,5}$=12Hz, J$_{3,6}$=8Hz); 6.38(dxd, H$_1$, J$_{1,2}$=13Hz, J$_{1,3}$=8Hz);

6.75 (d, H$_6$, J$_{6,3}$=8Hz); 6.97(d, H$_5$, J$_{5,3}$=12Hz); 7.49(q, H$_4$,

J$_{4,F}$=11Hz); 7.96(dxd, H$_2$, J$_{2,1}$=13Hz, J$_{2,3}$=6Hz); 8.87(s, 18H).

^{19}F n.m.r. 53.46("quin.", 3F, J$_{FF}$=11.0Hz, J$_{H_4F}$=11.0Hz);

60.48(qxd, 3F, J$_{FF}$=11.0Hz, J$_{RhF}$=1.2Hz).

Proton-proton decoupling experiments (see Figure 1.9)

Irradiated Signal	Affected Signal	Resultant Multiplicity
H$_3$	H$_1$ (dxd)	d (J=13Hz)
	H$_6$ (d)	s
	H$_5$ (d)	s
H$_6$	No obvious change	
H$_5$	No obvious change	
H$_2$	H$_1$(dxd)	d (J=6Hz)

ii) **With propene**

An excess of propene (1.0cm^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

[Rh(dpm)(1,2,4,5-η-CH$_2$=CHCH$_2$C(CF$_3$)=C(H)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

[Rh(dpm)(1,2,4,5-η-CH$_2$=C(CH$_3$)C{=C(CH$_3$)$_2$}C(CF$_3$)=C(H)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, 500w, 491w, 438w, 413w, 386w, 309w.

^{1}H n.m.r. 4.19(s, 1H); 6.74(s, 1H); 7.37(d, 1H, J_{RhH}=2.4Hz);

7.64(qxd, 1H, J_{HF}=9.0Hz, J_{RhH}=2.4Hz); 7.85(s,3H); 8.40(s,3H);

8.46(s,3H); 8.89(s, 9H); 8.91(s, 9H).

^{19}F n.m.r. 52.52(q, 3F, J_{FF}=9.0Hz); 53.86 ("quin"., 3F,

J_{FF}=9.0Hz, J_{HF}=9.0Hz).

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

i) With cyclopropane

     An excess of cyclopropane (1.0cm^3) was condensed (-196°C)

on to a solution of [Rh(dpm)(C$_8$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 [Rh(dpm)(1,2,4,5-η-CH$_2$=CHCH$_2$C(CF$_3$)=C(H)CF$_3$)]

by comparing its i.r. and ^{1}H n.m.r. spectra with those of the

complex prepared in (B)I(i). Yield=0.08g. 91%.

ii) With tetramethylallene

     Tetramethylallene (0.03g, 0.27mmol) was added to a

solution of [Rh(dpm)(C$_8$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 [Rh(dpm)(1,2,4,5-η-CH$_2$=C(CH$_3$)C=C(CH$_3$)$_2$C(CF$_3$)=C(H)CF$_3$)]

identified by comparing their ^{1}H 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 (1.0cm^3) was condensed

(-196°C) on to a solution of [Rh(dpm)(C$_7$H$_{12}$)(C$_4$F$_6$)]

(0.05g, 0.09mmol) in diethyl ether, contained in a

Carius tube. The tube was sealed and placed in an oven

at 60°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

[Rh(dpm)(1,2,4,5-η-CH$_2$=CHCH$_2$C(CF$_3$)=C(H)CF$_3$)] by comparing

its ^{1}H n.m.r. spectrum with that of the complex prepared

in (B)I(i). Yield = 0.04g, 95%.

ii)   With tetramethylallene

        Tetramethylallene (0.009g, 0.09mmol) was added to

a solution of [Rh(dpm)(C$_7$H$_{12}$)(C$_4$F$_6$)](0.05g, 0.09mmol) in

diethyl ether, and stirred for 24 hours. Evaporation of

the solvent gave an orange-yellow solid which was identified

as [Rh(dpm)(1,2,4,5-η-CH$_2$=C(CH$_3$)C{=C(CH$_3$)$_2$}C(CF$_3$)=C(H)CF$_3$)]

by comparing its ^{1}H n.m.r. spectrum with that of the

complex prepared in (B)I(iii). Yield = 0.04g, 80%.

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

i)   With tetramethylallene

        Tetramethylallene (0.05g, 0.52mmol) 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 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

$[Rh(acac)(1,2,4,5-\eta-CH_2=C(CH_3)C\{=C(CH_3)_2\}C(CF_3)=C(H)CF_3)]$
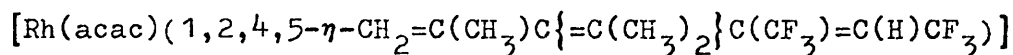
Yield = 0.19g, 81%.

M.P.   130-1°C

Analysis   Calculated for $C_{16}H_{19}O_2F_6Rh$:   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 [Rh(dpm)(1,2,4,5-η-CH$_2$=CHCH$_2$C(CF$_3$)=C(H)CF$_3$)]
      with triphenylphosphine.

        Triphenylphosphine (0.05g, 0.20mmol) was added to a

      solution of [Rh(dpm)(1,2,4,5-η-CH$_2$=CHCH$_2$C(CF$_3$)=C(H)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
      [Rh(dpm)(1,2,4,5-η-CH$_2$=C(CH$_3$)C{=C(CH$_3$)$_2${C(CF$_3$)=C(H)CF$_3$)]
      with carbon monoxide.

        Carbon monoxide was passed slowly through a solution of

      [Rh(dpm)(1,2,4,5-η-CH$_2$=C(CH$_3$)C{=C(CH$_3$)$_2${C(CF$_3$)=C(H)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 [Rh(dpm)(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 [Rh(acac)(C$_2$H$_4$)(C$_4$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

      [Rh(acac)(PPh$_3$)$_2$(C$_4$F$_6$)].   Yield = 0.36g, 79%.

M.P.   127-8°C

Analysis   Calculated for $C_{45}H_{37}O_2P_2F_6Rh$: 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_2Cl_2) 2.60(m,30H); 4.67(s, 1H); 8.27(s, 6H).

^{19}F n.m.r. (in CD_2Cl_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 $[Rh(acac)(C_2H_4)(C_4F_6)]$ (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 $[Rh(acac)(AsPh_3)_2(C_4F_6)]$ Yield = 0.39g, 78%.

M.P.   151-2°C.

Analysis   Calculated for $C_{45}H_{37}O_2As_2F_6Rh$: 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).

^{19}F n.m.r. (in CH_2Cl_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) <u>With triphenylstibine</u>

Triphenylstibine (0.09g, 0.26mmol) was added to a

solution of [Rh(acac)(C$_2$H$_4$)(C$_4$F$_6$)] (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)(SbPh$_3$)$_2$(C$_4$F$_6$)]. Yield = 0.11g, 75%.

<u>M.P.</u>   98-100°C (decomp.)

<u>Analysis</u>   Calculated for C$_{45}$H$_{37}$O$_2$Sb$_2$F$_6$Rh: C, 50.48%; H, 3.49%

Found: C, 50.67%; H, 3.80%

<u>Infra-red</u> 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.

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

^{19}F n.m.r. (room temperature) 52.57 (d,J$_{RhF}$=2.0Hz)

(-28°C) 52.12(s, 3F); 53.43(s, 3F).

iv) <u>With methyldiphenylphosphine</u>

Methyldiphenylphosphine (0.204g, 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. Slow

evaporation of the solvent and careful addition of methanol

gave yellow microcrystals which were identified as

[Rh(acac)(PPh$_2$Me)$_2$(C$_4$F$_6$)]. Yield = 0.38g, 97%.

<u>M.P.</u>   113-4°C.

<u>Analysis</u>   Calculated for C$_{35}$H$_{33}$O$_2$P$_2$F$_6$Rh: C,54.98%; H, 4.36%

Found: C,55.03%; H, 4.49%

<u>Infra-red</u> 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 acetylacetonatobis(triphenylphosphine)-
(hexafluorobut-2-yne)rhodium(I) with carbon monoxide.

Carbon monoxide was passed slowly through a solution

of [Rh(acac)(PPh$_3$)$_2$(C$_4$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, 85%.

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}=9Hz); 8.46(d, 3H, J_{PH}=9Hz); 8.84(s,9H); 9.23(s, 9H).

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

ii)   **With ethyldiphenylphosphine**

Ethyldiphenylphosphine (0.09g, 0.42mmol) was added to a solution of $[Rh(dpm)(C_2H_4)(C_4F_6)]$(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 $[Rh(dpm)(PPh_2Et)_2(C_4F_6)]$. Yield = 0.14g, 76%.

M.P.   98-99°C.

Analysis   Calculated for $C_{43}H_{49}O_2F_6P_2Rh$: 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}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}F n.m.r. 50.66(d, br, 3F, $J_{PF} \approx 11$Hz); 53.01(s, 3F).

iii) **With tricyclohexylphosphine**

Tricyclohexylphosphine (0.12g, 0.42mmol) was added

to a solution of $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (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

$[Rh(dpm)\{P(C_6H_{11})_3\}(C_4F_6)]$. Yield = 0.14g, 91%.

M.P.   184-6°C.

Analysis   Calculated for $C_{33}H_{52}O_2F_6$PRh: C, 54.39%; H, 7.19%

            Found: C, 54.23%; 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}H n.m.r. 4.21(s, 1H); 8.15(m, 33H); 8.87(s, 18H).

^{19}F n.m.r. 52.34(d, J_{RhF}=2.1Hz).

The same complex was subsequently prepared by the

reaction of one molar equivalent of tricyclohexylphosphine

with $[Rh(dpm)(C_2H_4)(C_4F_6)]$, giving a similar yield.

iv) With triphenylphosphine

Triphenylphosphine (0.055g, 0.21mmol) was added to a solution of [Rh(dpm)(C_2H_4)(C_4F_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 [Rh(dpm)(PPh_3)(C_4F_6)].

Yield = 0.14g, 90%.

M.P.   166-7°C.

Analysis   Calculated for $C_{33}H_{34}O_2F_6PRh$: 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}H n.m.r. 2.46(m, 15H); 4.17(s, 1H); 8.92(s, 9H); 9.22(s, 9H).

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

v)   With triphenylarsine

Triphenylarsine (0.04g, 0.21mmol) was added to a solution of [Rh(dpm)(C_2H_4)(C_4F_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 [Rh(dpm)($AsPh_3$)(C_4F_6)].

Yield = 0.13g, 82%.

M.P.   139-41°C.

Analysis   Calculated for $C_{33}H_{34}O_2AsF_6Rh$: 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}H n.m.r. 2.64(m, 15H); 4.24(s, 1H); 8.96(s, 9H); 9.18(s, 9H).

^{19}F n.m.r. 54.03(d, J_{RhF}=1.6Hz).

vi) With triphenylstibine

Triphenylstibine (0.12g, 0.32mmol) was added to a solution of [Rh(dpm)(C$_2$H$_4$)(C$_4$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 [Rh(dpm)(SbPh$_3$)$_2$(C$_4$F$_6$)] by its i.r. spectrum and m.p.

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

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

i) With triphenylphosphine

Triphenylphosphine (0.047g, 0.18mmol) was added to a solution of [Rh(dpm)(C$_8$H$_{14}$)(C$_4$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 $[Rh(dpm)(PPh_3)(C_4F_6)]$, 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 $[Rh(dpm)(C_7H_{12})(C_4F_6)]$ (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 $[Rh(dpm)(PPh_3)(C_4F_6)]$ 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 $[Rh(dpm)(C_7H_{12})(C_4F_6)]$ (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 $[Rh(dpm)(AsPh_3)(C_4F_6)]$ by comparing its i.r. spectrum with that of the complex prepared in (C)II(v). Yield = 0.28g, 86%.

V Reactions of dipivaloylmethanato(triphenylarsine)-
(hexafluorobut-2-yne)rhodium(I)

i) With tetrafluoroethene

An excess of tetrafluoroethene ($1.0cm^3$) was condensed
(-196°C) on to a solution of $[Rh(dpm)(AsPh_3)(C_4F_6)]$
(0.20g, 0.27mmol) in diethyl ether contained in a $50cm^3$
"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 $[Rh(dpm)(AsPh_3)(C_2F_4)]$ by their i.r.
spectrum and m.p.   Yield = 0.15g, 80%.

ii) With hexafluorobut-2-yne

An excess of hexafluorobut-2-yne ($1.0cm^3$) was
condensed (-196°C) on to a solution of $[Rh(dpm)(AsPh_3)(C_4F_6)]$
(0.10g, 0.13mmol) 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
$[Rh\{C(CF_3)=C(CF_3)-C(CF_3)=C(CF_3)\}(dpm)(AsPh_3)]$ by its i.r.
spectrum and m.p.   Yield = 0.09g, 76%.

VI Reaction of dipivaloylmethanatobis(triphenylstibine)-
(hexafluorobut-2-yne)rhodium(I)

i) With hexafluorobut-2-yne

An excess of hexafluorobut-2-yne (1.0cm^3) was

condensed (-196°C) on to a solution of

[Rh(dpm)(SbPh$_3$)$_2$(C$_4$F$_6$)] (0.30g, 0.26mmol) 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

[Rh{C(CF$_3$)=(C(CF$_3$)C(CF$_3$)=C(CF$_3$)}(dpm)(SbPh$_3$)] by their

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

(D) Reactions of pyridines with [Rh(dpm)(C$_2$H$_4$)(C$_4$F$_6$)]
and with [Rh(dpm)(C$_2$F$_4$)(C$_2$F$_4$)]

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

i) With pyridine

Pyridine (0.05g, 0.64mmol) was added to a solution

of [Rh(dpm)(C$_2$H$_4$)(C$_4$F$_6$)] (0.15g, 0.31mmol) in diethyl

ethyl. 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$_2$CH$_2$C(CF$_3$):C(CF$_3$)}(dpm)(C$_5$H$_5$N)$_2$].
Yield = 0.08g, 40%.

M.P.   48-9°C

Analysis   Calculated for $C_{27}H_{33}N_2O_2F_6Rh$:

                        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.

^1H 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. $112\text{-}4^\circ\text{C}$.

Analysis   Calculated for $C_{29}H_{37}N_2O_2F_6Rh$:

                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 2.88m (8H);

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 $[Rh(dpm)(C_2H_4)(C_4F_6)]$ (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 $[Rh\{\overline{CH_2CH_2C(CF_3)}\text{=}C(CF_3)\}(dpm)(3,5\text{-}(CH_3)_2C_5H_3N)_2]$

Yield = 0.23g, 79%.

M.P. $131\text{-}2^\circ\text{C}$.

Analysis: Calculated for $C_{31}H_{41}N_2O_2F_6Rh$:

                C, 53.92%; H, 5.98%; 4.05%

        Found: C, 53.75%; H, 5.76%; 4.06%

Infra-red. 1601m, 1589s, 1568s, 1554m, 1532s, 1500s, 1413s,

1327m, 1278s, 1243s, 1222s, 1196m, 1155s, 1146s, 1137s, 1120s,

1095s, 1062w, 1046w, 974w, 955w, 933w, 901w, 867w, 861w,

825w, 792w, 766w, 755w, 724w, 705m, 675w, 650w, 609w, 561w,

540w, 500w, 489w, 425w.

^{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}=12.7Hz); 58.26

(7 lines, 3F, J_{FF}=12.7Hz).

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

i)   With pyridine

     Pyridine (0.076g, 0.96mmol) was added to a solution of

[Rh(dpm)(C_2H_4)(C_2F_4)] (0.20g, 0.48mmol) 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_2F_4)], by analogy with the known complex

[Rh(acac)(py)$_2$(C_2F_4)]. Yield = 0.20g, 77%.

M.P.   122-40°C (decomp.)

Analysis   Calculated for $C_{23}H_{29}N_2O_2F_4Rh$:   C, 50.75%; H, 5,37%.

           Found: C, 50.98%; H, 5.41%.

Infra-red. 1609w, 1601w, 1587s, 1568s, 1550s, 1529s, 1500s,

1410s, 1249w, 1229m, 1220m, 1196m, 1155w, 1140w, 1092s, 1070m,sh,

1061s, 1042s,sh, 1039s, 1013w, 1002w, 980w, 936w, 829s, 791w,

782w, 764m, 759m,sh, 725w, 701m, 693m, 679w, 669w, 653w,br,

630w, 610w, 503w, 487w, 424w, 375w.

^{1}H n.m.r. 1.50(d), 1.76(d), 2.42(m) and 2.88(m) (10H);

4.62(s, 1H); 8.91(s, 9H), 9.02(s, 9H).

^{19}F n.m.r. 64.69, 66.25, 67.75, 69.06 (AB pattern,

J_{FF}=135Hz, $\Delta\nu$= 241Hz).

III   Reactions with triphenylphosphine and with carbon monoxide.

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

Triphenylphosphine (0.06g, 0.23mmol) was added to a solution of [Rh{CH$_2$CH$_2$C(CF$_3$)=C(CF$_3$)}(dpm)(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 [Rh{CH$_2$CH$_2$C(CF$_3$)=C(CF$_3$)}(dpm)(py)(PPh$_3$)].

Yield = 0.12g, 64%.

M.P.   136-8°C.

Analysis   Calculated for C$_{40}$H$_{43}$NO$_2$F$_6$PRh:

C, 58.76%; H, 5.30%; N, 1.71%.

Found: C, 58.65%; H, 5.45%; N, 1.85%.

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.

^{1}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 n.m.r. 53.85(m, 3F); 60.46(q, 3F, J_{FF}=13.1Hz).

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

ii)   Treatment of [Rh{CH$_2$CH$_2$C(CF$_3$)=C(CF$_3$)}(dpm)(py)$_2$] with
carbon monoxide.

Carbon monoxide was passed slowly through a solution

of [Rh CH$_2$CH$_2$C(CF$_3$)=C(CF$_3$)(dpm)(py)$_2$] (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$_2$H$_4$)$_2$] (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^3) was condensed (-196°C)

on to a solution of [Rh(hfacac)(C$_2$H$_4$)$_2$] (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) <u>With hex-3-yne</u>

An excess of hex-3-yne (0.10g, 1.22mmol) was added to a solution of $[Rh(hfacac)(C_2H_4)_2]$ (0.20g, 0.55mmol) 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

REACTIONS OF HEXAFLUOROPROPANONE WITH ALKYNEDIOL COMPLEXES

OF PLATINUM(0).

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, $K[PtCl_3(C_2H_4)].H_2O$, was isolated by Zeise, in

1827^1. 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 $[Pt(R^1R^2C(OH)C\equiv CC(OH)R^1R^2)_2]$, complexes

(I), have been synthesised by treating an aqueous

ethanolic solution of potassium tetrachloroplatinite

with the appropriate alkyne,^{2,3} as shown in Figure 2.1.

$$K_2PtCl_4 \quad + \quad R^1R^2C(OH)C\equiv CC(OH)R^1R^2 \longrightarrow \Big\downarrow EtOH$$

$$[Pt(R^1R^2C(OH)C\equiv CC(OH)R^1R^2)_2]$$

(I)

a) $R^1 = CH_3$, $R^2 = C_2H_5$ d) $R^1 = CH_3$, $R^2 = C_5H_{11}$

b) $R^1 = R^2 = C_2H_5$ e) $R^1 = C_2H_5$, $R^2 = C_4H_9$

c) $R^1 = CH_3$, $R^2 = C_3H_7$ f) Alkyne =
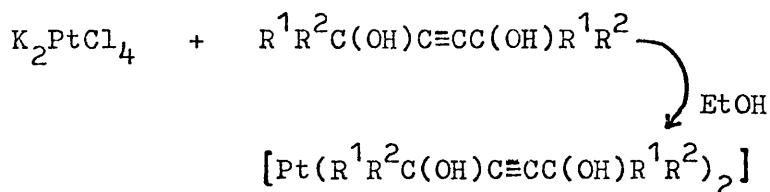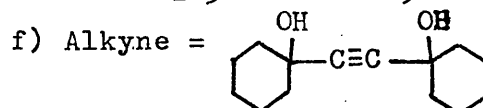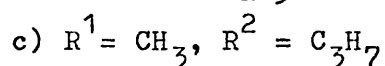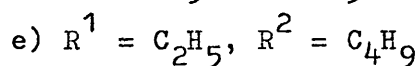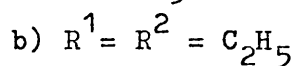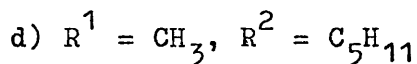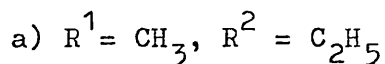
Figure 2.1

The X-ray crystal structure of complex (Ib) has been determined,[4] showing that the co-ordination at the platinum atom is essentially tetrahedral, with the two alkyne ligands being mutually perpendicular :

(Ib)
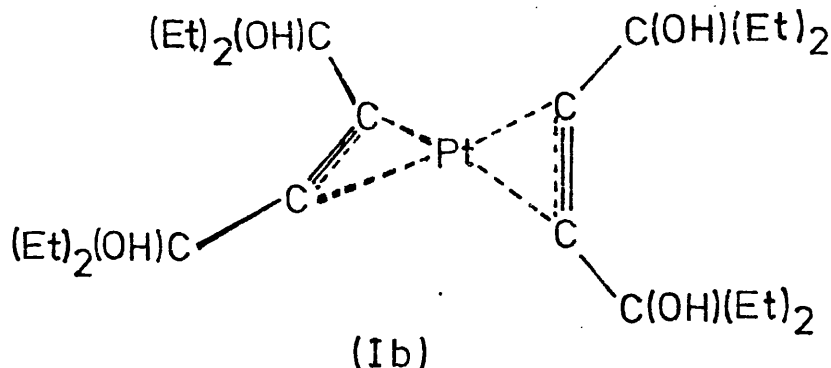
b) <u>Complexes of the type $[Pt(ac)L_2]$</u>

Most zerovalent platinum-alkyne complexes are of the general formula $[Pt(ac)L_2]$, where L is a phosphine ligand. These can be prepared by the reduction of an ethanolic suspension of <u>cis</u>-$[PtCl_2(PR_3)_2]$, 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 :

cis-$[PtCl_2(PPh_3)_2]$ $\xrightarrow{H_2NNH_2}$ $[PtHCl(PPh_3)_2]$

$\Bigg\downarrow H_2NNH_2$

$[Pt(ac)(PPh_3)_2]$ $\xleftarrow{\text{ac}}$ $[Pt(PPh_3)_2]$
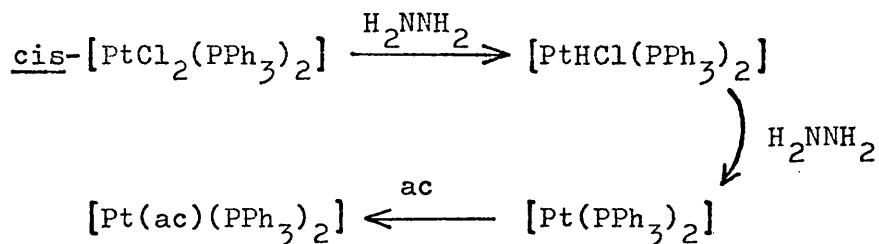
Figure 2.2

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;[6] 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,[7] and usually vinyl complexes are produced.[8-12]

The more likely mechanism is shown in Figure 2.3.[13]

The X-ray crystal structure of the bridged intermediate

showed it to be a mixture of complexes (II) and (III)[6].

The fact that hydroxyalkynes do not react with

complex III,[13] although the hydroxyalkyne complexes
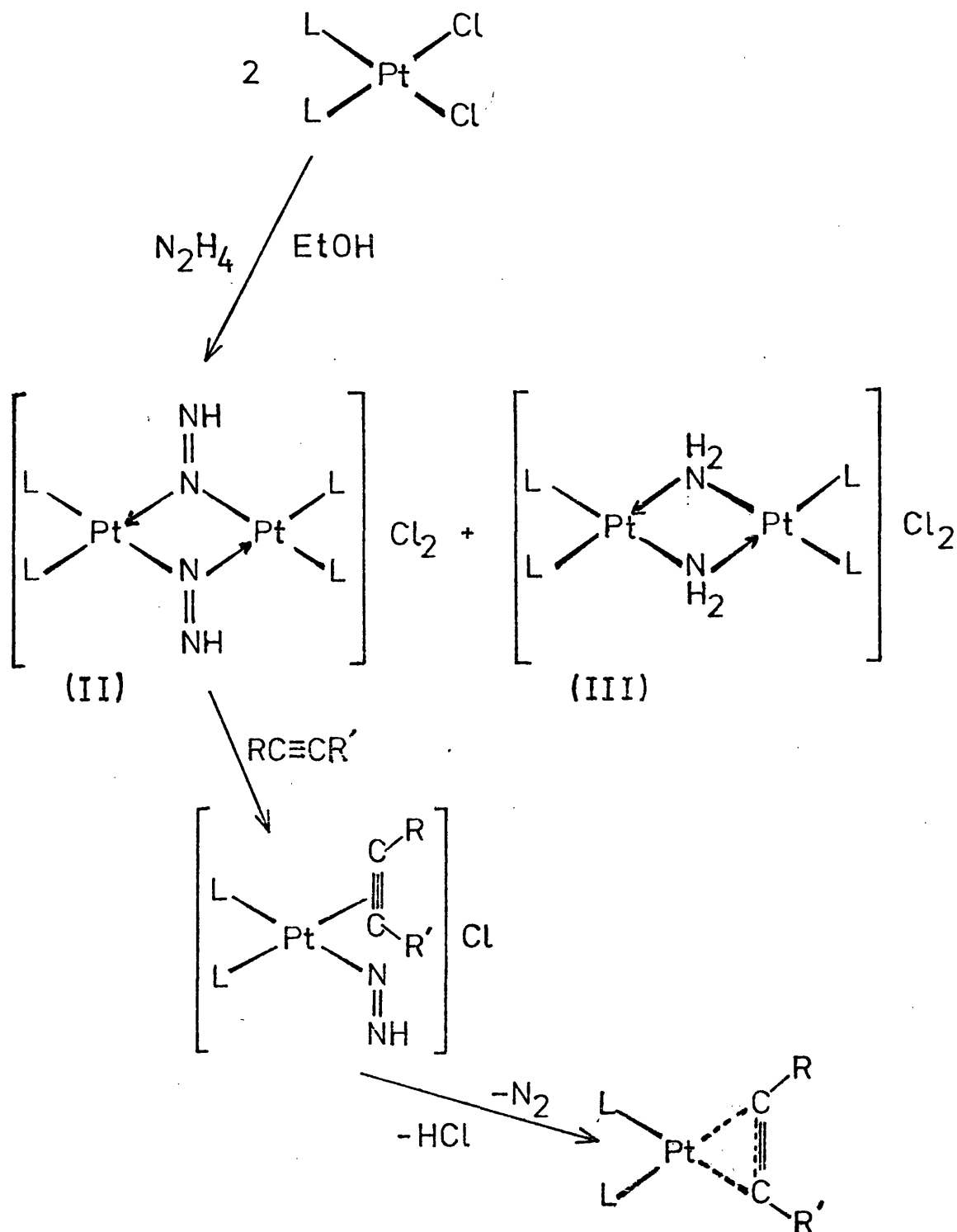
Figure 2.3

$[Pt(ac)(PPh_3)_2]$ 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.[14-19] It did not work, however, for $[PtCl_2(PBu_3)_2]$ or $[PtCl_2(PPh_2Me)_2]$.[16]
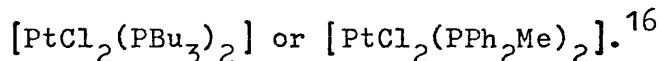
(ii) Ligand exchange in platinum(0) complexes

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

The complex $[Pt(PhC_2Ph)_2]$ has been synthesised from $[Pt(cod)_2]$ 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 $\overline{Pt-C=C}$ planes being $82°$.

b) Complexes of the type $[Pt(ac)L_2]$.

The complexes $[Pt(PR_3)_4]$[21] and $[Pt(PR_3)_3]$[21,22] are commonly used as starting materials in the preparation of complexes of the type $[Pt(ac)L_2]$. The exchange of ligands occurs readily due to the dissociation of phosphines, in solution:[23,24]

$$[Pt(PPh_3)_4] \underset{}{\overset{K_1}{\rightleftharpoons}} [Pt(PPh_3)_3] + PPh_3 \qquad K_1 \text{ large}$$

$$[Pt(PPh_3)_3] \underset{}{\overset{K_2}{\rightleftharpoons}} [Pt(PPh_3)_2] + PPh_3 \qquad K_2 = (1.6\pm1)\times10^{-4}$$
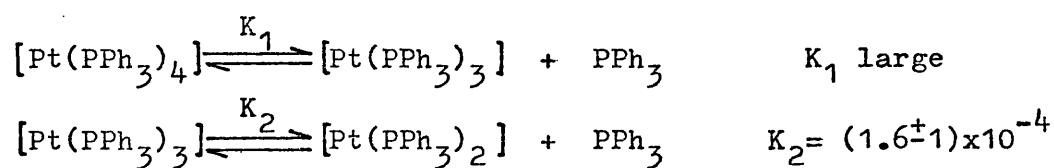
Hydroxyalkynes have been found to react with $[Pt(PPh_3)_4]$ to give two types of complex,[13] as shown in Figure 2.4. An excess of a bulky terminal alkyne gave complexes of type (V), while complexes (IV) were isolated from reactions with less bulky alkynes. The reaction with 1-ethynylcyclohexanol gave both complexes (IV) and (V),[13] and a single crystal X-ray study on the complex (IV)[25] confirmed that the alkyne is η^2-bonded.

A single crystal X-ray study of the complex of

type (V)[26] showed it to be a <u>trans</u> bis-alkynyl complex,

$$[PtL_4] \rightleftharpoons [PtL_3] + L$$

$$[PtL_3] + RC\equiv CH$$

(V)

[L=PPh₃]

(IV)
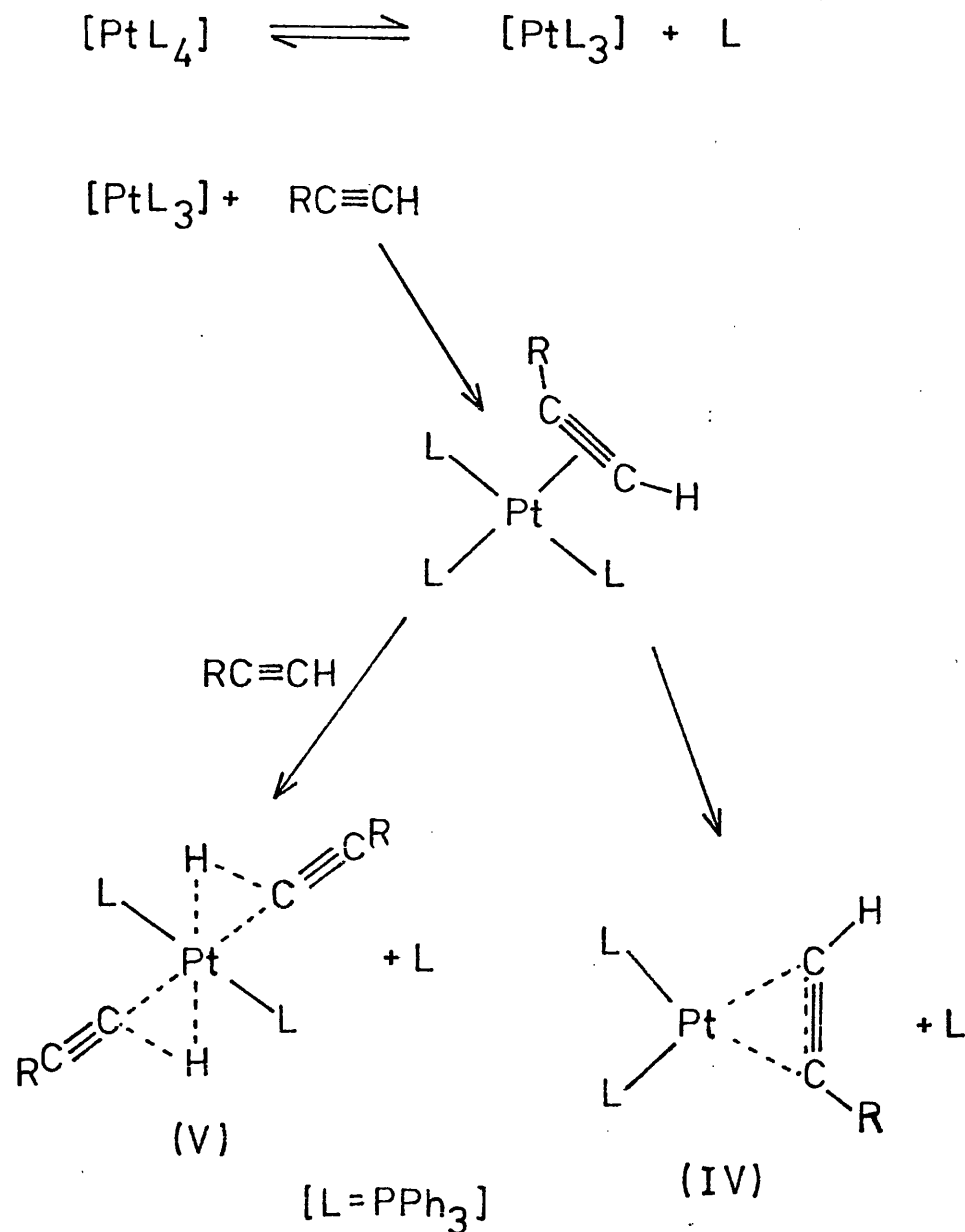
Figure 2.4

but the hydrogen atoms were not located. Evidence

for the platinum(IV) dihydride formulation is provided

by the ¹H n.m.r. spectrum[13] where a signal is seen

at 22.88τ, the region associated with metal hydride

species.

Using a similar method, the two cyclo-alkyne

a) n = 4

b) n = 5

c) n = 6

(VI)
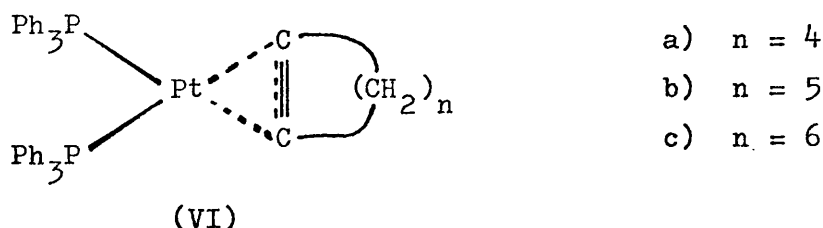
complexes (VIa) and (VIb) have been prepared by the

reactions of 1,2-dibromocyclohexene and

1,2-dibromocycloheptene respectively, with a sodium

amalgam in thf.,in the presence of $[Pt(PPh_3)_3]$.[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 cis-$[PtCl_2(PPh_3)_2]$,

in the presence of cyclo-octyne.[29]

An alternative ligand exchange method involves

platinum(0) complexes of the type $[Pt(alkene)(PPh_3)_2]$

or $[Pt(alkyne)(PPh_3)_2]$. Such reactions include, for

example, the displacement of co-ordinated ethene from

$[Pt(C_2H_4)(PPh_3)_2]$: [30]

$$[PtO_2(PPh_3)_2] \quad + \quad C_2H_4 \quad \xrightarrow{\text{NaBH}_4} \quad [Pt(C_2H_4)(PPh_3)_2]$$

$$\big\downarrow \text{PhC} \equiv \text{CPh}$$

$$[Pt(PhC_2Ph)(PPh_3)_2]$$
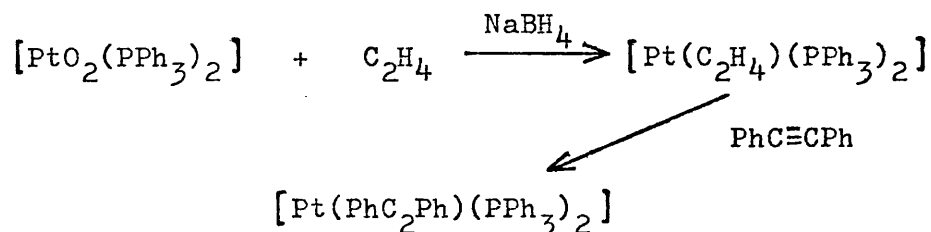
Similarly, alkene[31] and alkyne[32] complexes of platinum(0)

have been prepared by the displacement of trans-stilbene

from $[Pt(\underline{trans}\text{-}PhC(H)C=C(H)Ph)(PPh_3)_2]$. Likewise,

using an alkyne complex:[33]

$$[Pt(PhC_2H)(PPh_3)_2] \xrightarrow[70^\circ C]{F_3CC\equiv CF_3} [Pt(F_3CC\equiv CCF_3)(PPh_3)_2]$$
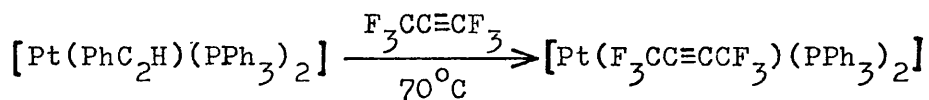
In a series of displacement reactions,[5] the

stability of the complexes $[Pt(alkyne)(PPh_3)_2]$ was

shown to increase in the order:

$$HC\equiv CH < RC\equiv CH < RC\equiv CR \sim PhC\equiv CH < PhC\equiv CPh < C_2(C_6H_4NO_2\text{-}\underline{p})_2$$

$$(R = alkyl)$$
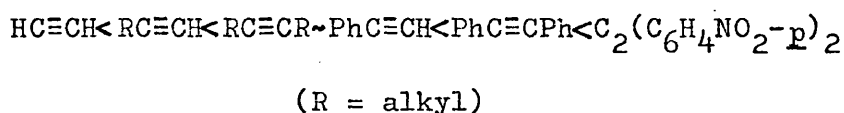
Usually, co-ordinated alkynes cannot be displaced

by alkenes, but exceptions to this behaviour arise

with electronegative alkenes, for example, with

tetracy anoethene (TCNE)[34]:

$$[Pt(PhC_2Ph)(PPh_3)_2] \xrightarrow{TCNE} [Pt(TCNE)(PPh_3)_2]$$
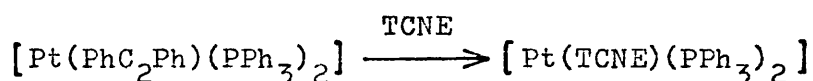
and with tetrafluoroethene (see Section 2 of this

chapter):

$$[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2] \xrightarrow{C_2F_4} [Pt(C_2F_4)(PPh_3)_2]$$
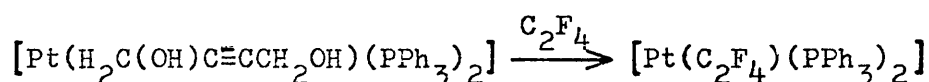
The mechanism first proposed[14] for these

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 $[Pt(PPh_3)_2]$[35] and its
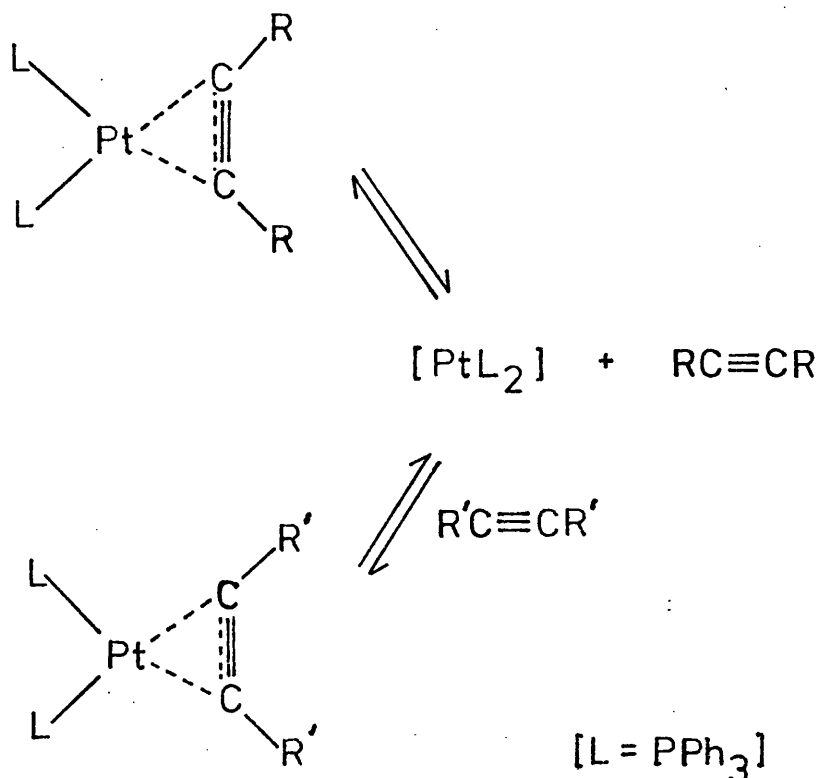
Figure 2.5

reaction with alkynes to give the complexes

$[Pt(alkyne)(PPh_3)_2]$[36]
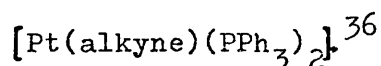
However, ^1H n.m.r. studies on $[Pt(PhC_2Me)(PPh_3)_2]$[37]

and later, on $[Pt(D_5C_6C\equiv CH)\{P(C_6D_5)_3\}_2]$,[38] showed no

indication of rotation or dissociation of the

co-ordinated alkyne, in solution. An alternative

mechanism for ligand exchange was therefore proposed,[38]

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 $90°$ about the platinum-alkyne bond.

The incoming alkyne can then be accommodated in a
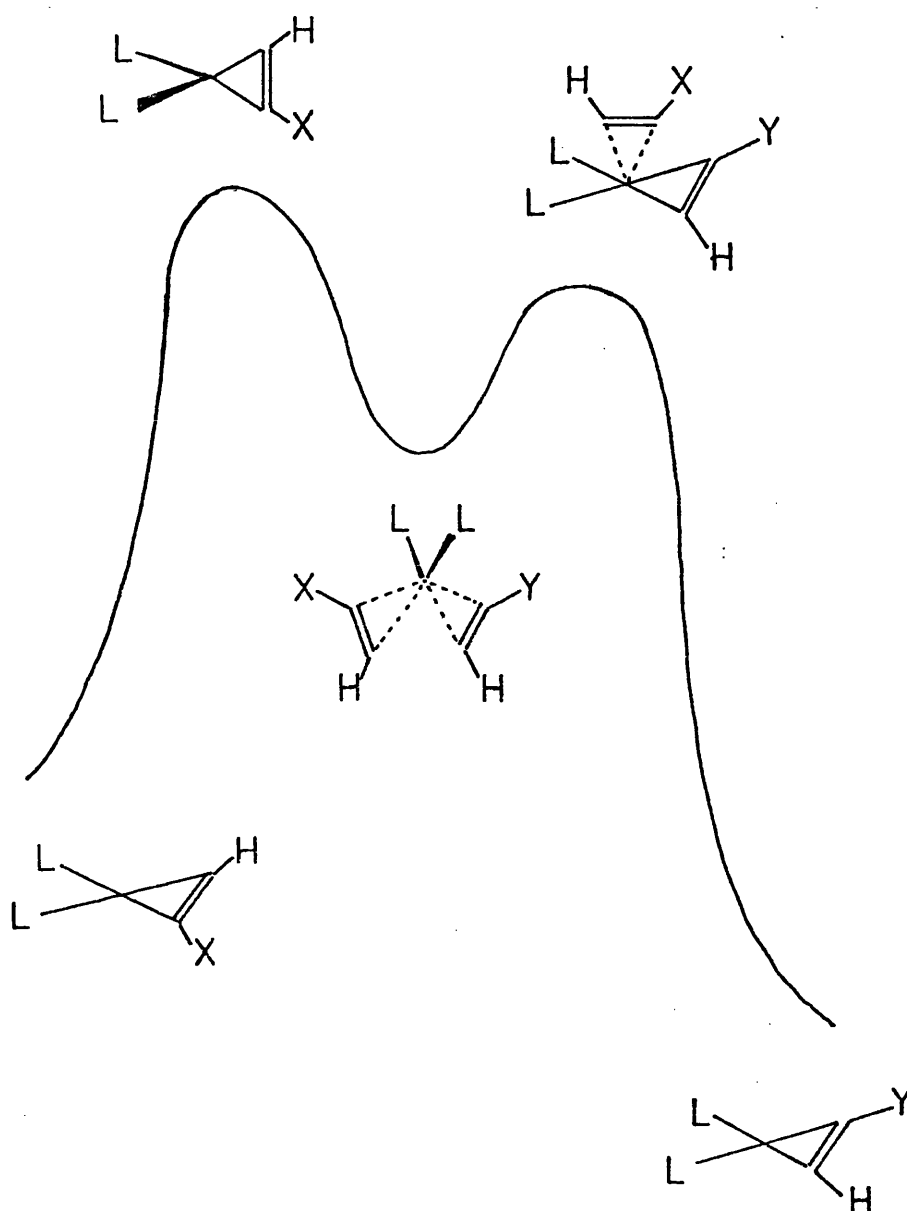
Figure 2.6

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 σ-π scheme first proposed by Dewar[39] for silver(I) alkene complexes, and later extended by Chatt and Duncanson[40] 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.[41]

The theory involves a σ-type bond formed from the overlap of a filled π 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 σ bond is supplemented by π back-donation of charge from a filled non-bonding metal d-orbital to an empty π^* antibonding orbital on the alkyne. Figure 2.7(A) illustrates this synergic bonding and shows (B) how π-type bonding is also possible out of the xy plane, for alkynes, due to their having two orthogonal π 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 C≡C stretching frequency observed in the infra-red spectrum).

TOP VIEW

A

SIDE VIEW

B
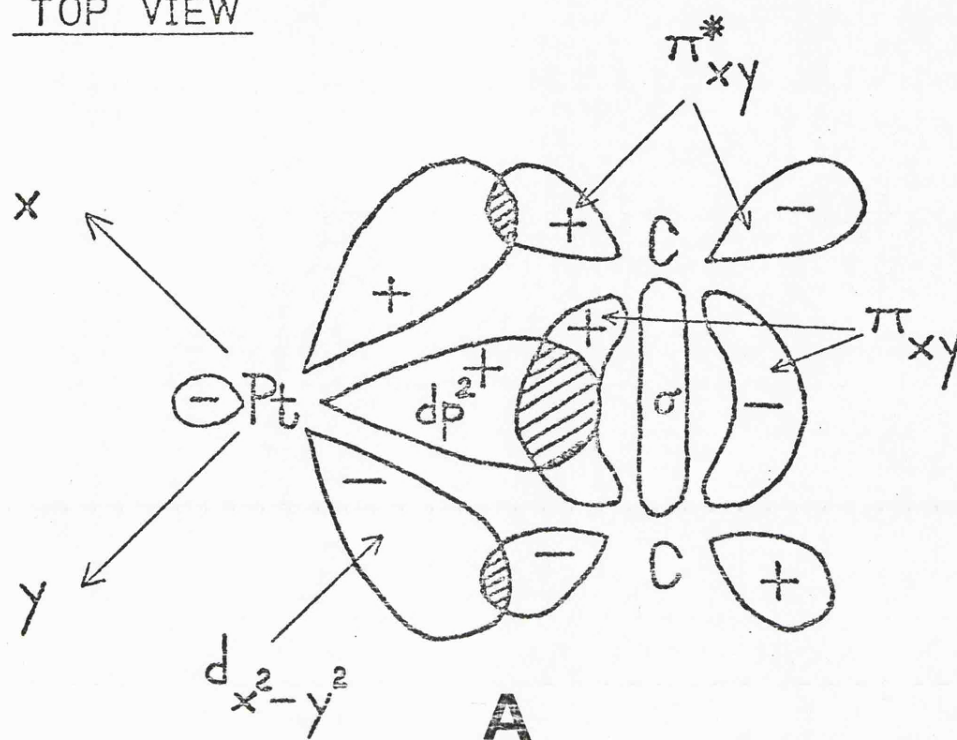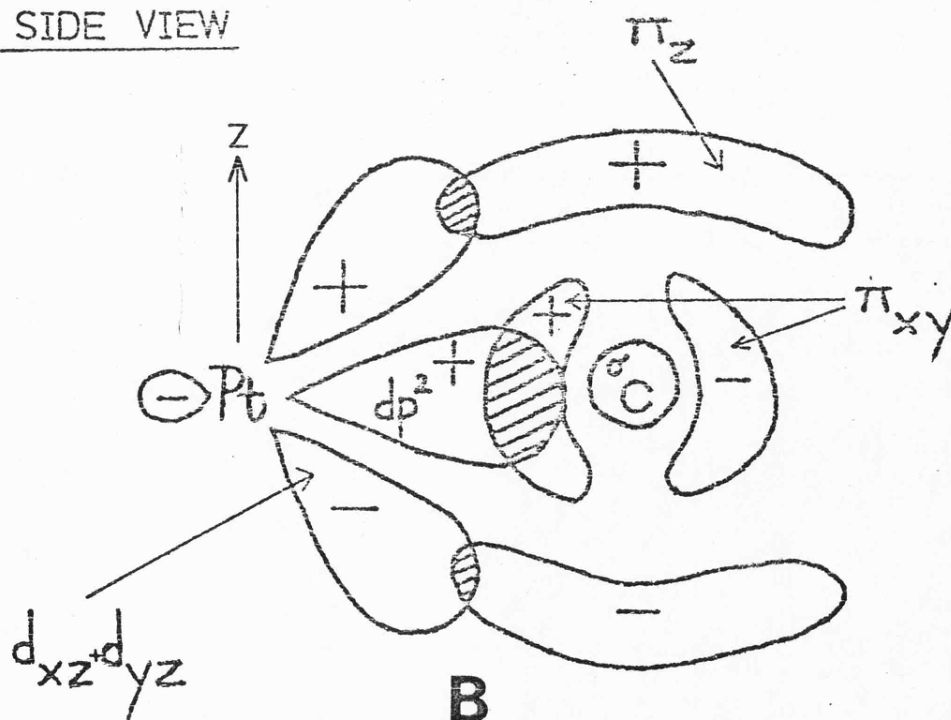
Figure 2.7

. (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 alkynic bond,

together with the observed change in geometry

suggests a change in orbital hybridisation from

sp towards sp^2 at the alkynic 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 σ and π 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 alkynic 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 π^* antibonding

orbital, together with the donation of electrons from

its π bonding orbital, reduces the bond order.

For unco-ordinated alkynes, the stretching frequency

occurs in the region $2000-2400 cm^{-1}$, and can be lowered

by as much as $600 cm^{-1}$ on co-ordination.

For platinum(II) complexes of the type

$[PtCl_2X(RC \equiv CR')]$, (X=Cl, amine, for example), the

C≡C stretch appears as a weak band, lowered by up

to $200cm^{-1}$ from that of the free alkyne. For these

complexes, it is proposed that the σ component of the

bonding model is important, but that π 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

observation of ν(C≡C) in the infra-red spectrum.

In platinum(0) complexes of the type $[Pt(RC \equiv CR')L_2]$,

(L=phosphine, for example), the stretching frequency can

be lowered by up to $600cm^{-1}$, due to a much higher

degree of back-bonding to the π* 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

A   B
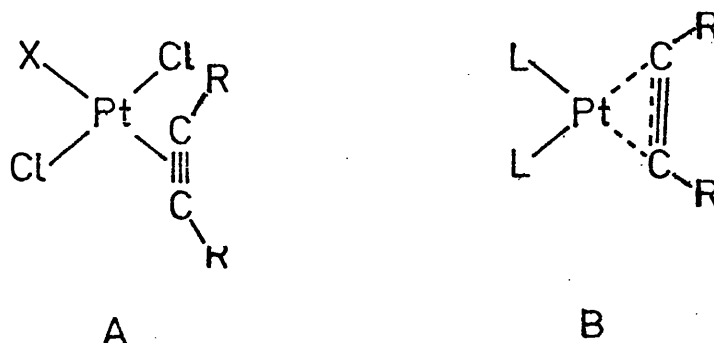
Figure 2.8

can be seen that in case B, the most extreme

representation of the bonding is a platinacyclopropene

system.

Table 2.1 presents the infra-red $C\equiv C$ stretching

frequencies for some alkyne complexes of platinum,

together with the values of $\Delta\nu(C\equiv C),[\Delta\nu(C\equiv C)=$

$\nu(C\equiv C)$(free alkyne)- $\nu(C\equiv C)$(co-ordinated alkyne)] .

As indicated above, the change in stretching frequency,

$\Delta\nu(C\equiv C)$, is often taken as an approximate quantitative

indication of the metal-alkyne bond strength.

Table 2.1

Alkyne stretching frequencies for platinum-alkyne complexes

	$\nu(C\equiv C)(cm^{-1})$	$\Delta\nu(cm^{-1})$	Reference
$K[PtCl_3(ac)]$; ac =			
$Me_2C(OH)C\equiv CCMe_2OH$	2010	38	42
$^tBuC\equiv CC(Me)_2OH$	2008	65	42
$[Pt(ac)(PPh_3)_2]$; ac=			
$HC\equiv CCMe_2OH$	1681	433	13
$HC\equiv CC(Me)(Et)OH$	1670	455	13
$HC\equiv CPh$	1675	445	16,33
$PhC\equiv CPh$	$1768,1740^a$	469	16
$F_3CC\equiv CCF_3$	1755	425	16,33
$NCC\equiv CCN$	1683	535	43

a. $\nu(C\equiv C)$ taken as the mean of the two observed values.

The metal-alkyne bond is stabilised, therefore, by strongly σ-donating ligands, which facilitate back-donation from the metal to the alkyne, and likewise, electronegative alkynes encourage greater π-type back-donation. This explains the stability series for $[Pt(ac)L_2]$ complexes,[5] 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.[44]

All $[Pt(alkyne)L_2]$ complexes have approximately planar geometry and the triple bond is lengthened from that of unco-ordinated alkynes ($1.204\text{\AA}$, on average[45]). The geometry of the distorted alkynes is cis, as suggested by theoretical considerations.[46-48]

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

Table 2.2

$C\equiv C$ bond lengths for platinum-alkyne complexes

Complex	Bond length ($\text{\AA}$)	Reference
$[Pt(ac)(PPh_3)_2]$; ac=		
$NCC\equiv CCN$	1.40	49
$F_3CC\equiv CCF_3$	1.255	45
$PhC\equiv CPh$	1.32	50
$K[PtCl_3(ac)]$; ac=		
$Et_2C(OH)C\equiv CCEt_2OH$	1.18	51
$[Pt(ac)_2]$; ac=		
$Et_2C(OH)C\equiv CCEt_2OH$	1.35	4
$PhC\equiv CPh$	1.28	20

The complexes $[Pt(alkyne)_2]$[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) N.m.r. spectroscopy

Complexes containing terminal alkynes show a

signal in their [1]H n.m.r. spectra in the range

~3.2 to 3.8τ, [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 n.m.r.

techniques, but the evidence suggests that for the

complexes $[Pt(alkyne)L_2]$ there is no rotation in

solution. For example, complex (VII) shows, in its

(VII)
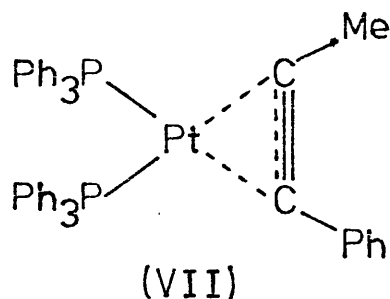
[1]H n.m.r. spectrum, coupling between the methyl

protons and the two inequivalent phosphorus nuclei.

This indicates that the alkyne is not rotating.[37,52]

Theoretical calculations[54] 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[5,14] have been outlined

in Section 2.1A.

(ii) Oxidation reactions

The complexes $[Pt(ac)(PPh_3)_2]$ react with acids,

(HX) according to the reaction whose proposed

mechanism is shown in Figure 2.9.[55] 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 F_3CCO_2H with complexes of the

type $[Pt(ac)(PPh_3)_2]$, where stable vinyl complexes of

platinum(II) were isolated.[56-58] The reaction of

HgX_2 (X=Cl,Br) with $[Pt(C_4F_6)(PPh_3)_2]$ gave the

cis-vinyl complex (VIII).[59] The geometry about the

(VIII)
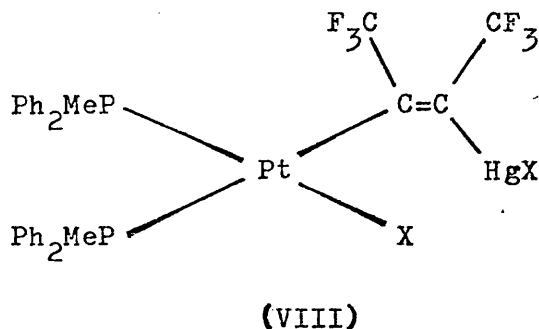
double bond is shown to be cis from the [19]F n.m.r.

data.
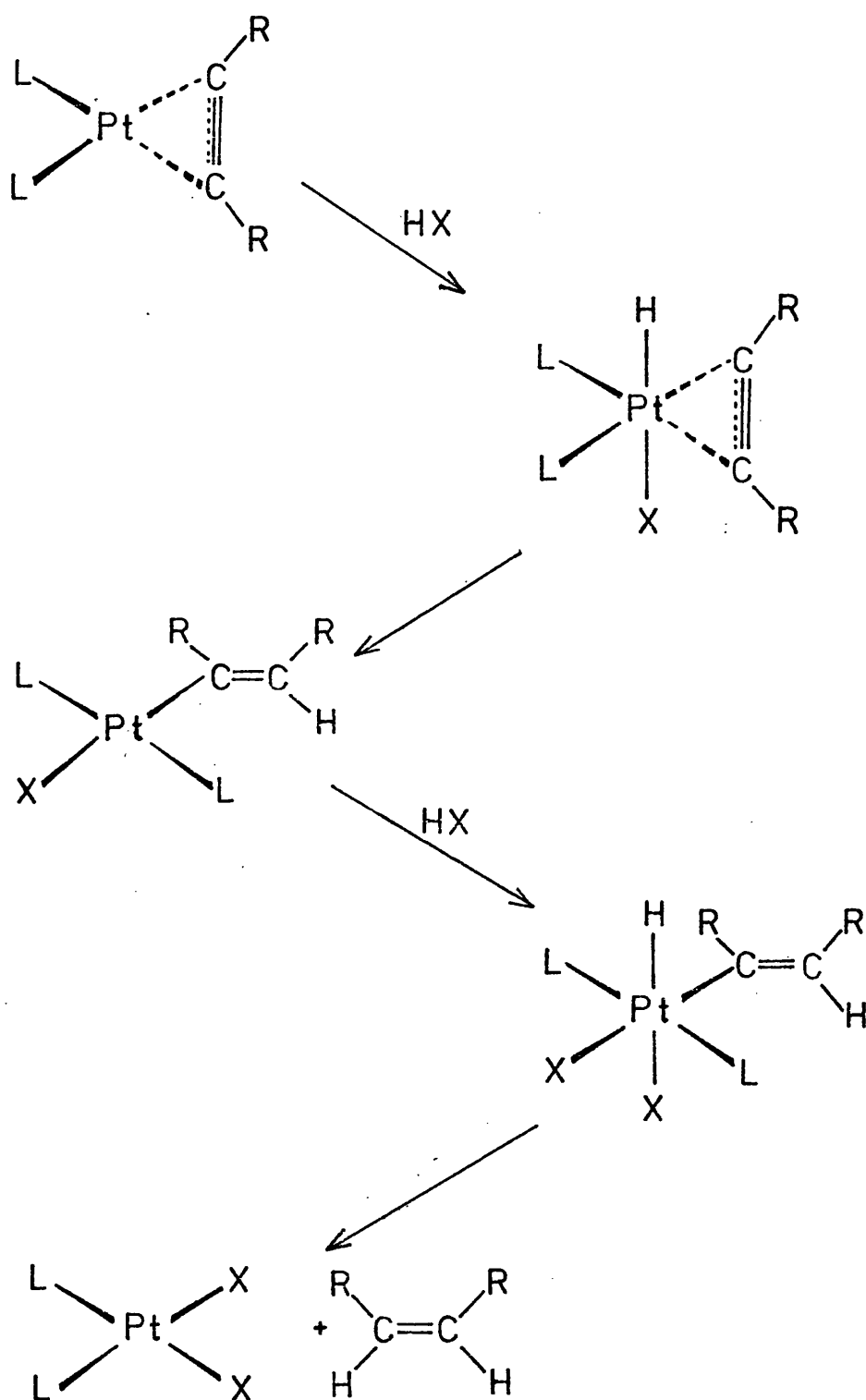
[L = PPh₃ ;   R = CH₃ ;

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 $[Pt(PhC_2Ph)(PPh_3)_2]$.[59,60] The alkyne

(IX)

[L = PPh$_3$; X = Cl, Br.]

(X)
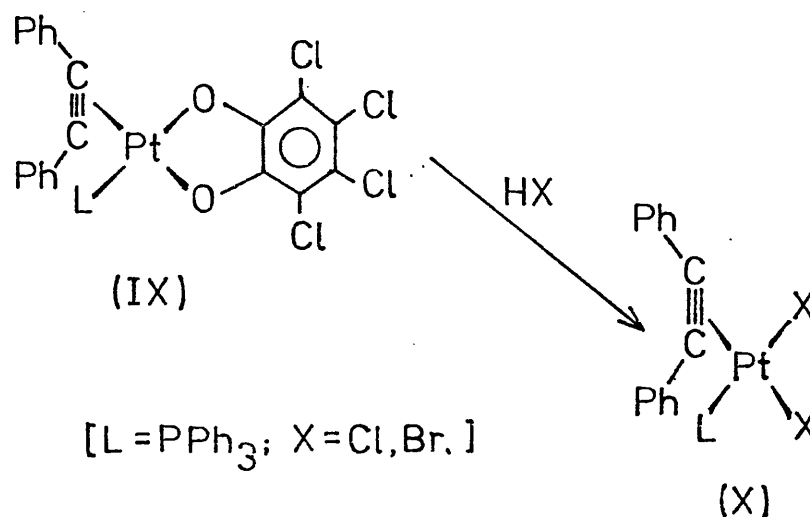
was displaced by the reaction with triphenylphosphine,

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

$[Pt(NCC\equiv CCN)(PPh_3)_2]$ to cis-$[PtCN(C_2CN)(PPh_3)_2]$.[61]

Recently, the complex $[Pt(PhC_2Cl)(PPh_3)_2]$ was prepared,

and shown to isomerise to the trans complex

$[PtCl(C_2Ph)(PPh_3)_2]$, via the cis complex, as shown

in Figure 2.10.[19]

Figure 2.10

2.2 Results and discussion

Platinum forms η^2-alkyne complexes[13,17,18,53,62] and alkynyl complexes[63-66] with α-hydroxyalkynes. Some interesting dehydration reactions of the alkynyl complexes have been reported.[65,66] Thus, on refluxing the bis-alkynyl complexes trans-$[Pt(C_2C(R_1)(R_2)OH)_2(PPhMe_2)_2](XI)$, in acetic anhydride containing a small amount of pyridine, the bis-enyne complex (XII)[65] was formed, as shown in Figure 2.11. The analogous bis-triphenylphosphine complexes

(XI)   (XII)
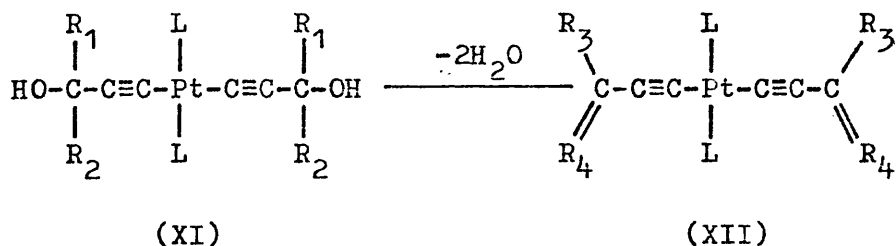
L=PPhMe$_2$;

a) $R_1=R_2=Me$; $R_3=Me$, $R_4=CH_2$

b) $R_1=Me$, $R_2=Et$; $R_3=Et$, $R_4=CH_2$, or $R_3=Me$, $R_4=C(H)Me$

Figure 2.11

Were prepared by refluxing cis-$[PtCl_2(PPh_3)_2]$ in neat α-hydroxyalkyne in the presence of ammonium hydroxide,[66] as shown in Figure 2.12, for 2-methylbut-3-yne-2-ol. The mono-enyne complex (XIII) was prepared by refluxing

$$\underset{\underset{PPh_3}{|}}{\overset{\overset{Cl}{|}}{Ph_3P-Pt-Cl}} \quad + \quad 2NH_3 \quad + \quad HC\equiv C-\underset{\underset{}{}}{\overset{\overset{OH}{|}}{CMe_2}}$$

$$\underset{\underset{PPh_3}{|}}{\overset{\overset{OH \quad PPh_3 \quad OH}{| \quad | \quad |}}{Me_2C-C\equiv C-Pt-C\equiv C-CMe_2}} \quad + \quad 2NH_4Cl$$

(XIc)

$-2H_2O$

(XIIc)
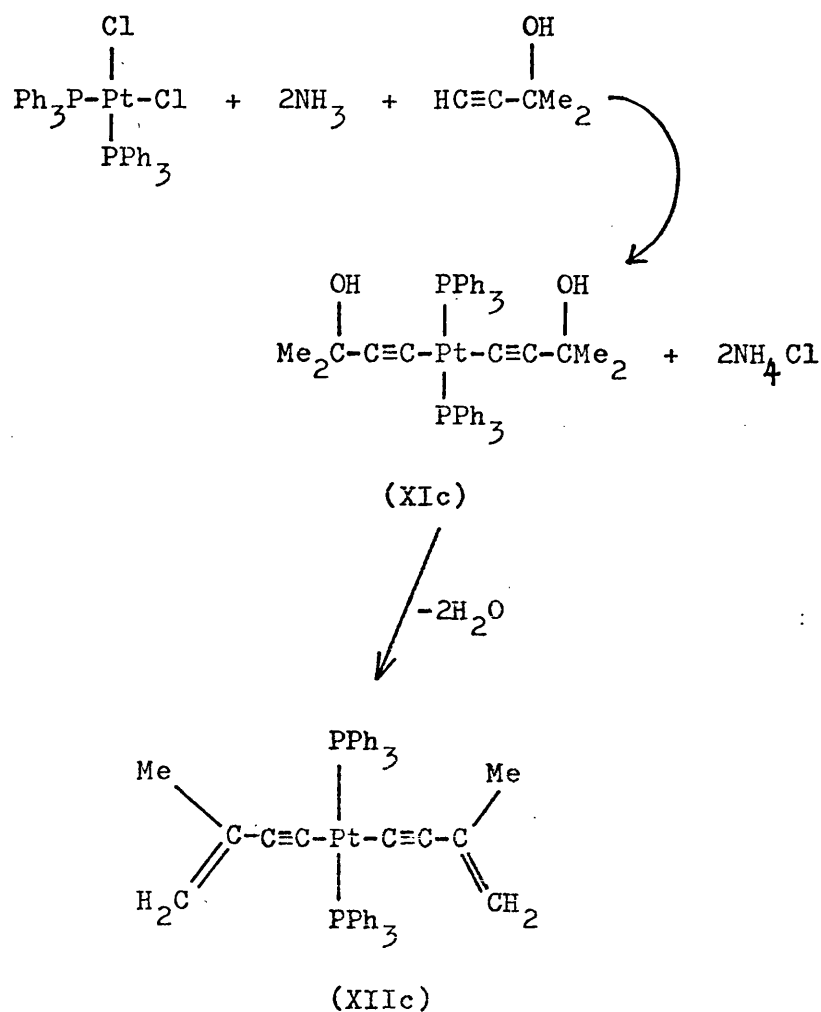
Figure 2.12

cis-$[PtCl_2(PPh_3)_2]$ in chloroform, with an α-hydroxyalkyne,[66] as exemplified in Figure 2.13, for 2-methylbut-3-yne-2-ol.

$$\underset{\underset{Cl}{|}}{\overset{\overset{PPh_3}{|}}{Ph_3P-Pt-Cl}} \quad + \quad H-C\equiv C-\underset{}{\overset{\overset{OH}{|}}{CMe_2}} \quad \xrightarrow{-HCl} \quad \underset{\underset{PPh_3}{|}}{\overset{\overset{PPh_3 \quad OH}{| \quad |}}{Cl-Pt-C\equiv C-CMe_2}}$$

$-H_2O$

(XIII)
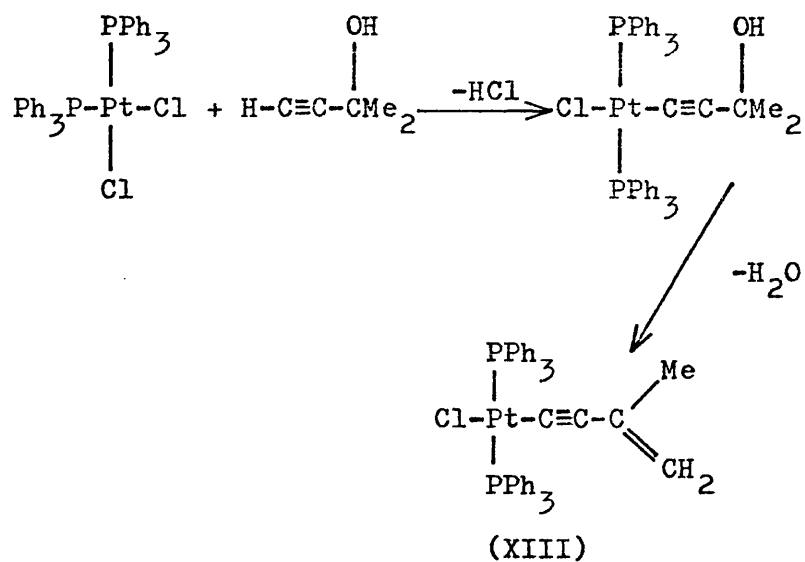
Figure 2.13

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 η^2-alkynediol

complexes (XIV)[60,62] were treated with hexafluoropropanone

a) $R_1=R_2=H$

b) $R_1=R_2=Me$

c) $R_1=Me$, $R_2=Et$

(XIV)
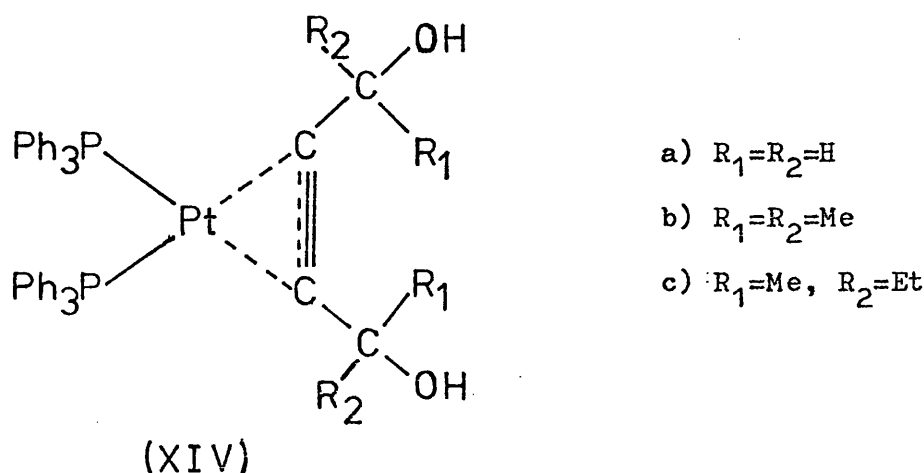
(HFP), to investigate the possibility of dehydration, and

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-yne-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

$1651cm^{-1}$ which is assigned as a carbonyl stretching frequency,

and a band of medium intensity at $551cm^{-1}$. It has been

proposed[67] that bands at $550\pm5cm^{-1}$ 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 4.45τ(1H)], and a double doublet centred at 7.41τ (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.[68] The crystals of complex (XV), $C_{43}H_{34}O_2F_6P_2Pt$ (molecular weight = 953.95) are monoclinic, with space group $P2_1/n$, and a = 12.881Å, b = 22.272Å, c = 13.572Å, β = 99°, U = 3845.67Å^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).[18,69] The expected value of J_{PtP} for cis bis-phosphine platinum(II) complexes is greater

$$[\mathrm{Pt(OC(CF_3)_2C(=CH_2)C(=O)CH_2)(PPh_3)_2}]$$

(XV)

Figure 2.14

($\sim$3500-3800Hz) than that for analogous trans complexes

($\sim$2200-2400Hz).[70,71] Therefore the signal at -28.04 p.p.m.,

which has the lower value for J_{PtP}(2378Hz) is assigned to

the phosphorus (P) which is trans to the σ-bonded carbon,

which has a strong 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 548cm^{-1}, indicating cis

configurations.

Besides the aromatic signals, the ^{1}H n.m.r. spectrum

of (XVI) shows a singlet resonance at 8.48τ (6H), and a

double doublet centred at 9.04τ (6H) which shows platinum

coupling (J_{PtH}=20Hz). This latter signal is assigned to

two equivalent methyl groups, which couple to the cis and

the trans phosphorus (J_{PcisH}=1.5Hz; $J_{PtransH}$=4Hz), in the

system:

$$
\begin{array}{c}
\text{Ph}_3\text{P} \\
\text{Pt} \\
\text{Ph}_3\text{P}
\end{array}
\quad
\begin{array}{c}
\text{C} \quad \text{CH}_3 \\
\text{C} \\
\text{CH}_3
\end{array}
$$

Figure 2.15

$[P=Ph_3P; \quad R=CF_3.]$
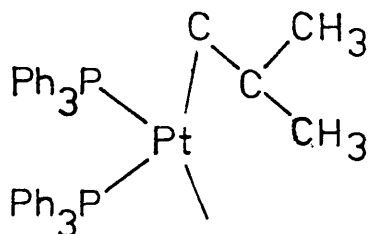
Complex (XVII) shows singlet resonances at 8.28τ(3H) and 8.42τ (3H), and a multiplet centred at 9.09τ(10H), as well as the aromatic signals, in its ^1H n.m.r. spectrum.

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), ($J_{PP'}$=14.6Hz; J_{PtP}=1899Hz; $J_{PtP'}$=4522Hz). For complex (XVII), the two doublets are at -25.00 p.p.m. (P), and -13.20 p.p.m. (P'), with $J_{PP'}$=14.6Hz, J_{PtP}=1885Hz and $J_{PtP'}$=4546Hz. These data give good evidence for a <u>cis</u> configuration of the phosphine ligands, with P <u>trans</u> to a σ-bonded carbon, and P' <u>trans</u> 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,[72]

Table 2.3

N.m.r. spectroscopic data[a] for complexes (XV), (XVI), (XVII)

	^{1}H n.m.r.[b]		^{19}F n.m.r.[c]	^{31}P n.m.r.[d]		
	Chemical Shift	Coupling Constant		Chemical Shift	Coupling Constant PtP	PP'
$[Pt(OC(CF_3)_2C(:CH_2)C(:O)CH_2)(PPh_3)_2]$ (XV)	2.73(m,30H) 4.20(s,1H) 4.54(s,1H) 7.41(dxd,2H)	(PcisH)=6 (PtransH)=12 (PtH)=68	75.94(s)	-28.04(d)	2378	14.6
				-10.59(d)	3975	14.6
$[Pt\{OC(CF_3)_2C(=C)C(Me)_2OC(Me)_2\}(PPh_3)_2]$ (XVI)	2.74(m,30H) 8.48(s,6H) 9.04(dxd,6H)	(PcisH)=1.5 (PtransH)=4 (PtH)=20	79.86(s)	-26.12(d)	1899	14.6
				-14.12(d)	4522	14.6
$[Pt\{OC(CF_3)_2C(=C)C(Me)(Et)OC(Me)(Et)\}(PPh_3)_2]$ (XVII)	2.78(m,30H) 8.28(s,3H) 8.42(s,3H) 9.09(m,10H)		81.41(m)	-25.00(d)	1885	14.6
				-13.20(d)	4546	14.6

a) Measured in CDCl$_3$ solution.

b) Recorded at 100MHz.; chemical shifts (τ) 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}H decoupling: chemical shifts (p.p.m.) relative to external PH$_4^+$, downfield shifts regarded as negative: coupling constants in Hz.
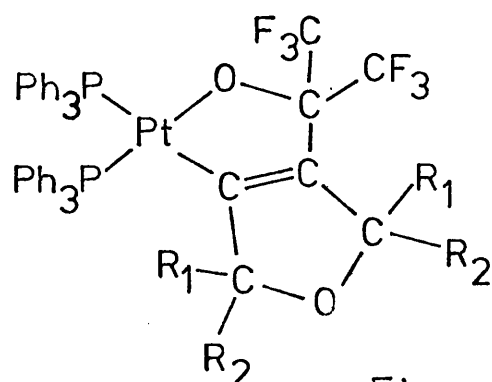
(XVI) $R_1=R_2=Me$

(XVII) $R_1=Me$, $R_2=Et$

Figure 2.16

rhodium[72] and platinum,[73] and some examples are summarised in Figure 2.17.

[R=CF_3]
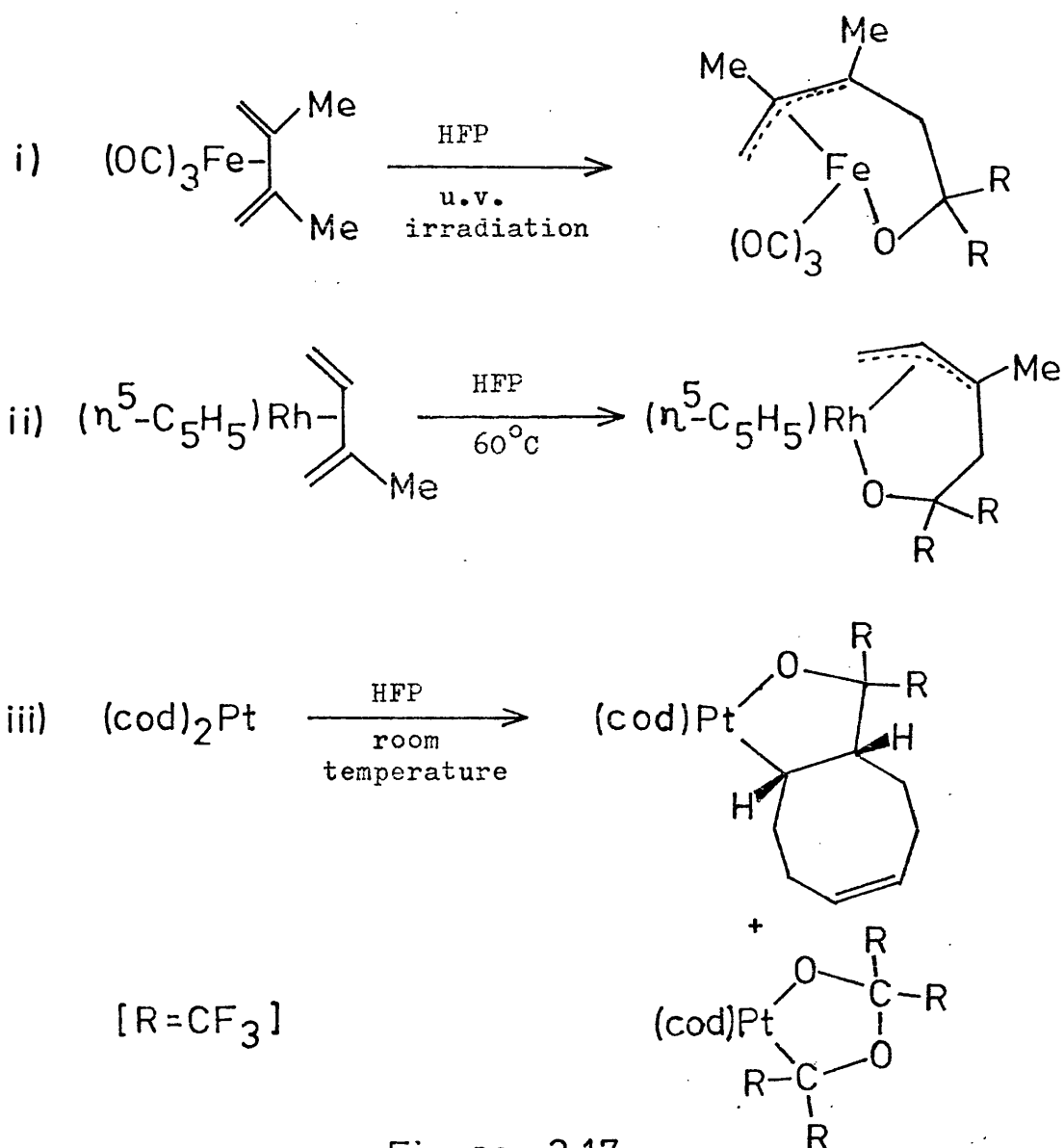
Figure 2.17

Ring-expansion reactions of HFP with bis-phosphine complexes of platinum(II) are well characterised.[74-76] Two examples are shown in Figure 2.18.
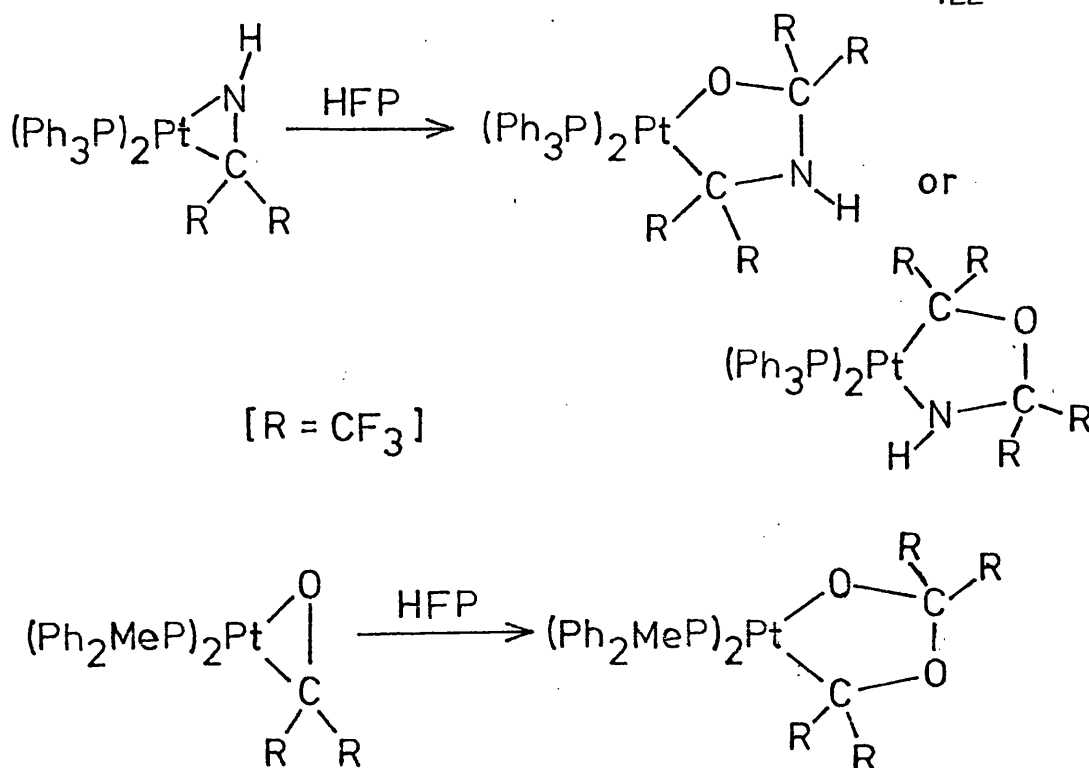
Figure 2.18

An interesting carbonylation reaction has been reported for the but-2-yne-1,4-diol complex (XIVa),[18] from which the platinalactone complex (XVIII) was isolated. No mechanism for this reaction was proposed.
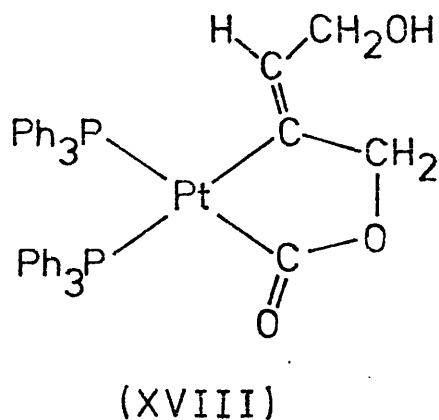
(XVIII)

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
tetracarboxylate at room temperature. The complex
$[Pt\{C_2(CO_2Et)_4\}(PPh_3)_2]$ could, however, be prepared by
the displacement of the alkene from the complex
$[Pt(trans-stilbene)(PPh_3)_2]$ at room temperature.

The but-2-yne-1,4-diol was also displaced by
N-sulphinylaniline, to give the known complex
$[Pt(PhNSO)(PPh_3)_2]$[77]. Acetonedicarboxylic acid dimethyl
ester, which is known to displace ethene and trans-stilbene
from the complexes $[Pt(alkene)(PPh_3)_2]$ 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}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-$[PtX_2(PBu_3)_2]$,
the coupling constants J_{PtP} decrease, and the ^{31}P chemical
shifts move to higher field, with a decrease in the
electronegativity of X (Cl-Br-I).[70] However, although
for the alkyne complexes the coupling constants decrease
in the order $C_2(CO_2Me)_2 > C_2(CF_3)_2 > C_2(CH_2OH)_2 > C_2Ph_2 > C_2(CMe_2OH)_2$
$\approx C_2(C(Me)(Et)OH)_2$, 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.

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Table 2.4

^{31}P n.m.r. data for complexes $[Pt(alkene)(PPh_3)_2]$ and $[Pt(alkyne)(PPh_3)_2]$

	Chemical Shift[a]	J_{PtP} (Hz)	$J_{PP'}$ (Hz)
$[Pt\{C_2(CN)_4\}(PPh_3)_2]$	-15.53(s)	3745	
$[Pt(C_2F_4)(PPh_3)_2]$	-25.41(7 lines)	2539	
$[Pt\{C_2(CO_2Et)_4\}(PPh_3)_2]$	-6.45(s)	3701	
$[Pt(\underline{trans}-HC(Ph)=C(H)Ph)(PPh_3)_2]$[b]	-29.04(s)	3867	
$[Pt\{C_2(CO_2Me)_2\}(PPh_3)_2]$	-24.20(s)	3726	
$[Pt(C_4F_6)(PPh_3)_2]$	-21.38(q)	3594	J_{PF}=9.8
$[Pt(C_2Ph_2)(PPh_3)_2]$	-27.23(s)	3447	
$[Pt(PhC_2C(:O)Me)(PPh_3)_2]$	-26.72(d) (P); -24.10(d) (P')	3799 (P); 3418 (P')	24.4
$[Pt\{C_2(CH_2OH)_2\}(PPh_3)_2]$[c]	-26.4(s)	3501	
$[Pt\{C_2(C(Me)_2OH)_2\}(PPh_3)_2]$[c]	-23.8(s)	3406	
$[Pt\{C_2(C(Me)(Et)OH)_2\}(PPh_3)_2]$	-23.60(s)	3403	
$\underline{cis}-[PtCl_2(PPh_3)_2]$	-13.92(s)	3677	

a. Measured in CDCl$_3$; chemical shifts (p.p.m.) relative to external PH$_4^+$ - downfield regarded as negative; all ^{1}H nuclei decoupled.

b. Measured in benzene; in CDCl$_3$, forms $\underline{cis}$-$[PtCl_2(PPh_3)_2]$

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 (τ) 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
⎫
⎬ Fluka AG
⎭

but-2-yne-1,4-diol

dimethylethynedicarboxylate

diphenylethyne

trans-stilbene

acetonedicarboxylic acid dimethyl ester

⎫
⎪
⎪
⎬ Koch Light Labs. Ltd.
⎪
⎪
⎭

tetracyanoethene

1-phenylbut-1-yne-3-one

⎫
⎬ Aldrich Chemical Co.Ltd.
⎭

tetraethylethene tetracarboxylate   — Lancaster Synthesis Ltd.

polytetrafluoroethene   — B.D.H. Chemicals Ltd.

hexafluoropropanone   — The Matheson Co.

hexafluorobut-2-yne   — 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.

Potassium tetrachloroplatinite 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)[18]

2,5-dimethylhex-3-yne-2,5-diolbis(triphenylphosphine)platinum(0)[18]

3,6-dimethyloct-4-yne-3,6-diolbis(triphenylphosphine)platinum(0)[60]

trans-stilbenebis(triphenylphosphine)platinum(0)[32]

diphenylethynebis(triphenylphosphine)platinum(0)[5]

cis-dichlorobis(triphenylphosphine)platinum(II)[81]

N-sulphinylaniline[78]

Authentic samples of the following were prepared for comparative purposes:

hexafluorobut-2-ynebis(triphenylphosphine)platinum(O)[33]

dimethylethynedicarboxylatebis(triphenylphosphine)platinum(O)[16]

1-phenylbut-1-yne-3-onebis(triphenylphosphine)platinum(O)[55]

tetrafluoroethenebis(triphenylphosphine)platinum(O)[79]

tetracyanoethenebis(triphenylphosphine)platinum(O)[80]

N-sulphinylanilinebis(triphenylphosphine)platinum(O)[77]

A. Reactions of hexafluoropropanone

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

An excess of hexafluoropropanone ($1.0cm^3$) was

condensed ($-196°C$) on to a suspension of

$[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2]$($0.18g$, $0.22mmol$) 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 $[\overline{Pt(OC(CF_3)_2C(:CH_2)C(:O)CH_2)}$-

$(PPh_3)_2]$.   Yield $= 0.13g$, 61%

<u>M.P.</u> $221-3°C$ (decomp)

<u>Analysis:</u>Calculated for $C_{43}H_{34}O_2F_6P_2Pt$:

$\qquad\qquad\qquad\qquad$ C, 54.14%; H, 3.59%; F, 11.95%

$\qquad$ Found:$\qquad\qquad$ C, 53.88%; H, 3.78%; F, 12.37%

<u>Infra-red.</u> 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.

^1H n.m.r. 2.73(m,30H); 4.20(s,1H); 4.54(s,1H);

7.41(dxd,2H,$J_{PcisH}=6Hz$, $J_{PtransH}=12Hz$; $J_{PtH}=68Hz$).

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

^{31}P n.m.r. -28.04(d, $J_{PP'}=14.6Hz$; $J_{PtP}=2378Hz$);

-10.59(d, $J_{PP'}=14.6Hz$; $J_{PtP'}=3975Hz$).

(ii)With 2,5-dimethylhex-3-yne-2,5-diolbis(triphenylphosphine)-

platinum(O)

An excess of hexafluoropropanone (1.0cm^3) was

condensed (-196°C) on to a suspension of

[Pt(Me$_2$C(OH)C≡CCMe$_2$OH)(PPh$_3$)$_2$] (0.20g, 0.23mmol) 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(CF$_3$)$_2$C(=C)C(Me)$_2$OC(Me)$_2$} (PPh$_3$)$_2$]. Yield=0.18g 78%

M.P.   212-3°C (decomp)

Analysis Calculated for C$_{47}$H$_{42}$O$_2$P$_2$F$_6$Pt

                   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.

^{1}H n.m.r. 2.74(m,30H); 8.48(s,6H); 9.04(dxd,6H,

J_{PcisH}=1.5Hz,$J_{PtransH}$=4Hz; J_{PtH}=20Hz).

^{19}F n.m.r. 79.86(s)

^{31}P n.m.r. -26.12(d, $J_{PP'}$=14.6Hz; J_{PtP}=1899Hz);

-14.12(d, $J_{PP'}$=14.6Hz; $J_{PtP'}$=4522Hz).

(iii)With 3,6-dimethyloct-4-yne-3,6-diolbis(triphenylphosphine)-
platinum(0)

An excess of hexafluoropropanone ($1.0cm^3$) was

condensed ($-196°C$) on to a suspension of

$[Pt(EtC(Me)(OH)C\equiv CC(Me)(Et)OH)(PPh_3)_2]$ ($0.28g$, $0.31mmol$)

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

$[\overline{Pt\{O\overline{C(CF_3)_2}C(=\overline{C})C(Me)(Et)O\overline{C}(Me)(Et)\}}(PPh_3)_2]$
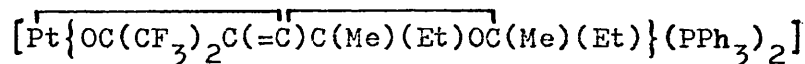
Yield = $0.15g$, 47%

M.P.   188-91°C (decomp)

Analysis: Calculated for $C_{49}H_{46}O_2P_2F_6Pt$:

                         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,

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

[19]F n.m.r. 81.41(m).

[31]P n.m.r. -25.00(d, $J_{PP'}=14.6Hz$; $J_{PtP}=1885Hz$);

-13.20(d, $J_{PP'}=14.6Hz$; $J_{PtP'}=4546Hz$).

B. <u>Reactions of electrophilic alkenes and alkynes with</u>

　　<u>but-2-yne-1,4-diolbis(triphenylphosphine)platinum(0)</u>

(i)<u>With hexafluorobut-2-yne</u>

　　　　An excess of hexafluorobut-2-yne ($0.5cm^3$) was

condensed ($-196°C$) on to a suspension of

$[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2]$ ($0.05g$, $0.06mmol$), 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 to give an

impure solid. Recrystallisation from dichloromethane/

methanol gave crystals which were identified as

$[Pt(C_4F_6)(PPh_3)]$ by their i.r. and ^{19}F n.m.r. spectra.

Yield = $0.05g$, 94%.

^{31}P n.m.r.-21.38 p.p.m. (q, $J_{PF}=9.8Hz$; $J_{PtP}=3594Hz$);

$[$Lit. value:$J_{PF}=10.3Hz^{33}]$.

(ii) <u>With dimethylethynedicarboxylate</u>

　　　　A slight excess of dimethylethynedicarboxylate

($0.01g$, $0.07mmol$) was added to a solution of

$[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2]$ ($0.05g$, $0.06mmol$) 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 $[Pt\{C_2(CO_2CH_3)_2\}(PPh_3)_2]$, by their i.r.

spectrum and m.p. Yield = $0.05g$, 97%.

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

(iii) <u>With 1-phenylbut-1-yne-3-one</u>

　　　　1-phenylbut-1-yne-3-one ($0.009g$, $0.06mmol$) was

added to a suspension of $[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2]$

(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 $[Pt(PhC\equiv CC(:O)Me)(PPh_3)_2]$ by their

i.r. spectrum, and m.p. Yield = 0.045g, 87%.

^{31}P n.m.r. -26.72 (d, $J_{PP'}$=24.4Hz; J_{PtP}=3799Hz);

-24.10(d, $J_{PP'}$=24.4Hz; $J_{PtP'}$=3418Hz).

(iv) With diphenylethyne

Diphenylethyne, (0.022g, 0.12mmol) was added to

a suspension of $[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2]$ (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 (0.5cm^3) was

condensed (-196°C) on to a suspension of

$[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2]$ (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 $[Pt(C_2F_4)(PPh_3)_2]$ by their i.r.

and ^{19}F n.m.r. spectra. Yield = 0.04g, 82%.

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

(vi) <u>With tetracyanoethene</u>

Tetracyanoethene (0.16g, 0.12mmol) was added to $[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2]$ (0.10g, 0.12mmol) suspended in diethyl ether, and stirred for 4 hours. A white microcrystalline solid was filtered, washed with diethyl ether, and identified as $[Pt(C_2(CN)_4)(PPh_3)_2]$ by its i.r. spectrum and m.p. Yield = 0.07g, 69%.

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

(vii) <u>With tetraethylethenetetracarboxylate</u>

Tetraethylethenetetracarboxylate (0.02g, 0.06mmol) was added to a suspension of $[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2]$ (0.05g, 0.06mmol) 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) <u>With N-sulphinylaniline</u>

An excess of N-sulphinylaniline (0.05g, 0.36mmol) was added to a suspension of $[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2]$ (0.10g, 0.12mmol) 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 $[Pt(PhNSO)(PPh_3)_2]$ by its i.r. spectrum and m.p. Yield = 0.09g, 87%.

(ix) <u>With acetonedicarboxylic acid dimethyl ester</u>

An excess of acetonedicarboxylic acid dimethyl ester (0.05g, 0.28mmol) was added to a suspension of $[Pt(H_2C(OH)C\equiv CCH_2OH)(PPh_3)_2]$ (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. <u>Preparation of tetraethylethenetetracarboxylatebis-</u>
<u>(triphenylphosphine)platinum(O)</u>

Tetraethylethenetetracarboxylate (0.20g, 0.63mmol) was added to a suspension of $[Pt(\underline{trans}\text{-stilbene})(PPh_3)_2]$ (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 $[Pt\{(C_2(CO_2Et)_4\}(PPh_3)_2]$. Yield = 0.07g, 61%.

<u>M.P.</u> 130-32°C (decomp)

<u>Analysis</u>: Calculated for $C_{50}H_{50}O_8P_2Pt$:

C, 57.96%; H, 4.86%

Found: C, 57.49%; H, 4.78%

<u>Infra-red</u>: 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_{HH}=7Hz); 9.04(t,12H,J_{HH}=7Hz).

^{31}P n.m.r. -6.45(s; J_{PtP}=3701Hz).

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[1], who found that chloroplatinic acid reacted with cyclopropane to give $[PtCl_2(C_3H_6)]_n$ (I). Treatment with pyridine gave $[PtCl_2(C_3H_6)(py)_2]$ (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.

(IA)   (IB)
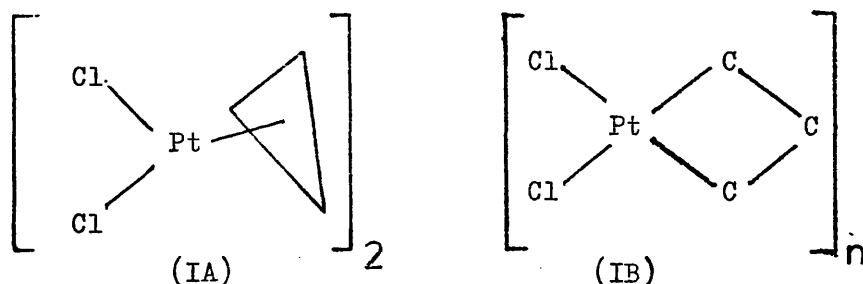
Spectroscopic,[2,3] chemical[3] and X-ray[4] data showed the complex (I) to be polymeric and to contain the trimethylene-platinum moiety (IB). The X-ray analysis of complex (II) showed a similar structure, with the C_1-C_3 distance of 2.55 Å being too long for there to be significant bonding between these two atoms. N.m.r. studies on

(II)
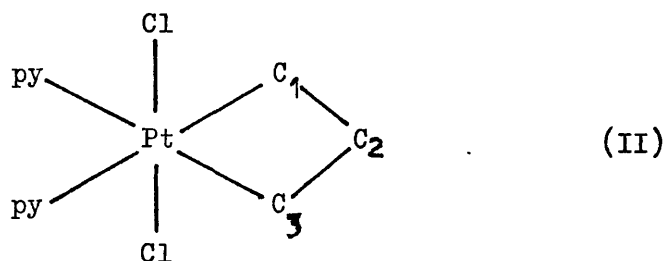
complex (II)[6], together with ^{1}H n.m.r.[7] and X-ray data

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.

$$
\begin{array}{c}
\text{Cl} \\
| \\
\text{py} \diagdown \quad | \quad \diagup \text{C}_1 \diagdown \\
\text{Pt} \qquad\qquad \text{C}_2\!\!-\!\!\text{R} \qquad\qquad \text{(III)} \\
\text{py} \diagup \quad | \quad \diagdown \text{C}_3 \diagup \\
| \quad\quad | \\
\text{Cl} \quad\quad \text{R}
\end{array}
$$
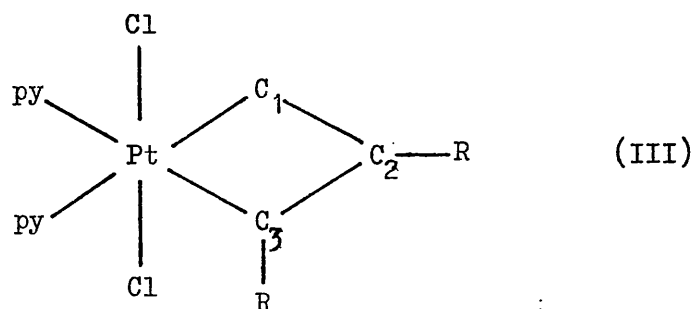
These platinum(IV) complexes were synthesised according

to the following reaction ^{7,9}. (Figure 3.1)

$$
\begin{array}{ccc}
\text{Cl}\diagdown \diagup\text{Cl}\diagdown \diagup|| \\
\text{Pt} \qquad \text{Pt} \qquad + \qquad \triangleright\!-\!\text{R} \qquad \longrightarrow \qquad C_2H_4 \\
||\diagup \diagdown \text{Cl}\diagup \diagdown \text{Cl}
\end{array}
$$

$$
+
$$

$$
\left[\begin{array}{c}
\text{Cl}\diagdown \quad \overset{\text{R'}}{\square}\!\!-\!\!\text{R} \\
\text{Pt} \\
\text{Cl}\diagup
\end{array}\right]_n
$$

$$
\begin{array}{c}
\text{Cl} \quad \text{R'} \\
\text{py}\diagdown | \quad \square\!\!-\!\!\text{R} \\
\text{Pt} \qquad\qquad \xleftarrow{\;\;\text{py}\;\;} \\
\text{py}\diagup | \\
\text{Cl}
\end{array}
$$

(III)
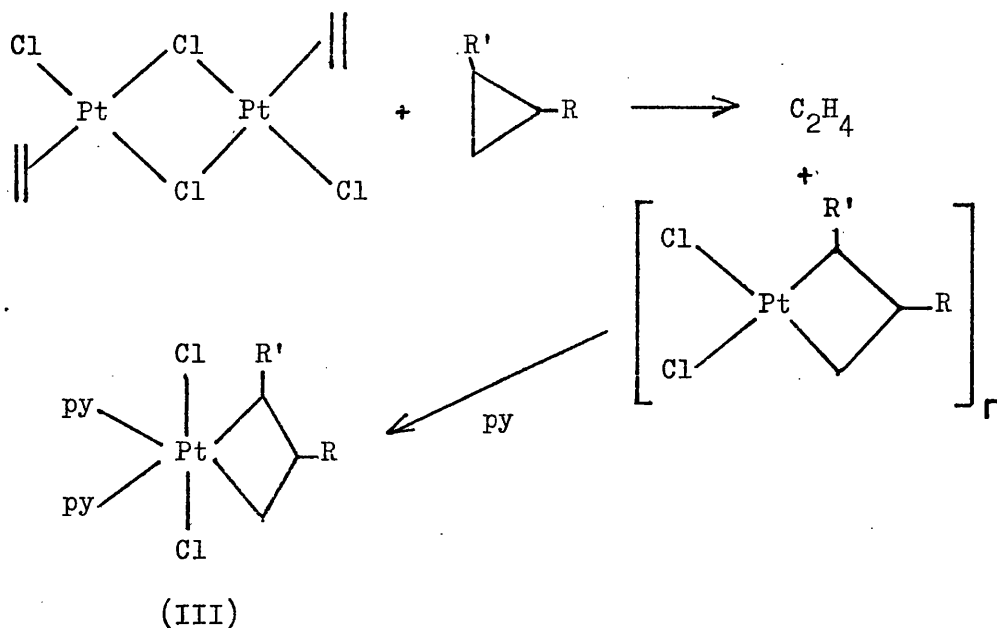
R=n-C_6H_{13}, PhCH$_2$, Ph, $\underline{o}$-NO$_2C_6H_4$; R'=H

R=H; R'=$\underline{p}$-MeC$_6H_4$.

R=R'=Ph(<u>trans</u>). R= n-C_4H_9; R'=Me(<u>trans</u>)

R=CO$_2$Me, COMe, CN; R'=H: no reaction

<u>Figure 3.1</u>

The proposed mechanism involves electrophilic attack by $PtCl_2$ on the cyclopropane ring, and the position of the insertion of the $PtCl_2$ moiety into the ring was studied, using a series of monosubstituted cyclopropanes, by recording the ^1H n.m.r. spectra of the bis-pyridine adducts (III)[7,10]. It was found that, with the exception of $R=p\text{-}MeC_6H_4$, insertion occurred preferentially into the less substituted cyclopropane bond ($R=n\text{-}C_6H_{13}$, $PhCH_2$, Ph, $o\text{-}NO_2C_6H_4$).

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[11], so that characterisation of the complexes (III)[7,10] 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[11].
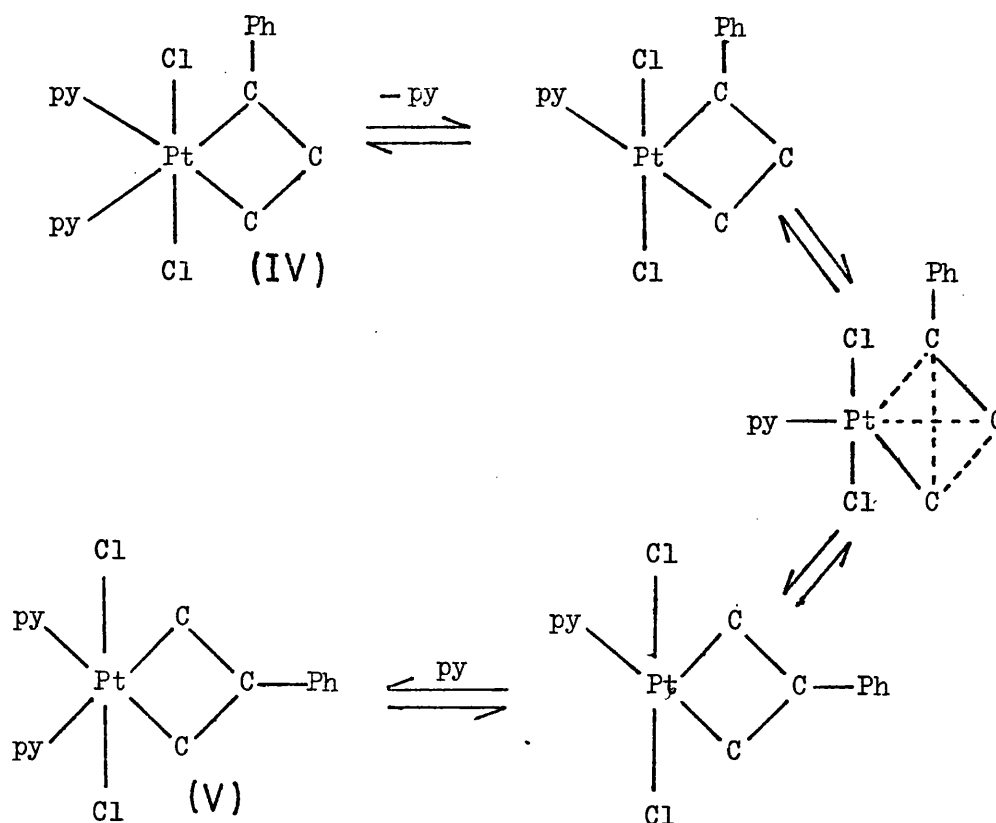
Figure 3.2

Complex (IB) was not obtained when cyclopropane was reacted with $[PtCl_2(C_2H_4)]_2$ or with $H_{(aq)}[PtCl_3(C_2H_4)]$. Instead, $[PtCl_2(CH_3CH=CH_2)]_2$(VI) was formed[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).

(VI)   (IB)
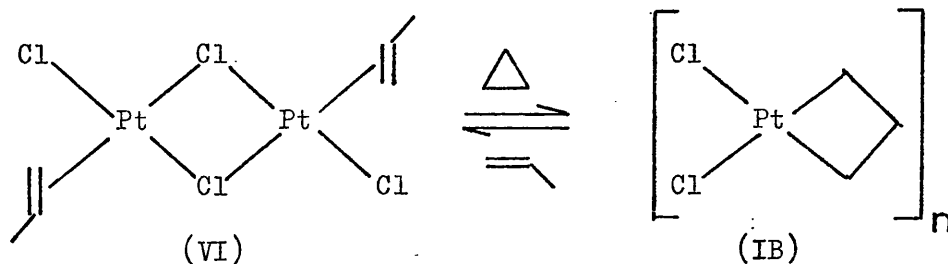
Figure 3.3

A series of studies on the thermal decomposition of,[13,14] and the chemical displacement of cyclopropane from [15] $[PtX_2(C_3H_6)]_n$, $[PtX_2(C_3H_6)L_2]$, (X=Cl, Br; L=C_5H_5N, 4-$CH_3C_5H_4N$) and $[PtX_2(C_3H_6)(L-L)]$ (X=Cl, Br, L-L= ethylenediamine,2,2'-bipyridyl) has been reported, and an estimate was made, of 113-124kJ 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, trans-$[PtCl_2(C_5H_5NCHEt)(py)]$ (VII).
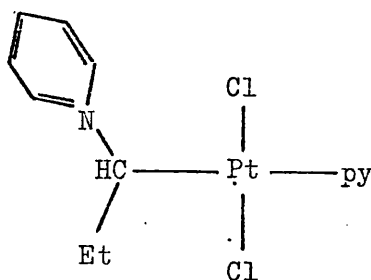
(VII)

The crystal structure of this platinum(II) complex has been reported[4,16], together with that of the platinum(IV) analogue $[PtCl_4(C_5H_5NCHEt)(py)]$. The mechanism of this isomerisation has been studied[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[18,19,20].
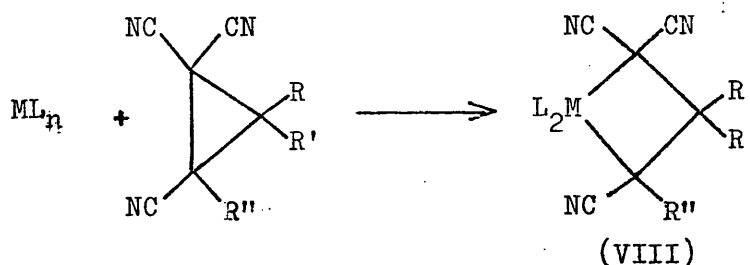
(VIII)

M= Pt, Pd.   L=PPh$_3$, AsPh$_3$, PPh$_2$Me.   n=3,4.

R''= CN: R=R'=H; R=R'=CH$_3$; R=CH$_3$, R'=C$_2$H$_5$; R+R'=(CH$_2$)$_5$.

R''= CO$_2$C$_2$H$_5$: R=H, R'=Ph.

Figure 3.4

$[Pt(C_2H_4)(PPh_3)_2]$ also gave complexes (VIII), and in some cases, the ligands L in (VIII) could be exchanged[19].

These complexes were characterised by their i.r. and ^{1}H n.m.r. spectra[19], and later by X-ray crystallography[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[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 $[Pt(PPh_3)_4]$ does not react with

1,2-dicyanocyclopropane[19].

The platinum(II) and palladium(II) complexes (IX)

have been synthesised from the reaction of tetracyano-

oxacyclopropane [22,23] (TCNEO), with zerovalent palladium or

platinum. The structure of the triphenylarsine
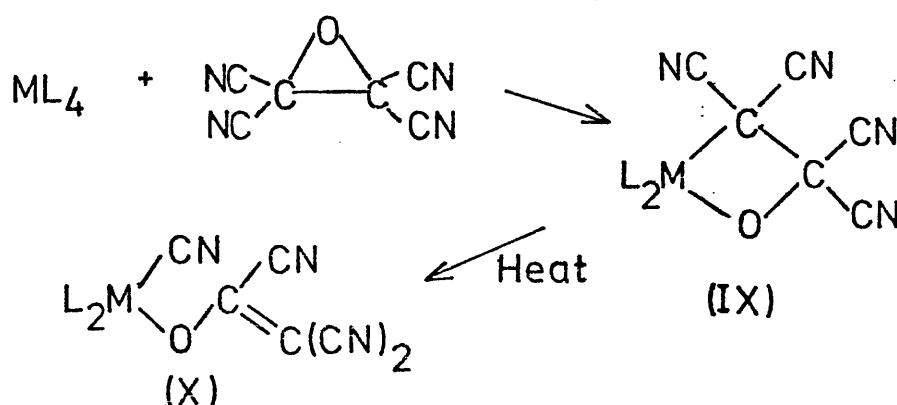
$L=PPh_3$, PPh_2Me, PEt_3, $P(p\text{-}MeC_6H_4)_3$, $AsPh_3$.

$M=Pt$, Pd.

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[24]. The complexes (IX) were not

thermally stable[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[22]. The reaction of

$[Pt(C_2H_4)(PPh_3)_2]$ 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[25].
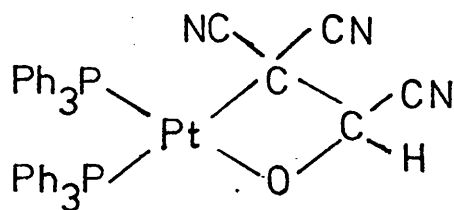
(XI)

Reactions of cyclopropene derivatives with [Pt(C_2H_4)(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 [Pt(C_2H_4)(PPh_3)$_2$][29]. (Figure 3.5). The reaction of diphenylcyclopropenone with [Pt(PPh_3)$_4$][30] gave the ring-opened complex.
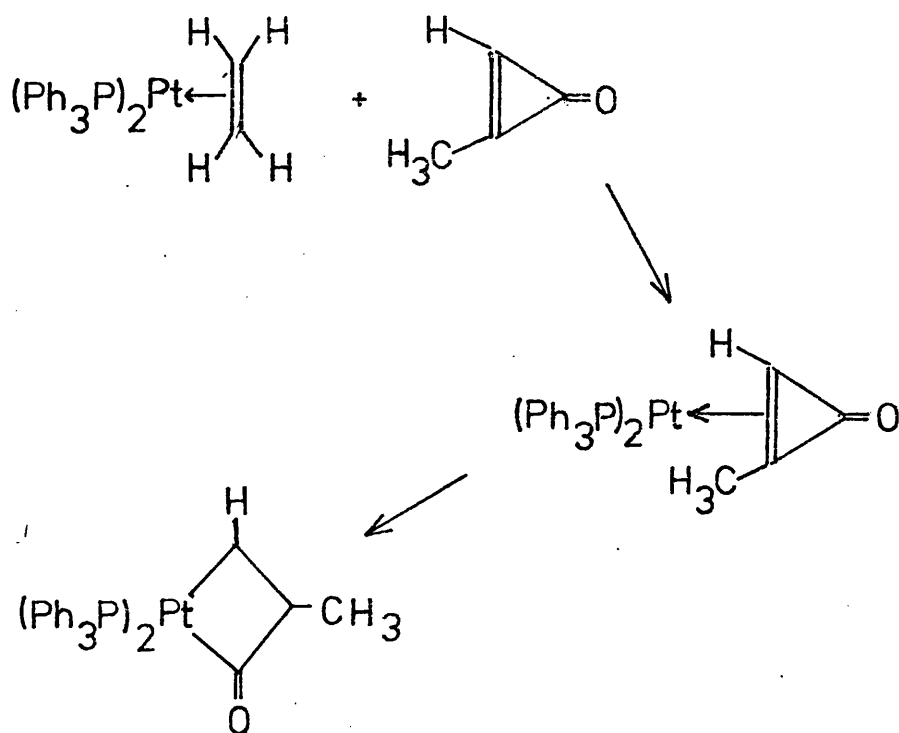
Figure 3.5

Ring-opening was not observed in the reaction of

methylenecyclopropanes with $[Pt(C_2H_4)(PPh_3)_2]$, and only

the η^2-alkene complexes (XII) were isolated[31]. Similarly,

only alkene complexes were obtained from the reaction of

$$Ph_3P \diagdown \quad Pt \leftarrow \diagup\!\!\diagup$$

(XII)

$R_1 = R_2 = R_3 = H.$

$R_1 = R_3 = CO_2CH_3; \quad R_2 = H.$

$R_1 = R_2 = CO_2CH_3; \quad R_3 = H.$
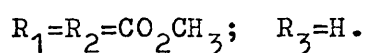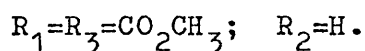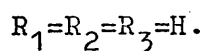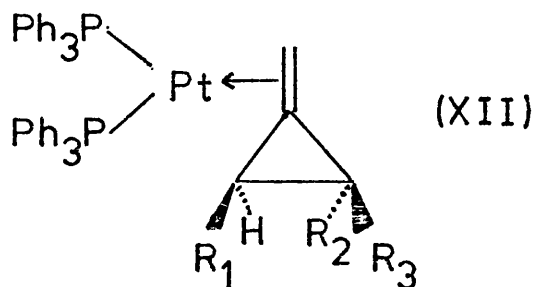
methylenecyclopropanes with trans-$[PtCl_2(C_2H_4)(py)]$.

However, the reaction of 1,2-diphenyl-3-dicyanomethylene-

cyclopropane with $[Pt(C_2H_4)(PPh_3)_2]$[32] 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[32].
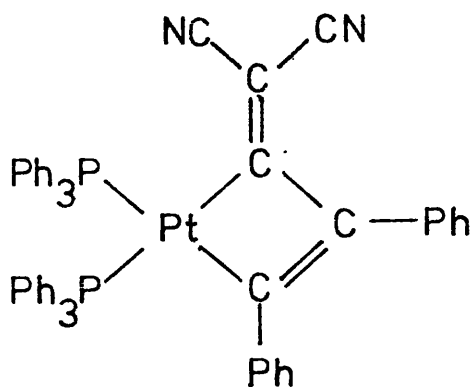
(XIII)
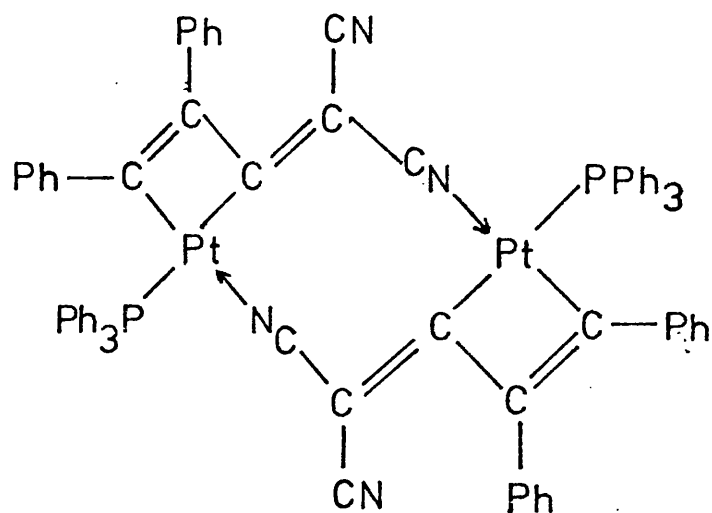
(XIV)

Despite much work on the preparation and reactivity

of cyclopropanones[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 $[Pt(PPh_3)_4]$ in benzene solution, in air, with acetonedicarboxylic acid dimethyl ester, $MeO_2CCH_2COCH_2CO_2Me$, (ACADME) gave a white precipitate, after about 24 hours. The infra-red spectrum of this complex, (XV), had sharp bands in the carbonyl region ($1620-1710cm^{-1}$) and its ^1H 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}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 $[Pt(\underline{trans}-stilbene)(PPh_3)_2]$, in benzene solution with ACADME, in the presence of air.

The reaction of $[PtO_2(PPh_3)_2]$ 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 ^1H n.m.r.

(XV)

(XVI)

$$(Ph_3P)_2PtO_2 \ + \ O=C\overset{R}{\underset{R'}{}} \ \longrightarrow \ Ph_3P\underset{Ph_3P}{}Pt\overset{O-O}{\underset{O}{}}C\overset{R}{\underset{R'}{}}$$

R	R'
CH_3	CH_3
C_2H_5	CH_3
H	CH_3
H	C_6H_5

R	R'
C_2H_5	H
CH_2Cl	CH_3
C_6H_5	CH_3
CH_3	CH_3

R	R'
CH_3	$COCH_3$
C_6H_5	COC_6H_5
CH_3	COC_2H_5
C_6H_5	$COCH_3$
$p-CH_3OC_6H_4$	$COCH_3$

R	R'
CF_3	CF_3
CF_3	CH_3

R	R'
CH_3	$C(CH_3)_3$
CH_3	$CH_2CH(CH_3)_2$
$(CH_2)_4$	
$(CH_2)_5$	

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

$[PtO_2(PPh_3)_2]$ (Figure 3.6). These peroxo-ring complexes

can also be prepared by reacting the appropriate aldehyde

or ketone with $[Pt(PPh_3)_4]$, in the presence of dioxygen[35].

The five-membered ring peroxo-complexes give a characteristic

band in the infra-red spectrum at about 780 cm^{-1}, which has

been assigned to $\nu(O-O)$[35]. Complex (XVI) showed a weak

band at 776 cm^{-1} in the infra-red spectrum, together with

strong broad bands in the carbonyl region (1690-1750 cm^{-1}).

The ^1H n.m.r. spectrum of (XVI) showed a singlet at $\tau = 6.61(6H)$,

and four more peaks at $\tau = 6.66$, 6.80, 6.93 and 7.07(4H),

characteristic of an AB pair. Further evidence for the

structure of (XVI) as $[\overline{Pt(OOC(CH_2CO_2CH_3)_2O}(PPh_3)_2]$ was

provided by its reaction with hexafluoropropanone (HFP). The

product of this reaction was identified as the known complex

$[\overline{Pt(OOC(CF_3)_2O})(PPh_3)_2]$ [37]. An analogous reaction in which

propanone was replaced by HFP in the complex $[\overline{Pt(OOC(CH_3)_2O})(PPh_3)_2$

has been reported.[37]

The reaction of ACADME with $[Pt(PPh_3)_4]$ suspended in

diethyl ether[39] 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 ^1H n.m.r. spectrum it was clear that the major component

of this mixture was complex (XVI). However, it had been found

$$[Pt\{CH(CO_2CH_3)C(=O)CH(CO_2CH_3)\}(PPh_3)_2]$$

(XV)

⊗ = P, ⊕ = C, ○ = O.
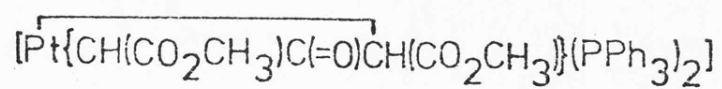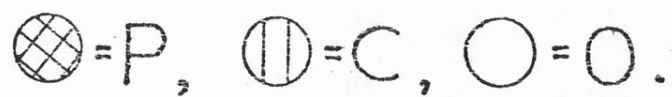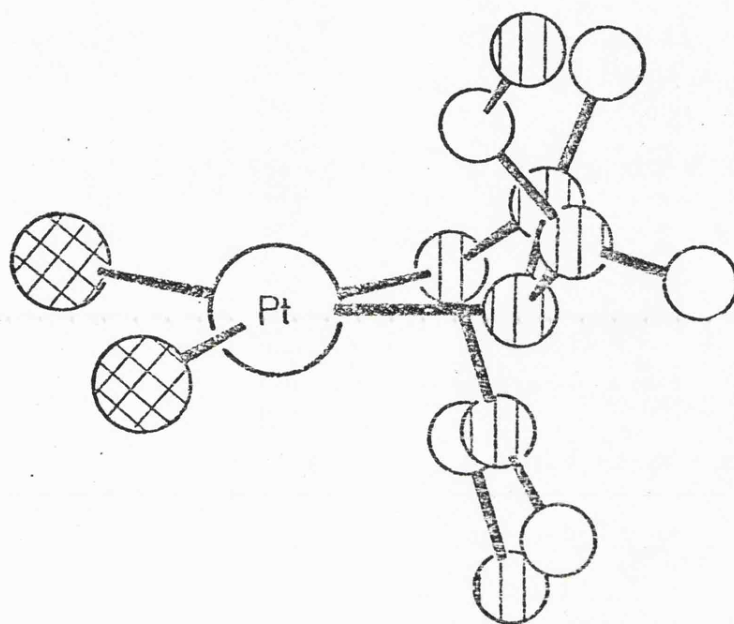
(The phenyl rings have been omitted for clarity.)

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[39], 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,[40]

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.
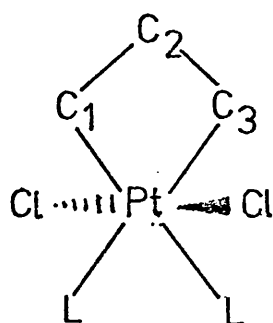
(XVII)
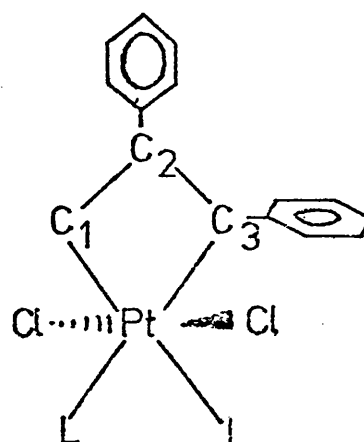
(XVIIIa)
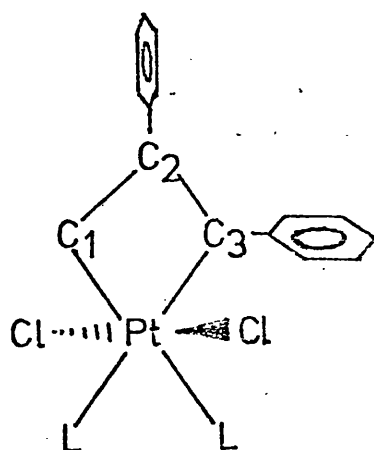
(XVIIIb)
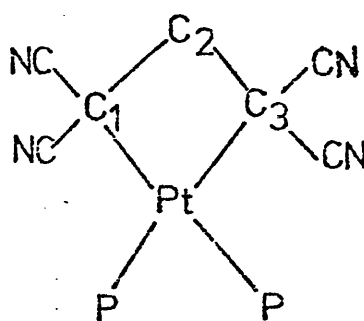
(XIX)
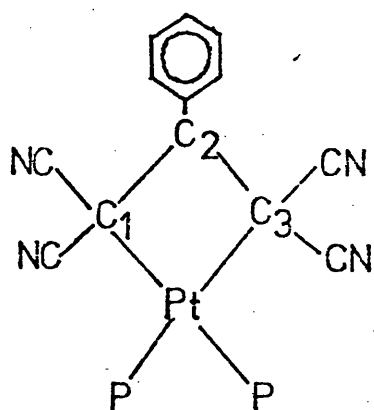
(XX)
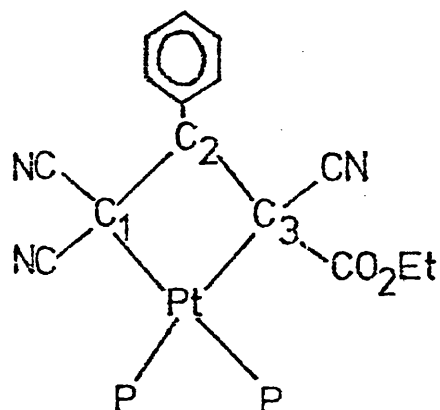
(XXI)

L = py., P = PPh$_3$.

Figure 3.9

It is interesting to compare some of the important features of the crystal structure of complex (XV), which was found (Figure 3.8)[39] to contain a novel metallacyclobutanone ring, with those of the known structures for the metallacyclobutane complexes of platinum(IV), (XVII)[5], (XVIIIa)[8], (XVIIIb)[8], and of platinum(II), (XIX)[21], (XX)[20] and (XXI)[20], which are shown in Figure 3.9.
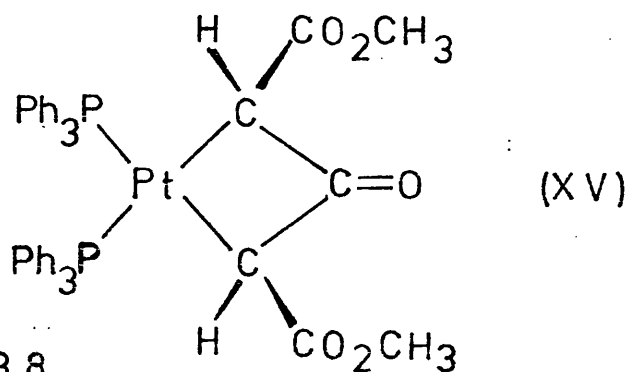
Figure 3.8

The crystals of (XV), $C_{43}H_{38}O_5P_2Pt$, (molecular weight = 891.88) are triclinic, with space group $P\bar{1}$, and a = 17.591Å, b = 12.736Å, c = 10.272Å, α = 118.19°, β = 94.71°, γ = 73.98°, U = 1946.44Å^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-Pt-C_3 and C_1-C_2-C_3 is much greater in (XV), that is, the ring is more puckered;

ii) the angle C_1-C_2-C_3 is larger in (XV);

iii) the angles Pt-C_1-C_2 and Pt-C_3-C_2 are smaller in (XV);

iv) the bond lengths C_1-C_2 and C_2-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 2.4Å.

Table 3.1

Crystallographic data for platinacyclobutane complexes, and for the platinacyclobutanone complex

	(XVII)[1]	(XVIIIa)[1]	(XVIIIb)[1]	(XIX)	(XX)	(XXI)	(XV)
Intramolecular distances (Å)							
$Pt - C_1$	2.04(5)	2.06(3)	2.05(3)	2.137(6)	2.137(6)	2.158(14)	2.149(6)
$Pt \ldots C_2$	2.69(4)	2.60(4)	2.62(3)	2.712(6)	2.694(6)	2.687(14)	2.420(6)
$Pt - C_3$	2.19(5)	2.11(5)	2.17(3)	2.139(6)	2.159(6)	2.200(14)	2.128(6)
$C_2 - C_3$	1.82(9)	1.48(5)	1.71(4)	1.584(9)	1.548(10)	1.509(19)	1.457(10)
$C_2 - C_1$	1.48(8)	1.59(7)	1.59(4)	1.545(9)	1.557(9)	1.556(19)	1.497(9)
$C_1 \ldots C_3$	2.55(10)	2.39(7)	2.60(4)	2.404(9)	2.394(9)	2.403(20)	2.397(10)
Bond Angles (°)							
$Pt - C_1 - C_2$	99(4)	90(2)	91(2)	93.5(4)	92.3(4)	91.2(8)	81.1(4)
$Pt - C_3 - C_2$	84(3)	91(3)	84(2)	92.3(4)	91.7(4)	90.8(8)	82.6(4)
$C_1 - C_2 - C_3$	101(4)	102(3)	104(2)	100.4(5)	100.9(6)	103.2(11)	108.5(5)
$C_1 - Pt - C_3$	74(2)	70(2)	76(1)	68.4(2)	67.7(2)	66.9(5)	68.2(3)
Dihedral Angles (°)							
$C_3 - Pt - C_1$ / $C_1 - C_2 - C_3$	12(5)	28(3)	22(2)	24.4(4)	28.6(6)	29.7(13)	49.7

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[41], it can be seen that the $C_1....C_3$ distance is greater in the platinacyclobutanes. In contrast to the platinacyclobutanone ring, <u>cis</u>-2,4-dibromo-2,4-di-t-butylcyclobutanone has four internal angles of approximately 90°, and a fold angle of only 10° [42].

The Pt....C_2 distance of 2.4Å in (XV) is interesting. Interaction between these two atoms has been proposed previously, on the basis of theoretical considerations[8], and supported by ^{13}C n.m.r. data[6]. A bonding model was proposed[8] 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[43] of the cyclopropane moiety (Figure 3.10).

i,ii,iii) Electron donation to empty metal σ-orbital.

iv) Back donation from metal π-orbital to empty cyclopropane orbital.
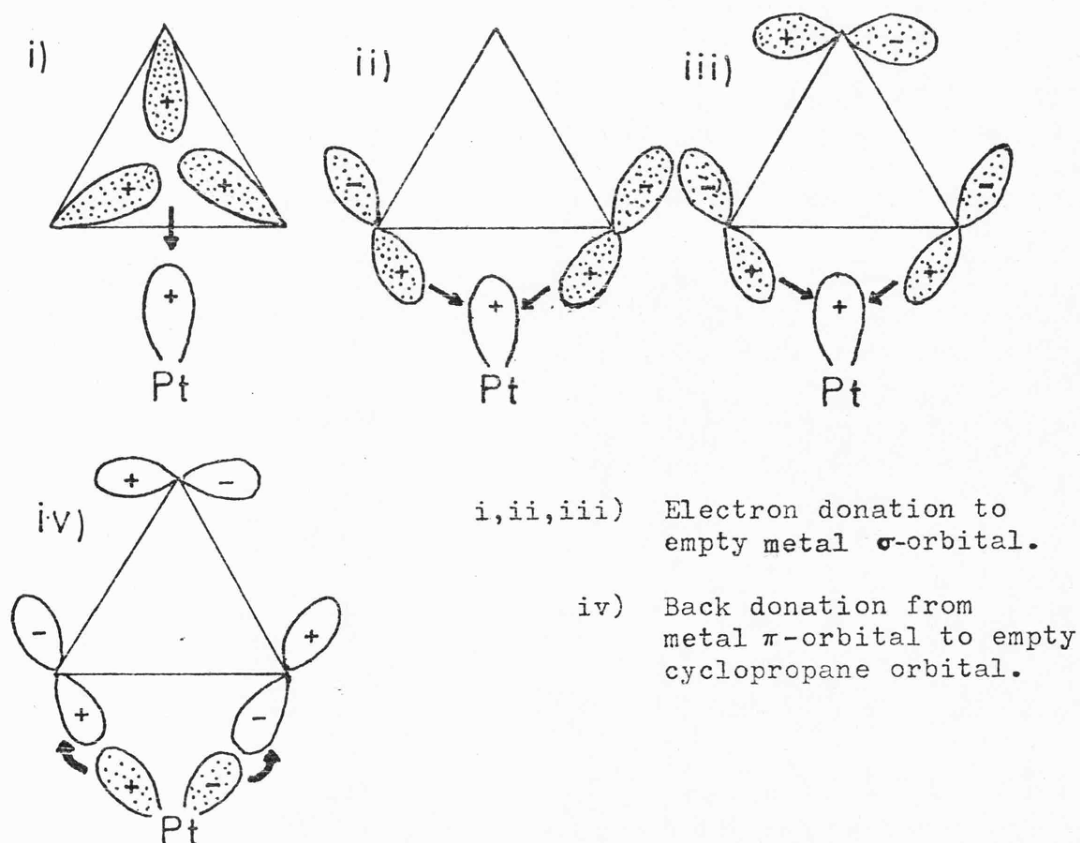
Figure 3.10

Relatively large $^{195}Pt-^{13}C_2$ coupling constants were recorded for complexes of type (XVII)[6], where $^2J_{PtC}$=103-110Hz. This was contrasted with $^2J_{PtC}$= 0-38Hz for ethylplatinum complexes, and suggested that there may be some bonding interaction between the platinum atom and the carbon atom(C_2). The even shorter Pt....C_2 distance in complex (XV) therefore suggests that ^{13}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 C_1-Pt-C_3 and C_1-C_2-C_3 is nearly 50°, and the substituents on C_1 and 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 ^1H 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
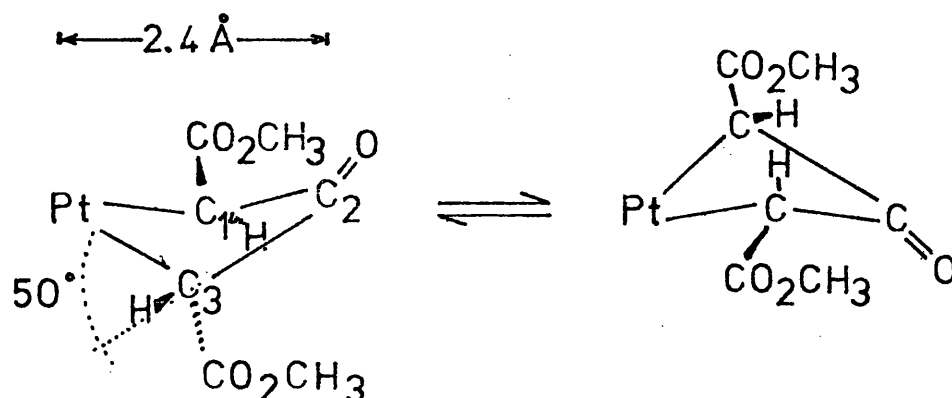
Figure 3.11

temperature ^1H n.m.r. spectra were recorded (-26°C), to endeavour to "freeze out" the two environments by slowing down the

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
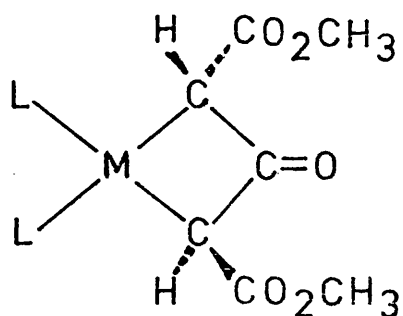
XXII : $L=PPh_2Me$, $M=Pt$

XXIII : $L=PPhMe_2$, $M=Pt$

XXIV : $L=PPh_3$, $M=Pd$

the reaction of ACADME with $[Pt(PPh_2Me)_4]$, $[(Pt(PPhMe_2)_4]$

and $[Pd(PPh_3)_4]$ respectively[39]. The ^1H 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

TABLE 3.2

^1H n.m.r. data for complexes $[M\{ CH(CO_2CH_3)C(=O)CH(CO_2CH_3)\} L_2]$

M	L	CH_3	CH	$^3J_{PtransH}$ (Hz)	$^2J_{PtH}$ (Hz)
Pt	PPh_3	7.00(s)	6.12(d)	6	52
Pt	PPh_2Me	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	

data, suggested the metallacyclobutanone formulation for

(XXII), (XXIII) and (XXIV).

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-[PtCl$_2$(PPh$_3$)$_2$] and cis-[Pt(OCOCF$_3$)$_2$(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 [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 (τ) 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.
trifluroethanoic 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(0)[44]

tetrakis(triphenylarsine)platinum(0)[44]

peroxobis(triphenylphosphine)platinum(II)[45]

trans-stilbenebis(triphenylphosphine)platinum(0)[46]

N-sulphinylaniline[47]

t-butylisocyanide[48]

A.   Reactions of acetonedicarboxylic acid dimethyl ester

i)   With tetrakis(triphenylphosphine)platinum(0) in benzene
      solution

      An excess of acetonedicarboxylic acid dimethyl ester

(0.10g, 0.57mmol) was added to a yellow solution of

$[Pt(PPh_3)_4]$(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 $[\overline{Pt\{CH(CO_2CH_3)C(:O)CH(CO_2CH_3)\}}(PPh_3)_2]$.

Yield = 0.14g, 60%

M.P.   212-3°C (decomp.)

Analysis. Calculated for $C_{43}H_{38}O_5P_2Pt$:

                    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, 1316s,

1298m,sh, 1236m, 1191w, 1180w, 1161m,sh, 1148s, 1135s, 1106m,

1095m, 1090m, 1073w, 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_{PH}=6Hz;

J_{PtH}=52Hz); 7.00(s, 6H).

^{31}P n.m.r.-16.74(s, J_{PtP}=3066Hz).

ii)   With trans-stilbenebis(triphenylphosphine)platinum(0)

      An excess of acetonedicarboxylic acid dimethyl ester

(0.20g, 1.15mmol) was added to a pale yellow solution of

$[Pt(\underline{trans}-stilbene)(PPh_3)_2]$ (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

$[\overline{Pt\{CH(CO_2CH_3)C(:O)\dot{C}H(CO_2CH_3)}\}(PPh_3)_2]$, by its i.r. and

^1H 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 $[PtO_2(PPh_3)_2]$(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

$[\overline{Pt\{OOC(CH_2CO_2CH_3)_2O}\}(PPh_3)_2]$. Yield = 0.25g, 68%.

M.P. 158-9°C (decomp.)

Analysis. Calculated for $C_{43}H_{40}O_7P_2Pt$:

C, 55.78%; H, 4.35%; O, 12.10%

Found: 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, 361w, 320w.

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

(AB pattern, 4H, $J_{HH}=14Hz$, $\Delta\nu=23.1Hz$).

iv) <u>With tetrakis(triphenylphosphine)platinum(0), suspended</u>
<u>in diethyl ether.</u>

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 ^1H 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 ^1H 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. <u>Attempted conversions of $[Pt\{OOC(CH_2CO_2CH_3)_2O\}(PPh_3)_2]$ (XVI)</u>
<u>into $[Pt\{CH(CO_2CH_3)C(:O)CH(CO_2CH_3)\}(PPh_3)_2]$ (XV).</u>

1. <u>In suspension</u>

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 ^{1}H 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.

iii)   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 $[Pt\{CH(CO_2CH_3)C(:O)CH(CO_2CH_3)\}(PPh_3)_2]$ (XV)

i)   With concentrated hydrochloric acid

An excess of concentrated hydrochloric acid

$(36\%w/w, 0.1cm^3)$ was added to $[Pt\{CH(CO_2CH_3)C(:O)CH(CO_2CH_3)\}$-

$(PPh_3)_2]$ (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 $\underline{cis}$-$[PtCl_2(PPh_3)_2]$

by its i.r. spectrum $[\nu(Pt-Cl)=319, 293$ cm^{-1};

(Lit. 316, 297cm^{-1})$^{40}]$ and its m.p. $[310°C;$ (Lit.$=310-312°C)^{49}]$

Yield = 0.19g, 86%.

ii)   With trifluoroethanoic acid

Trifluoroethanoic acid (0.026g, 0.228mmol) was added to

$[Pt\{CH(CO_2CH_3)C(:O)CH(CO_2CH_3)\}(PPh_3)_2]$(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 $\underline{cis}$-$[Pt(OCOCF_3)_2(PPh_3)_2]$, by their

i.r. spectrum $[\nu(OCO)=1727, 1700$ cm^{-1}; (Lit. 1727, 1700,

1400 cm^{-1})^{50}] and their m.p. $[$ 223°C; (Lit.220-5°C)^{50}].

Yield = 0.18g, 87%.

iii) <u>With t-butylisocyanide</u>

t-Butylisocyanide (0.037g, 0.44mmol) was added to

$[Pt\{CH(CO_2CH_3)C(:O)CH(CO_2CH_3)\}(PPh_3)_2]$ (0.20g, 0.22mmol)

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) <u>With N-sulphinylaniline</u>

A slight excess of freshly prepared N-sulphinylaniline

(0.04g, 0.28mmol) was added to $[Pt\{CH(CO_2CH_3)C(:O)CH(CO_2CH_3)\}-$

$(PPh_3)_2]$ (0.20g, 0.22mmol) 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. <u>An attempt to prepare $[Pt\{CH(CO_2CH_3)C(:O)CH(CO_2CH_3)\}(AsPh_3)_2]$</u>

An excess of acetonedicarboxylic acid dimethyl ester

(0.08g, 0.46mmol) was added to a suspension of $[Pt(AsPh_3)_4]$

(0.32g, 0.23mmol) in diethyl ether, and stirred in an open

flask overnight. The cream powder was filtered and washed

with diethyl ether and identified as unreacted $[Pt(AsPh_3)_4]$

by its i.r. spectrum.

E.   Attempts to displace PPh_3 from $[Pt\{OOC(CH_2CO_2CH_3)_2O\}(PPh_3)_2]$ (XVI)

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

1,2-Bis(diphenylphosphino)ethane (0.043g, 0.16mmol) was added to $[Pt\{OOC(CH_2CO_2CH_3)_2O\}(PPh_3)_2]$ (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 $[Pt\{OOC(CH_2CO_2CH_3)_2O\}(PPh_3)_2]$ (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.

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