

SOME REACTIONS OF ACETYLENES WITH
GROUP VIII METAL COMPLEXES

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 1974 and September 1977, under the supervision of Dr. R. D. W. Kemmitt. The work has not been, and is not concurrently being presented for any other degree.

R. E. Fowden

September 1977

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SUMMARY

Chapter 1 presents an outline of the bonding in π -bonded acetylene complexes of metals, and also contains a survey of mono-acetylene complexes of four Group VIII metal systems - rhodium(I), iridium(I), palladium(0) and platinum(0).

In chapter 2, some reactions of rhodium(I)- β -ketoenolate complexes with the electrophilic acetylene hexafluorobut-2-yne are described. Compounds of the type $(\text{Rh}(\beta\text{-ketoenolate})(\text{C}_2\text{H}_4)_2)$ as well as $(\text{Rh}(\text{apeo})(\text{C}_2\text{H}_4)_2)$ and $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$, react with C_4F_6 to give products in which the acetylene adds 1,4 across the rhodium-chelate ring. In addition, the C_4F_6 is either trimerised to give a hexakis(trifluoromethyl)benzene ring, or dimerised, with incorporation of ethylene, to a 1,2,3,4-tetrakis(trifluoromethyl)cyclohexa-1,3-diene ligand. These ligands become coordinated to the rhodium, with the π -bonded ethylene ligands being displaced, and it is found that the basicity of the chelating anion is influential in determining which ligand is formed. With $(\text{Rh}(\text{acac})(\text{C}_8\text{H}_{14})_2)$, a 9,10,11,12-tetrakis(trifluoromethyl)-bicyclo(6,4,0)dodeca-9,11-diene ligand is formed by combination of two C_4F_6 molecules and one cyclo-octene molecule.

Low temperature (-78°C) reactions of C_4F_6 with the compounds $(\text{Rh}(\beta\text{-ketoenolate})(\text{olefin})_2)$ give a new class of complexes, $(\text{Rh}(\beta\text{-ketoenolate})(\text{olefin})(\text{C}_4\text{F}_6))$, containing both a π -bonded olefin and a π -bonded acetylene ligand. These complexes are probable intermediates in the room temperature formation of cyclohexa-1,3-diene and bicyclododeca-9,11-diene ligands, and may also be involved in the build-up of the benzene-type ligands.

The crystal structures of two of these compounds, $(\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$

and $(\text{Rh}(\text{acac})(\text{C}_8\text{H}_{14})(\text{C}_4\text{F}_6))$ are described.

Starting from $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$, a series of complexes $(\text{Rh}(\text{dpm})(\text{EPh}_3)_2(\text{C}_4\text{F}_6))$ ($\text{E} = \text{P, As, Sb}$) can be prepared; it is found that one of the EPh_3 ligands is dissociated in chloroform solution. A preliminary investigation of the reactions of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ with other acetylenes is also reported.

Chapter 3 contains the results of an investigation into the reactions of phenylhaloacetylenes with complexes of platinum(0), palladium(0), rhodium(I) and iridium(I). These results are compared with those obtained for halo-olefins, which have been previously reported. In the case of phenylhaloacetylenes, the products are largely metal-acetylide complexes, many of them previously unknown. Two π -bonded acetylene complexes are obtained, these being $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ and $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$, and gentle warming of these in hydroxylic solvents results in isomerisation to metal-acetylide compounds.

In chapter 4 the kinetics of these two metal-acetylene to metal-acetylide isomerisations are described. In both cases, the reaction is found to exhibit considerably more intramolecular character than is found for metal-olefin to metal-vinyl rearrangements. This result is related to the greater strength of the carbon-halogen bond being broken in acetylene-acetylide isomerisation.

Chapter 5 discusses the preparation of some platinum and palladium acetylide and σ -allene complexes containing dimethyldithiocarbamate as a ligand. In the case of the palladium complex, $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$, stable products, involving insertion of the acetylene into the palladium-carbon bond, are formed in reactions with hexafluorobut-2-yne and dimethylacetylenedicarboxylate.

No reactions occur in the case of the platinum analogue. These results are compared with those for reactions of the acetylenes with $(\text{PdX}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ ($\text{X} = \text{halogen}$), in which no stable mono-insertion products are formed, although multiple insertion into the palladium-carbon bond may be occurring.

Reaction of C_4F_6 with $(\text{Pd}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$ is postulated to give a product derived from insertion of the acetylene into the palladium- σ -allene bond, followed by rearrangement of the allene moiety to an acetylenic group.

ABBREVIATIONS

aan	anion of acetoacetanilide
acac	anion of acetylacetone
apemino	anion of 4-aminopent-3-ene-2-imine
apeo	anion of 4-aminopent-3-ene-2-one
br	broad
cod	<u>cis-cis</u> -cyclo-octa-1,5-diene
d	doublet
dbm	anion of dibenzoylmethane, (1,3-diphenyl-1,3-propanedione)
dmdtc	anion of dimethyldithiocarbamic acid
dpdtc	anion of diphenyldithiocarbamic acid
dpm	anion of dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione)
dtc	anion of dithiocarbamic acid
dtp	anion of diethyldithiophosphoric acid
m	multiplet (in n.m.r.) or medium (in i.r.)
Ph	phenyl
p.p.m	parts per million
q	quartet
s	strong
sh	shoulder
t	triplet
T.M.S.	tetramethylsilane
vs	very strong
vw	very weak
w	weak

"He is before all things, and in Him all things hold together."

Colossians 1¹⁷

CHAPTER 1

MONO-ACETYLENE COMPLEXES OF RHODIUM(I), IRIDIUM(I), PALLADIUM(O)
AND PLATINUM(O)

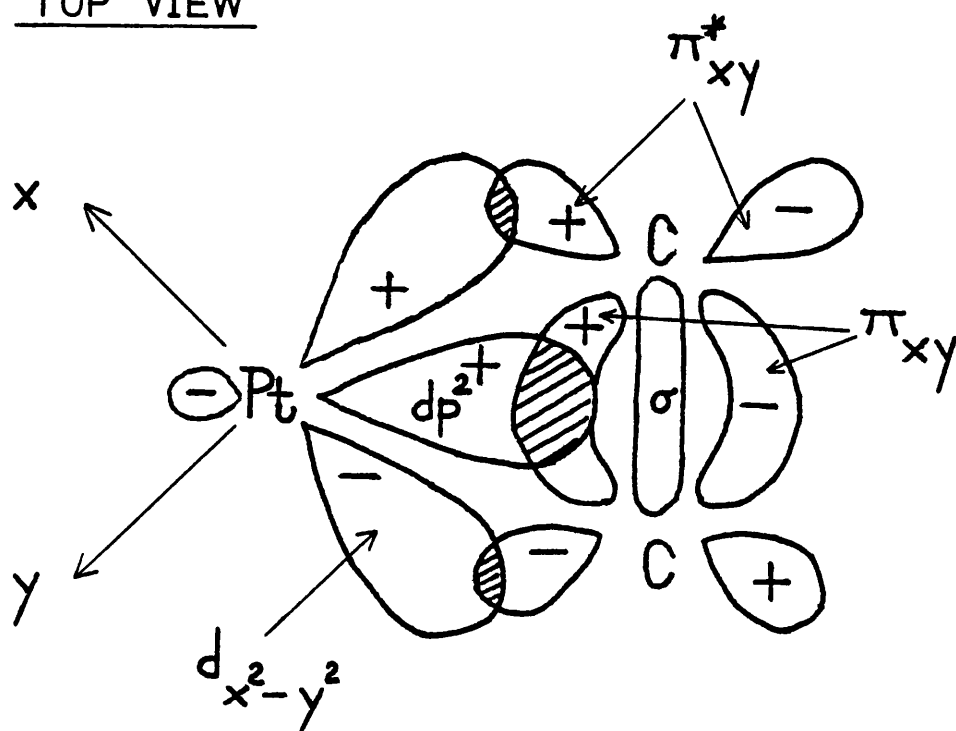
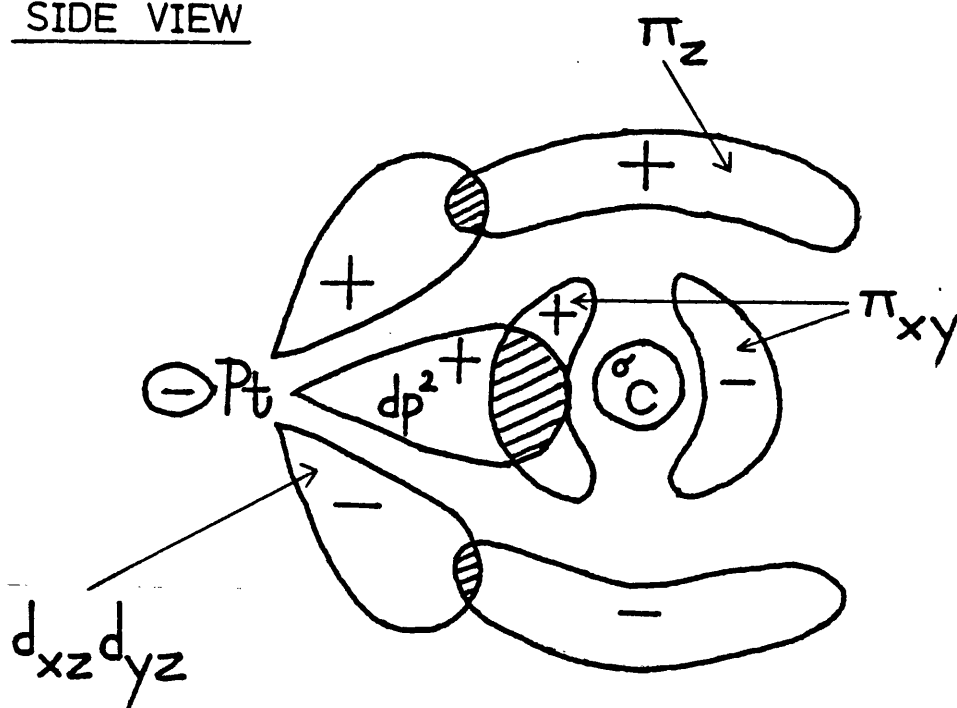
1.1 Bonding in acetylene complexes

Speculation as to the nature of the bonding in metal-olefin and metal-acetylene complexes has existed ever since 1827, when Zeise made $K(PtCl_3(C_2H_4))H_2O$ the first compound of this type.¹ The scheme first outlined by Dewar² for silver(I)-olefin complexes, and used by Chatt and Duncanson³ for platinum(II)-olefin complexes, may also be used as a basis for explaining the bonding in metal-acetylene compounds.

The first part of the bond involves the σ -overlap of a filled π -bonding orbital of the acetylene and a vacant hybrid σ -orbital on the metal, resulting in the transfer of electron density to the metal. The bond is completed by the π -overlap of a filled d-orbital on the metal and an empty π^* -antibonding orbital of the acetylene, resulting in back-donation of electron density from the metal to the acetylene. It is this synergic effect which is thought to give the metal-acetylene bond its stability, and systems of this type are usually described as having the acetylene π -bonded to the metal. This bonding scheme is illustrated for the system platinum(0)-acetylene in Figure 1.1 which also shows how it is possible to get both in-plane and out-of-plane π -bonding in these zerovalent complexes, since an acetylene has two filled π -orbitals.

Any scheme for the bonding in metal-acetylene complexes must account for the following general experimental observations:

- (i) a weakening of the acetylenic triple-bond on

TOP VIEWSIDE VIEWFigure 1.1

coordination, as indicated by X-ray and infra-red evidence:

- (ii) the substituents on the acetylene become cis bent out or the plane of the triple-bond, away from the metal:
- (iii) the bending back of the substituents, combined with n.m.r. studies ⁷² suggests that the sp hybridisation of the carbon atoms moves towards sp² hybridisation on coordination.

The theory readily accounts for a weakening of the acetylene triple-bond on coordination, since both loss of electron density through the σ -bonding contribution to the metal-ligand bond, and gain of electron density in the π^* -antibonding orbital as a result of the π -bonding contribution will result in a weakening of the triple-bond. X-ray diffraction studies on a number of metal-acetylene complexes confirm that the triple-bond is lengthened on coordination. The average length⁴ of the triple-bond in uncoordinated acetylenes is 1.204(2) \AA : Table 1.1 lists the triple-bond lengths in some metal-acetylene complexes.

Table 1.1 Triple-bond lengths in some metal-acetylene complexes

<u>Compound</u>	<u>Triple-bond length (\AA)</u>	<u>Reference</u>
$(\text{Pt}(\text{PPh}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$	1.255(9)	4
$(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CPh}))$	1.32(9)	5
$(\text{Ir}(\text{dmdtc})(\text{cod})(\text{F}_3\text{CC}\equiv\text{CCF}_3))$	1.27(2)	6
$\text{K}(\text{PtCl}_3((\text{C}_2\text{H}_5)_2\text{C}(\text{OH})\equiv\text{CC}(\text{OH})(\text{C}_2\text{H}_5)_2))$	1.18(3)	7

Further evidence for the weakening of the triple-bond is provided by infra-red data: the stretching frequency of the

bond is lowered considerably on coordination, indicating a decrease in the bond-order. Some representative figures are given in Table 1.2 below:

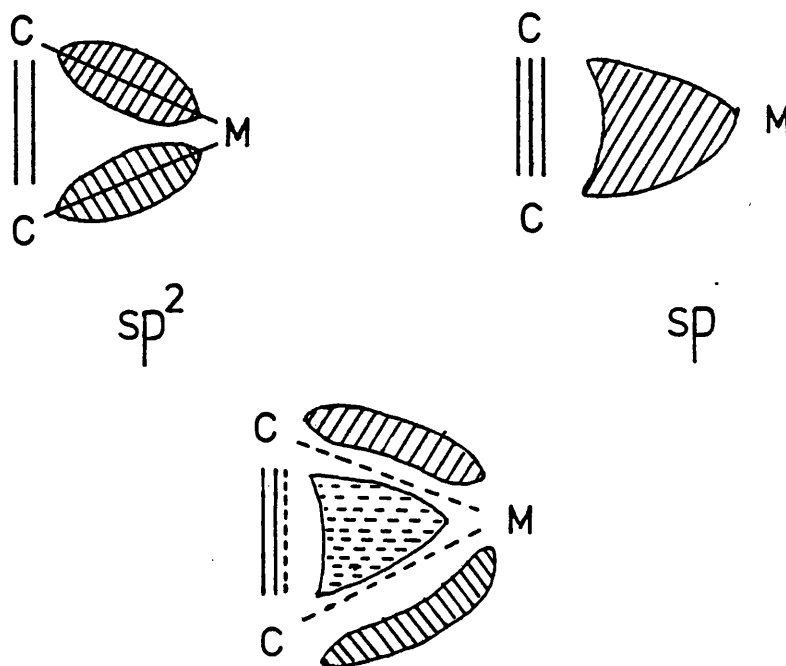
Table 1.2 Infra-red data for some metal-acetylene compounds

<u>Compound</u>	<u>Decrease in C≡C stretching frequency (cm⁻¹)</u>	<u>Reference</u>
(Pt(PPh ₃) ₂ (NCC≡CCN))	535	8
(RhCl(PPh ₃) ₂ (F ₃ CC≡CCF ₃))	383	9
(Ni(C≡NC(CH ₃) ₃) ₂ (PhC≡CPh))	412	10
K(PtCl ₃ ((CH ₃) ₂ C(OH)C≡CC(OH)(CH ₃) ₂))	38	11
(IrCl(cod)(F ₃ CC≡CCF ₃)) ₂	440	22

As can be seen from this X-ray and infra-red evidence, the degree of weakening of the acetylene triple-bond can vary considerably, depending on the acetylene used, the metal involved and its oxidation state, and the substituents on the metal. Thus, for example, platinum(0)-acetylene complexes commonly show a greater weakening of the triple-bond than do platinum(II)-acetylene complexes. This is in accordance with the Dewar, Chatt, Duncanson model, since platinum(0)-acetylene complexes would be expected to be stabilised by a greater degree of back-donation from the platinum(0) - a d¹⁰ electron system - into the π*-antibonding orbitals of the acetylene than is favourable in platinum(II) - a d⁸ electron system.

The change in hybridisation of the acetylene carbon atoms from sp towards sp² is best considered by examining the two extreme situations of sp and sp² hybridisation, and then

considering the intermediate case.¹² In the case of sp^2 , the acetylene is thought of as a dicarbanion, forming two σ -bonds with the metal (Figure 1.2).



Intermediate case.

High electron density.

Low electron density.

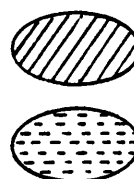


Figure 1.2

With sp^2 hybridisation, the electron density is located largely on the lines between the metal and carbon atoms, whereas with pure sp hybridisation, electron density is largely inside the metal-carbon-carbon triangle. The intermediate example,

shown here, indicates the electron-density distribution in metal-acetylene complexes where there is a σ -donation from acetylene to metal, and a more important π -donation from metal to acetylene. On the basis of this theory, an increased back-donation from metal to acetylene should result in an increase in the sp^2 character of the hybridisation at carbon, and in turn a greater distortion of the acetylene from planarity. This distortion results from a shift of electron density towards the C-R bonds (R = substituent on the acetylene), causing a bond-pair/bond-pair repulsion, and forcing R away from the metal.¹³ Mason¹⁴ also rationalised this distortion as being evidence for π -bonding, since this process would be expected to give an electron distribution on the acetylene analogous to that of the 1A_u excited state of acetylene, which is known to be bent.

Further calculations based on donation of electron density to the π^* -antibonding orbital indicate that either a cis or trans bent acetylene could result, with the cis form being slightly lower in energy.¹⁵ It can also be shown by symmetry arguments that trans bending of the acetylene would lead to a weakening of the metal-acetylene bond, whereas cis bending away from the metal probably has little effect on the bond. These theories are in accordance with experimental observation, which indicates that the substituents on the coordinated acetylene are bent back in a cis manner.

Davies and Payne⁴ have subdivided metal-acetylene complexes into three classes, based on the degree of σ - and π -bonding involved.

(a) Complexes with "electron-rich" metal atoms (e.g.

(Pt(PPh₃)₂(acetylene)) compounds). In these complexes, the more important component of the bonding is π -donation from the metal to the acetylene π^* -antibonding orbitals. These compounds exhibit the largest decrease in the C \equiv C i.r. stretching frequency, and the greatest distortion of the acetylene, on coordination.

(b) Complexes with "electron-deficient" metal atoms (e.g.

complexes of the type K{PtCl₃(acetylene)}). These compounds have a small ($\sim 200\text{ cm}^{-1}$) reduction in C \equiv C i.r. stretching frequency, and only a small ligand distortion (bend-back angles $\sim 20^\circ$) on coordination. In these complexes, acetylene to metal σ -bonding is more important, although there is some π -back-bonding.

(c) Five-coordinate complexes - the intermediate situation

(e.g. (Pt(CH₃)(HB(N₂C₃H₃)₃)(F₃CC \equiv CCF₃))). These intermediate compounds show quite a large decrease in C \equiv C i.r. stretching frequency, and bend-back angles in the range $30\text{--}40^\circ$. The large distortions suggest that metal π -bonding to the acetylene is the dominating component of the bonding, and therefore that class (c) more closely resembles class (a) than class (b).

The complexes listed in Table 1.3 clearly illustrate the three classes suggested by these authors. As yet, however, no clear relationship between bend-back angle and acetylenic bond length has been observed.

Rotation of the olefin in metal-olefin complexes is a well characterised phenomenon. e.g. ^{24,25,26}. Thus, for example, the series of complexes (Rh(π -C₅H₄X)(C₂H₄)₂) (X=H,CN,CO₂CH₃) and the complex (Rh(π -(CH₃)₅C₅)(C₂H₄)₂) have been studied by variable

Table 1.3 Division of metal-acetylene complexes into three classes on the basis of changes occurring to the acetylene on coordination.

<u>Complex</u>	<u>Class</u>	<u>Bend-back angle (degrees)</u>	<u>Decrease in ν C\equivC stretch (cm$^{-1}$)</u>	<u>Reference</u>
$(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CPh}))$	a	40	468	5,16
$(\text{W}(\text{CO})(\text{PhC}\equiv\text{CPh})_3)$	a	40*	542	17,18
$\text{trans}-(\text{Pt}(\text{CH}_3)((\text{CH}_3)_2\text{Ph})\text{P})_2(\text{H}_3\text{CC}\equiv\text{CCH}_3)\text{PF}_6$	b	8,16 (3)	156	19
$\text{trans}-(\text{PtCl}_2((\text{CH}_3)_3\text{CC}\equiv\text{CC}(\text{CH}_3)_3)(\text{p-toluidine}))$	b	15	~ 200	20,21
$(\text{IrCl}(\text{cod})(\text{F}_3\text{CC}\equiv\text{CCF}_3)_2)$	c	38 (2)	440	6,22
$(\text{Pt}(\text{CH}_3)(\text{HB}(\text{N}_2\text{C}_3\text{H}_3)_3)(\text{F}_3\text{CC}\equiv\text{CCF}_3))$	c	34.4 (4)	457	23

* This figure represents a mean value

temperature ^1H n.m.r., and shown to contain rotating ethylene ligands.²⁷ The experimental evidence does not differentiate between a rotation about the metal-olefin bond axis, or about the ethylene bond axis. Rotation about the ethylene bond axis, however, would result in a breaking of both the σ - and π - components of the bond, leading to dissociation of the ethylene, which is not observed, whereas a rotation about the metal-olefin bond axis would not require a rupture of the π -component, since some $d-\pi^*$ overlap would always be present. Consequently, it seems more probable that it is this 'propeller-like' rotation of the ethylene which is taking place.

Some more recent work by Johnson and Segal²⁸ on $(\text{Os}(\text{CO})(\text{NO})(\text{PPh}_3)_2(\text{C}_2\text{H}_4))(\text{PF}_6)$, in which each end of the ethylene molecule is in a different chemical environment, shows, using a combination of ^{13}C and ^1H n.m.r., that the ethylene rotation in this compound is, as expected, about the metal-olefin bond, and it therefore seems probable that this is always the case.

The barrier to rotation would be expected to increase with the amount of metal-olefin π -bonding, and this theory is supported by the results observed for the rhodium(I) compounds²⁷. (See Table 1.4)

Increasing the electron density at the metal should result in increased π -bonding with the olefin, and this is reflected in the value of ΔF_T^* for the compound $(\text{Rh}(\pi-(\text{CH}_3)_5\text{C}_5)(\text{C}_2\text{H}_4)_2)$, whereas introducing an electron-withdrawing group, such as CN or CO_2CH_3 , into the cyclopentadienyl ring should reduce the amount of metal-olefin π -bonding, producing a decrease in ΔF_T^* ,

as is observed. This theory is given further support by the fact that olefin rotation is more often observed in platinum(II) complexes e.g.^{26,29}, than in platinum(0) complexes, where a greater degree of back-bonding is expected.

Table 1.4 The barrier to rotation of ethylene in some bis-ethylene rhodium-cyclopentadienyl complexes.

<u>Complex</u>	<u>ΔF_T^* (kcal/mole)</u>
$(\text{Rh}(\pi\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4)_2)$	15.7
$(\text{Rh}(\pi\text{-C}_5\text{H}_4\text{CN})(\text{C}_2\text{H}_4)_2)$	14.1
$(\text{Rh}(\pi\text{-C}_5\text{H}_4\text{CO}_2\text{CH}_3)(\text{C}_2\text{H}_4)_2)$	14.1
$(\text{Rh}(\pi\text{-(CH}_3)_5\text{C}_5)(\text{C}_2\text{H}_4)_2)$	>16.9

ΔF_T^* is obtained from ^1H n.m.r. data, and reflects principally differences in the activation energy for rotation.

Jonassen et al.³⁰ have performed semi-empirical one-electron molecular orbital calculations on some platinum(II) and platinum(0) olefin and acetylene complexes, and their conclusions are in accordance with a greater barrier to rotation in platinum(0) systems than in platinum (II) complexes.

Since the π -bonding and π^* -antibonding levels are closer in energy to each other in acetylene than they are in ethylene, acetylene should be both a better σ -donor and π -acceptor than ethylene,³¹ and as a consequence would be expected to form a stronger bond, and to have a greater barrier to rotation in its complexes. In addition, acetylene has the ability to form two

sets of π -bonds with the metal, and this should also result in a more rigid structure for metal-acetylene complexes.

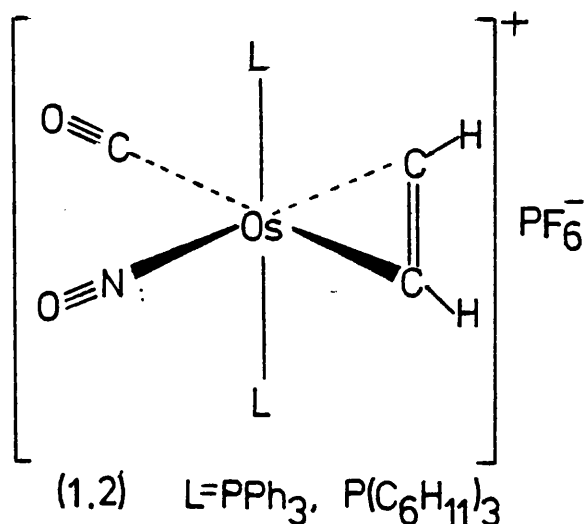
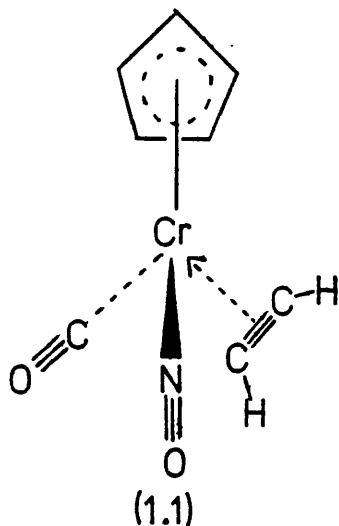
Jonassen's calculations³⁰ show that the energy barrier to rotation is greater for complexed acetylenes than for complexed olefins.

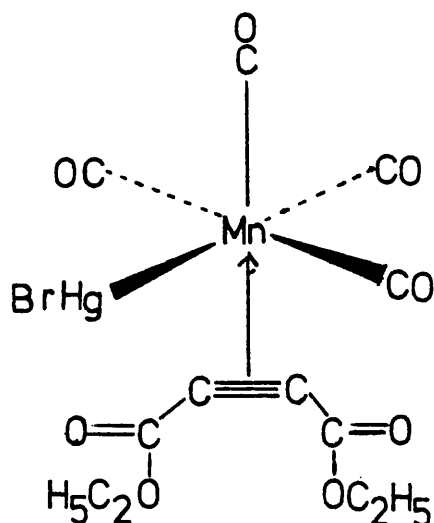
Table 1.5 Calculated energy-barrier to rotation of some olefin and acetylene complexes of platinum.

<u>Compound</u>	<u>Rotational energy barrier (eV)</u>
<u>trans</u> -(PtCl ₂ (NH ₃)(C ₂ H ₄))	1.1
(Pt(PH ₃) ₂ (C ₂ H ₄))	3.3
(Pt(PH ₃) ₂ ((NC) ₂ C=C(CN) ₂))	2.6*
(Pt(PH ₃) ₂ (H ₃ CC≡CCH ₃))	3.6
(Pt(PH ₃) ₂ (H ₃ CC≡CH))	3.8*

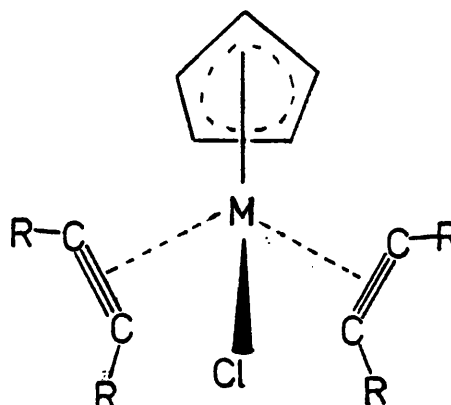
* These results are obtained by assuming the same angular dependence of the total energy of the molecule as is obtained for the other platinum(0) systems.

These workers conclude, however, that acetylene rotation about a metal-acetylene bond should be observable, and such a process has now been discovered in several systems, including (1.1),³² (1.2),³³ (1.3),³⁴ and (1.4).³⁵





(1.3)



(1.4)

A series of compounds of the type (1.4) has been studied using ^{19}F and ^1H n.m.r. techniques: at low temperatures, the compounds can be trapped in one isomeric form, but on raising the temperature, the acetylenes start to rotate, with associated changes in ^1H and ^{19}F n.m.r. spectra. Table 1.6 lists some of these compounds, as well as the transition temperatures at which the acetylenes become freely rotational on the n.m.r. time scale.

A comparison of the results for compounds having the same acetylene ligands, but a different central metal atom, shows good agreement with theory, since the barrier to rotation in tungsten(II)-acetylene complexes would be expected to be greater, due to increased overlap between metal d-orbitals and acetylene π^* -orbitals, causing a greater π -bonding contribution to the metal-acetylene bond. However, when the results for different acetylene complexes of the same metal are examined, some anomalies appear to be present. It would be expected that the presence of electron-withdrawing substituents on the acetylenes would lead

Table 1.6 Acetylene rotation in some compounds of the type
 $(MCl(\pi^5-C_5H_5)(acetylene)_2)$

<u>Compound</u>	<u>Transition Temperature ($^{\circ}C$)</u>
$(MoCl(\pi^5-C_5H_5)(F_3CC\equiv CCF_3)_2)$	-28
$(WCl(\pi^5-C_5H_5)(F_3CC\equiv CCF_3)_2)$	-22
$(MoCl(\pi^5-C_5H_5)(F_3CC\equiv CCF_3)(PhC\equiv CPh))$	+ 8
$(WCl(\pi^5-C_5H_5)(F_3CC\equiv CCF_3)(PhC\equiv CPh))$	+40
$(MoCl(\pi^5-C_5H_5)(PhC\equiv CCH_3)_2)$	-20 \rightarrow -45
$(WCl(\pi^5-C_5H_5)(PhC\equiv CCH_3)_2)$	-10 \rightarrow -15
$(MoCl(\pi^5-C_5H_5)(F_3CC\equiv CH)_2)$	-30

to a greater degree of back-bonding in the compounds, and therefore to higher transition temperatures, but this does not always seem to be the case. For example, a higher transition temperature might be expected for the complex $(WCl(\pi^5-C_5H_5)(F_3CC\equiv CCF_3)_2)$ than for $(WCl(\pi^5-C_5H_5)(PhC\equiv CCH_3)_2)$, but the reverse is observed. This is probably caused by having two acetylenes present rather than one, since for example a hexafluorobut-2-yne ligand will compete strongly for metal d-electron density, thus reducing the back-bonding to the other hexafluorobut-2-yne molecule, so that an unusually low transition temperature results.

Having considered the basic theories of metal-acetylene bonding, it is then instructive to consider some more specific examples of acetylene complexes, in order to see how these fit the general trends which have been outlined. In the next few pages, this is done for mono-acetylene complexes of rhodium(I), iridium(I), palladium(0) and platinum(0).

1.2 Rhodium(I) complexes

The purpose of these short reviews of specific metal-acetylene systems is not to list every compound known for a particular metal oxidation-state, but rather to pick out some of the different classes of compounds and to examine some of their properties. Thus, for example, for rhodium(I), there exists a class of acetylene complexes of the general formula $(\text{Rh Cl}(\text{EPh}_3)_2(\text{acetylene}))$ ($\text{E}=\text{P}, \text{As}, \text{Sb}$), the first complex of this type having been made by Mays and Wilkinson⁹ in 1965.

These workers reacted chlorotris(triphenylphosphine)rhodium(I) with the highly electrophilic acetylene hexafluorobut-2-yne to form a compound in which the acetylene has displaced one of the phosphine ligands. In the original work³⁶ on chlorotris(triphenylphosphine)rhodium(I), Wilkinson et al. proposed that the complex dissociates in solution, with loss of triphenylphosphine, giving $(\text{RhCl}(\text{PPh}_3)_2(\text{solvent}))$, in which the solvent molecule is quite easily displaced by ligands such as ethylene. Later work, however, shows that the species $(\text{RhCl}(\text{PPh}_3)_2(\text{solvent}))$ is not present in solution to a spectroscopically detectable extent³⁷, but rather that the complex is in equilibrium with the dimer $(\text{RhCl}(\text{PPh}_3)_2)_2$, and it is this which reacts with ligands such as olefins and acetylenes, with cleavage of the chlorine bridges, to give the compounds $(\text{RhCl}(\text{PPh}_3)_2(\text{olefin/acetylene}))$. Jonassen's calculations²⁹ for the platinum(II)-acetylene system show that the most stable configuration for these complexes is the pseudotetrahedral form, in which the acetylene is perpendicular to the plane defined by the metal and the other three ligands, and since rhodium(I) is a d^8 system like platinum(II), it would be expected that rhodium(I)-acetylene complexes would also adopt

this pseudotetrahedral structure. Further information useful in defining the structure is provided by ^{19}F n.m.r. evidence, which shows that, in the presence of a large excess of free C_4F_6 , there is no exchange of coordinated and free ligand, and also by the i.r. spectrum, which has a band due to coordinated C_4F_6 at 1917 cm^{-1} (a decrease of 383 cm^{-1} from the band in the free ligand). The metal-acetylene bond does not therefore appear, on the basis of i.r., to be as strong as that in, for example, $(\text{Pt}(\text{PPh}_3)_2(\text{F}_3\text{C}\equiv\text{CCF}_3))$, where the decrease in the acetylene frequency 16 is 525 cm^{-1} , and therefore it is not surprising that the coordinated C_4F_6 in the rhodium(I)-complex can be displaced by tetrafluoroethylene.

Further complexes of the type $(\text{Rh}(\text{PPh}_3)_2(\text{acetylene}))$ include the diphenylacetylene derivative 38 , and a series of compounds 39 where the acetylene is of the type $\text{R}^1-\text{C}\equiv\text{C}-\text{CO}-\text{R}^2$. This latter series of compounds is prepared by room-temperature reaction of $(\text{RhCl}(\text{PPh}_3)_3)$ with the appropriate acetylene, but if the reactions are repeated under more drastic conditions (boiling xylene), decarbonylation occurs, leading, in the cases where R^2 contains an acetylenic linkage, to the conjugated diyne, $(\text{RhCl}(\text{CO})(\text{PPh}_3)_2)$, and triphenylphosphine. A mechanism for this decarbonylation has been proposed (Figure 1.3).

Very little work has been done on $(\text{RhCl}(\text{EPh}_3)_2(\text{acetylene}))$ complexes, where $\text{E}=\text{As}$ or Sb , but the diphenylacetylene derivative has been prepared in each case. 38 In the case where $\text{M}=\text{Sb}$, the complex is not obtained pure, and satisfactory analytical data have not been obtained.

The reactions of these arsine and stibine derivatives with hexafluorobut-2-yne have also been studied. 40 When $\text{E}=\text{Sb}$, a five

coordinate adduct, $(\text{RhCl}(\text{SbPh}_3)_3(\text{F}_3\text{CC}\equiv\text{CCF}_3))$, is formed, and this reacts further, in benzene solution at 80°C , to give a rhodiacyclopentadiene complex, $(\text{RhCl}(\text{C}_8\text{F}_{12})(\text{SbPh}_3)_2)$. In the case where $\text{E}=\text{As}$, no mono-acetylene complex is isolated, and even at room temperature the product is $(\text{RhCl}(\text{C}_8\text{F}_{12})(\text{AsPh}_3)_2)$. No polymers of hexafluorobut-2-yne are observed in these reactions, which is in contrast to the reaction of the phosphine derivative, in which the excess fluorocarbon gives a high polymer.

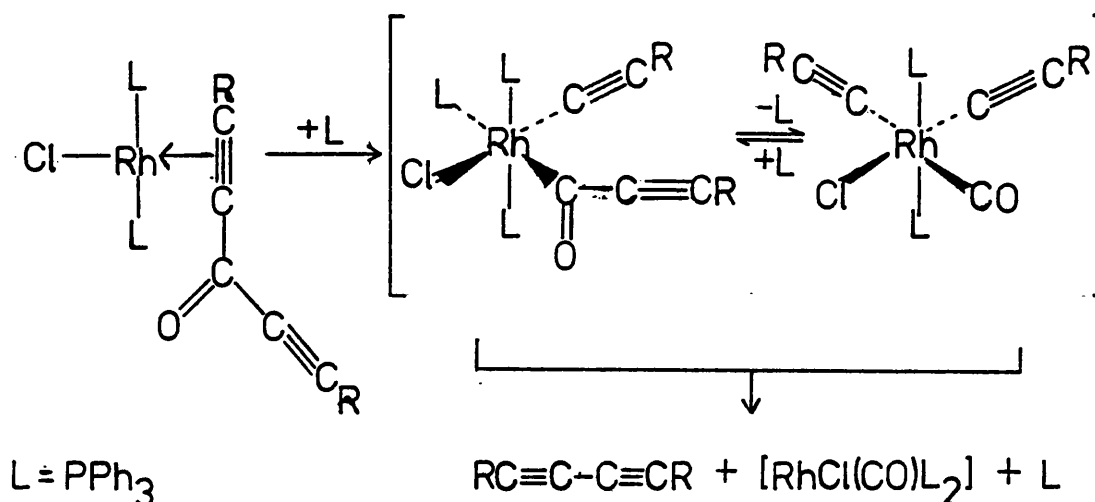
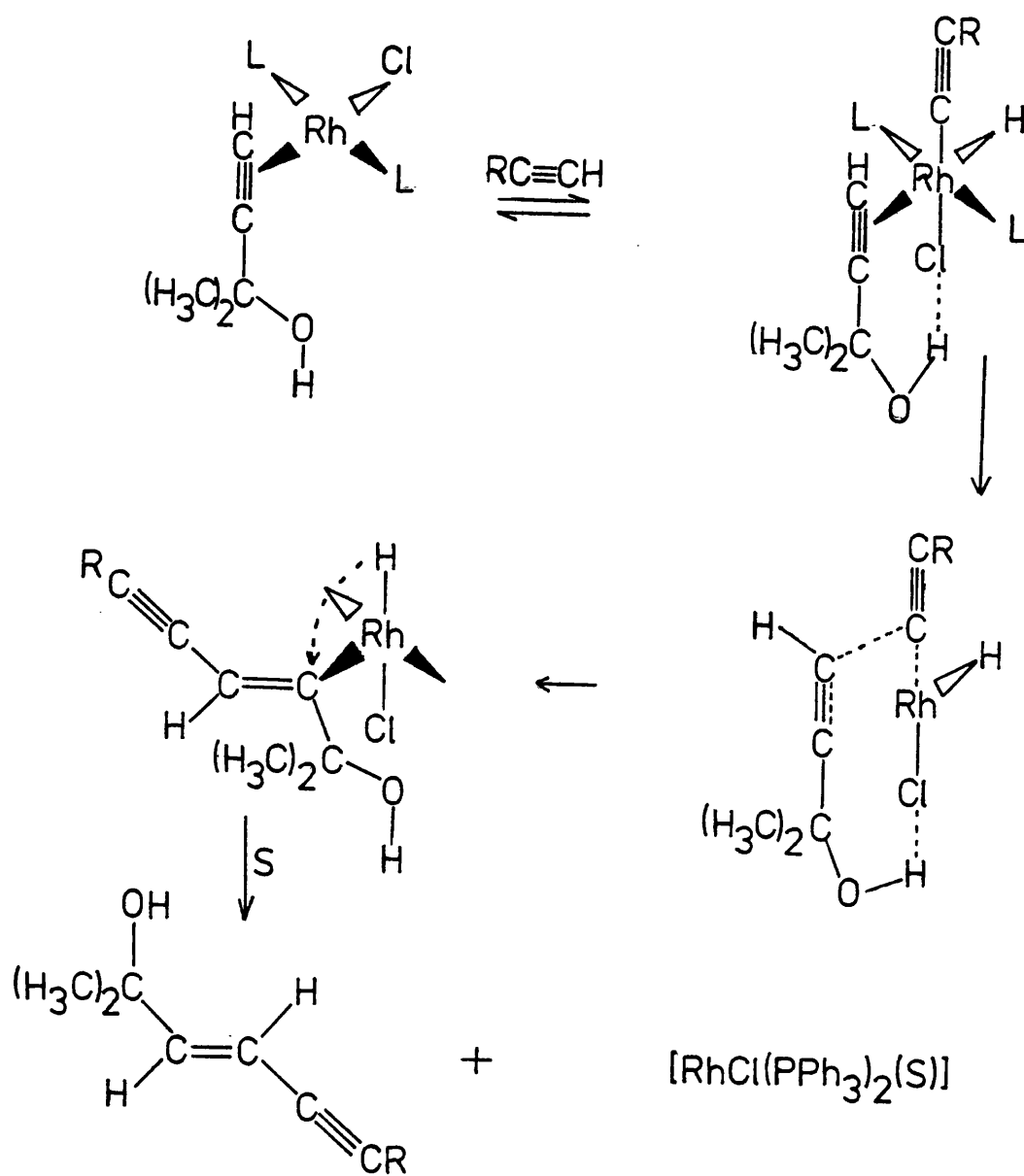
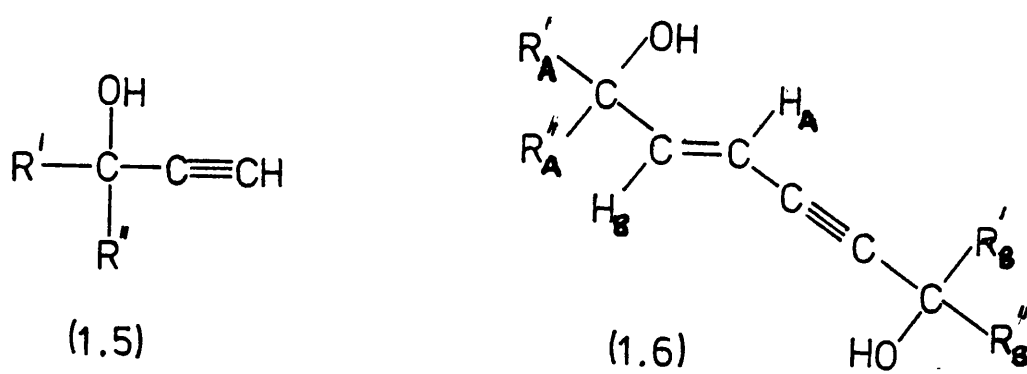


Figure 1.3

Studies on the reaction between $(\text{RhCl}(\text{PPh}_3)_3)$ and α -hydroxyacetylenes of the general formula (1.5), where R^1 is an aliphatic group and R^2 either an aliphatic group or hydrogen, show that the acetylenes are converted almost exclusively to the dimers (1.6) by catalytic amounts of the rhodium(I) complex, in benzene, chloroform, or dichloromethane solution.⁴¹

In the case where $\text{R}^1=\text{R}^2=\text{CH}_3$, a complex is obtained in which the dimer is coordinated to the metal via the triple-bond, possibly forming a polymeric compound through coordination of the double-bond to a neighbouring rhodium atom. A scheme for the dimerisation of the α -hydroxyacetylenes has been proposed (Fig. 1.4).



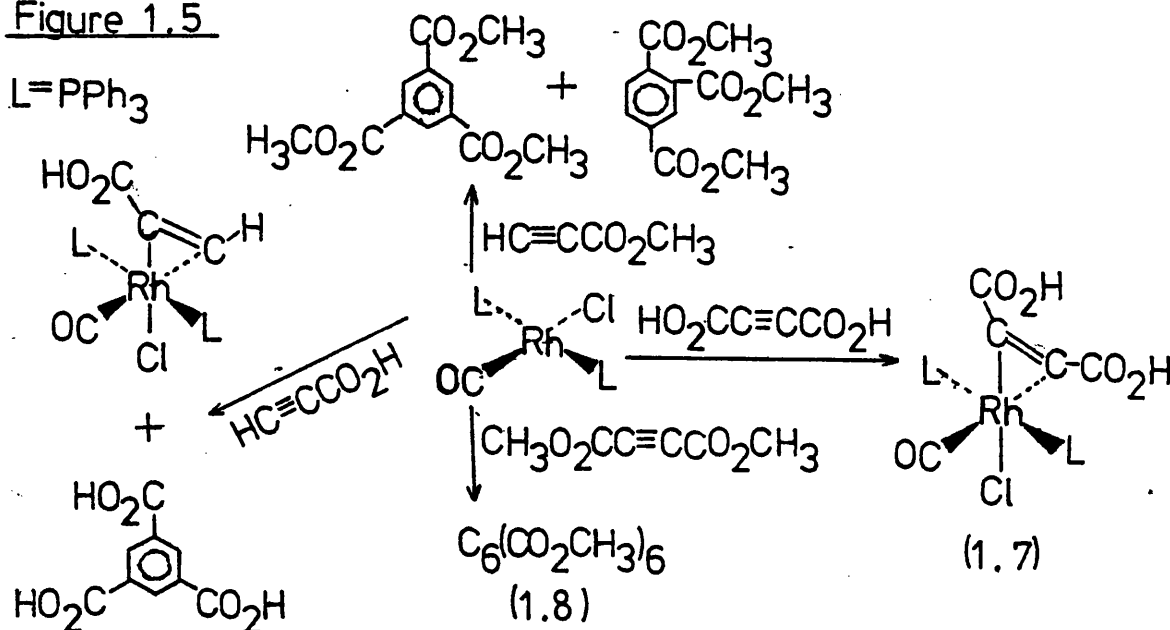
$\text{L} = \text{PPh}_3$
 $\text{S} = \text{solvent}$

Figure 1.4

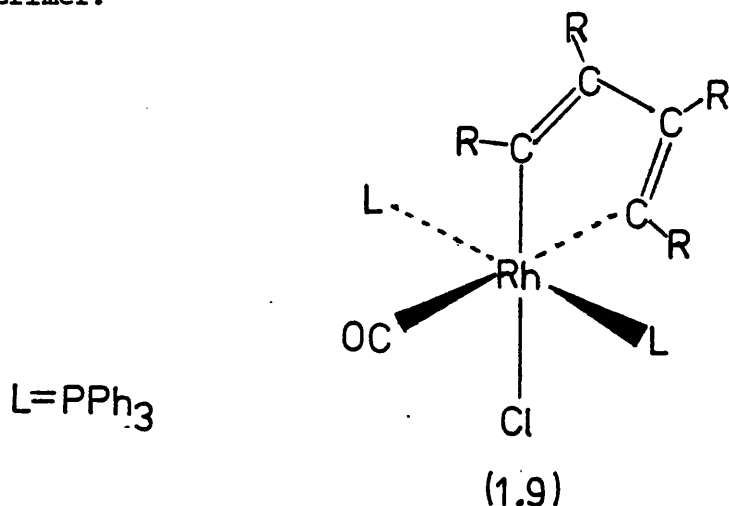
It is also possible to co-dimerise phenylacetylene and the acetylene (1.5) where $R^1=R^2=CH_3$: phenylacetylene alone is rapidly dimerised to trans-1,4-diphenylbutenyne, as well as reacting to form a higher polymer.

Other metal complexes often react with acetylenes either with trimerisation of the acetylene to an aromatic compound, or with linear polymerisation, e.g.^{57,58}. In this context, trans-(RhCl(CO)(PPh₃)₂) is an interesting complex since it gives both mono-acetylene complexes and aromatic trimers.⁴² With acetylenedicarboxylic acid, a stable acetylene complex is formed (1.7): this compound is unusual, in that the coordinated acetylene appears to have a C≡C stretching frequency of 1600cm^{-1} in the i.r., a very low value indeed. Reaction of the dimethyl ester of this acid, however, does not produce an isolable mono-acetylene complex, but instead results in catalytic trimerisation to hexa(carbo-methoxy)benzene (1.8). Further examples of mono-acetylene complexes, as well as trimerisation products, formed from trans-(RhCl(CO)(PPh₃)₂) and acetylenes are given in Figure 1.5.

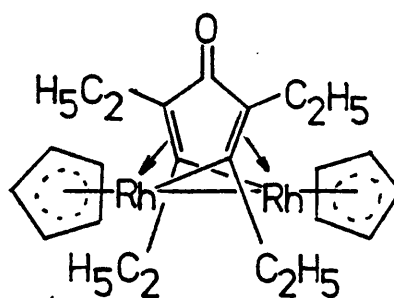
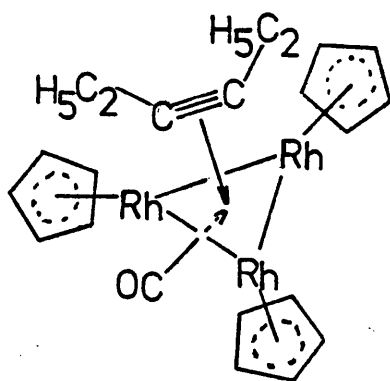
Figure 1.5



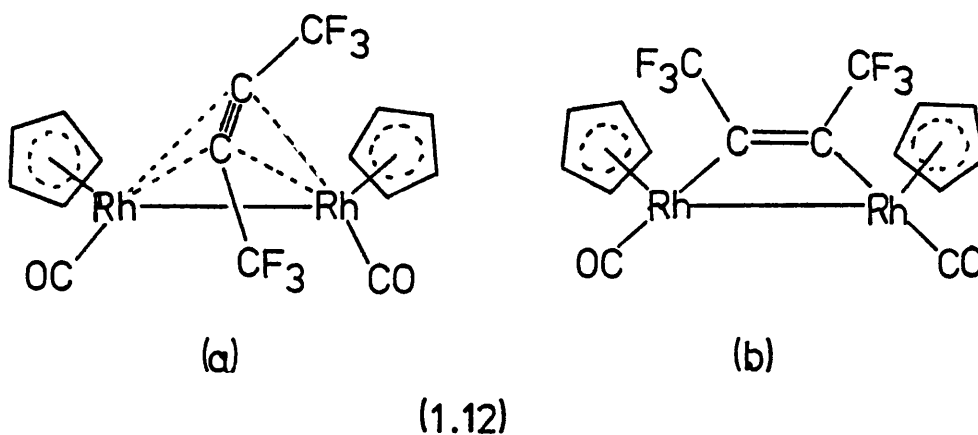
These trimerisation products are probably formed by step-wise reaction of the acetylene to give initially compounds of the type (1.7), followed by a metalocyclopentadiene (1.9), and finally the trimer.



A further interesting group of rhodium(I)-acetylene compounds are those involving a trinuclear rhodium-cyclopentadienide framework. Reaction of hex-3-yne with $(\text{Rh}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2)$ in boiling cyclooctane⁴³ gives the mono-acetylene complex (1.10), as well as complex (1.11).

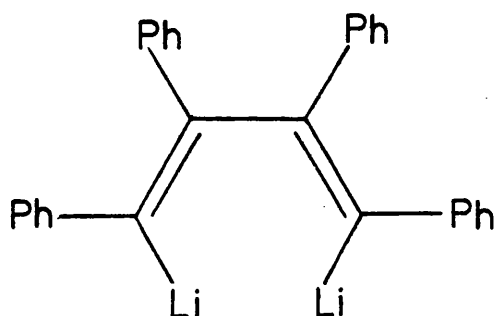


Completely analogous compounds to (1.10) and (1.11) can be obtained from the reaction of the acetylene $\text{F}_3\text{C}\equiv\text{CCF}_3$ with $(\text{Rh}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2)$ at temperatures between 120 and 125°C. In addition at temperatures between 105 and 110°C, a mono-acetylene complex, which is believed to be either (1.12a) or (1.12b) is formed.⁴⁴



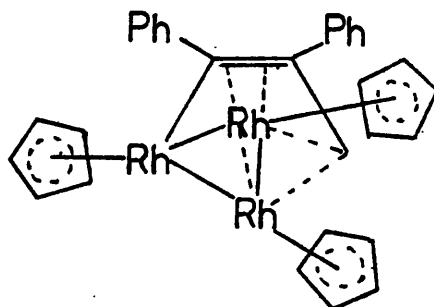
This complex is thought to be an intermediate in the formation of (1.10), (1.11) and several other organorhodium complexes.

Complexes analogous to (1.10) have also been obtained from the acetylenes $\text{PhC}\equiv\text{CPh}$ and $\text{F}_5\text{C}_6\text{C}\equiv\text{CC}_6\text{F}_5$ in reaction with $(\text{Rh}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2)$.^{45,46} The diphenylacetylene complex has also been obtained by an unusual route⁴⁷, involving $(\text{RhI}_2(\pi\text{-C}_5\text{H}_5)(\text{CO}))$ and the dilithium reagent (1.13), although it is possible that the complexed diphenylacetylene ligand arises from unreacted diphenylacetylene used in the preparation of (1.13).



(1.13)

In addition to these complexes, a carbonyl-free compound (1.14) can be isolated from the reaction of diphenylacetylene with $(\text{Rh}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2)$ in boiling cyclooctane.⁴³



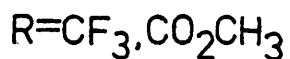
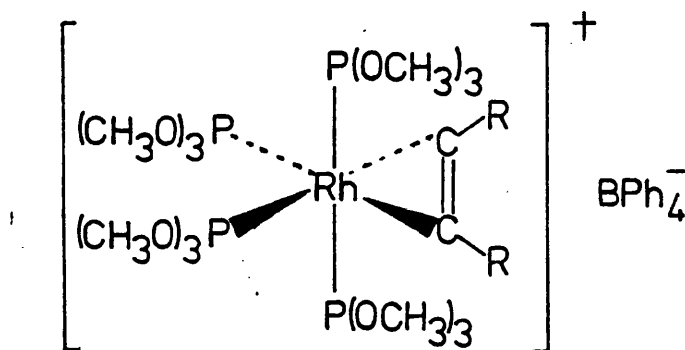
(1.14)

The acetylene component is regarded as a coordinated olefin with two normally π -electrons in a σ -type sp^2 orbital on the carbon atom nearest the unique rhodium atom. The olefinic π -electrons form a three-centre π -bond with the two remaining rhodium atoms, and the empty sp^2 orbital on the remaining olefinic carbon is used in forming a three-centre bonding-orbital with two rhodium atoms.

Some of these rhodium(I)-acetylene complexes have been the subject of variable temperature n.m.r. studies, which in some cases have shown the acetylene to be fluxional. Fluxionality is observed in the compound $(Rh_3(\pi-C_5H_5)_3(CO)(F_5C_6C\equiv CC_6F_5))$ at $+85^\circ C$, but this is due to migration of the carbonyl group from rhodium to rhodium. Interestingly, in this compound, the carbonyl group is only bridging two rhodium atoms.⁴⁸ Using ^{13}C -enriched diphenylacetylene, it is possible to prepare the compounds $(Rh_3(\pi-C_5H_5)_3(CO)(Ph^{13}C\equiv CPh))$ and $(Rh_3(\pi-C_5H_5)_3(Ph^{13}C\equiv CPh))$ and study their variable temperature ^{13}C n.m.r. spectra.⁴⁹ These show that in the former compound, the acetylene is fluxional in solution at room-temperature, but static at $-87^\circ C$, whereas in the latter compound the acetylene is fluxional even at $-127^\circ C$.

In the case of the carbonyl compound, the process appears to involve migration of the carbonyl group around a quasi-threefold axis on one side of the Rh_3 plane, and simultaneous migration of the acetylene about the axis on the opposite side of the plane. The bridging acetylene in $(\text{Rh}_2(\pi\text{-C}_5\text{H}_5)_2(\text{CO})_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$ is static.

As a final example of a class of rhodium(I)-acetylene compounds, some cationic rhodium-acetylene complexes (1.15) can be prepared by reaction of $(\text{Rh}(\text{P}(\text{OCH}_3)_3)_4)(\text{BPh}_4^-)$ with the appropriate electrophilic acetylene.⁵⁰ Using phenylacetylene, only polymeric products are obtained.

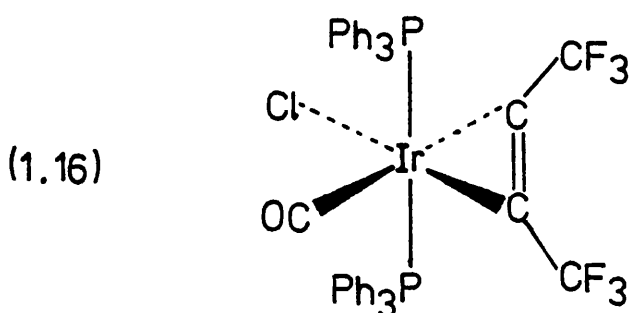


(1.15)

1.3 Iridium (I) complexes

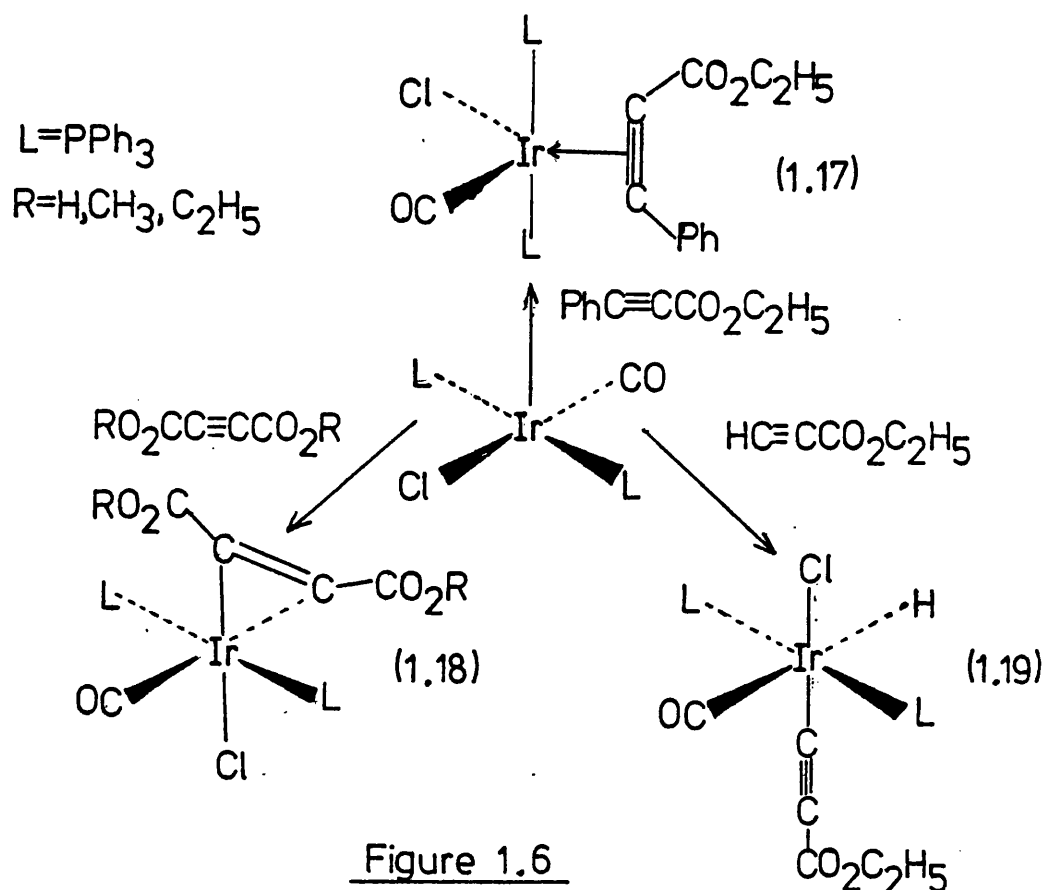
It would be expected that iridium(I)-acetylene complexes would, in general, be more stable than rhodium(I)-acetylene complexes, due to iridium being a third-row, as opposed to a second-row, transition element, and therefore having the ability to form greater d- π^* -overlap with an acetylene ligand. In addition, the outer d-electrons are held less tightly in iridium(I) than in rhodium(I), and this also enhances its back-bonding capability. This expectation is borne out in practice, since mono-acetylene compounds of iridium(I) are more stable, and more numerous, than those of rhodium(I), and also iridium(I) shows far less tendency to polymerise acetylenes.

The largest class of iridium(I)-acetylenes are those derived from trans-(IrCl(CO)(PPh₃)₂) - Vaska's complex. The first such compound made by Parshall and Jones,⁵¹ was the hexafluorobut-2-yne derivative (1.16) and this was rapidly followed by a series of acetylene derivatives prepared by Collmann and Kang.⁴²



This series shows a wide variation in the observed i.r. stretching frequencies of the coordinated triple-bonds, ranging from 2060cm^{-1} for $\text{PhC}\equiv\text{CCO}_2\text{C}_2\text{H}_5$, to 1600cm^{-1} for $\text{HO}_2\text{CC}\equiv\text{CCO}_2\text{H}$, and this leads these workers to propose the two limiting structures shown for (1.17) and (1.18). It is also possible that these stretching

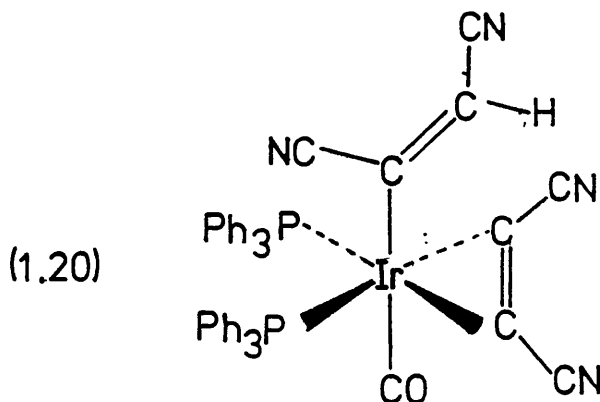
frequencies simply reflect differences in back-bonding to the acetylene as illustrated in Figure 1.2, although a value of 1600 cm^{-1} is extraordinarily low. Figure 1.6 illustrates some of the acetylene compounds prepared from Vaska's complex by Collmann and Kang.



The terminal acetylene ethyl propiolate forms a different type of complex (1.19). The formation of this iridium-acetylide-hydride is an example of the common oxidative-addition reactions of iridium(I) producing iridium(III) complexes, e.g.^{52,53}.

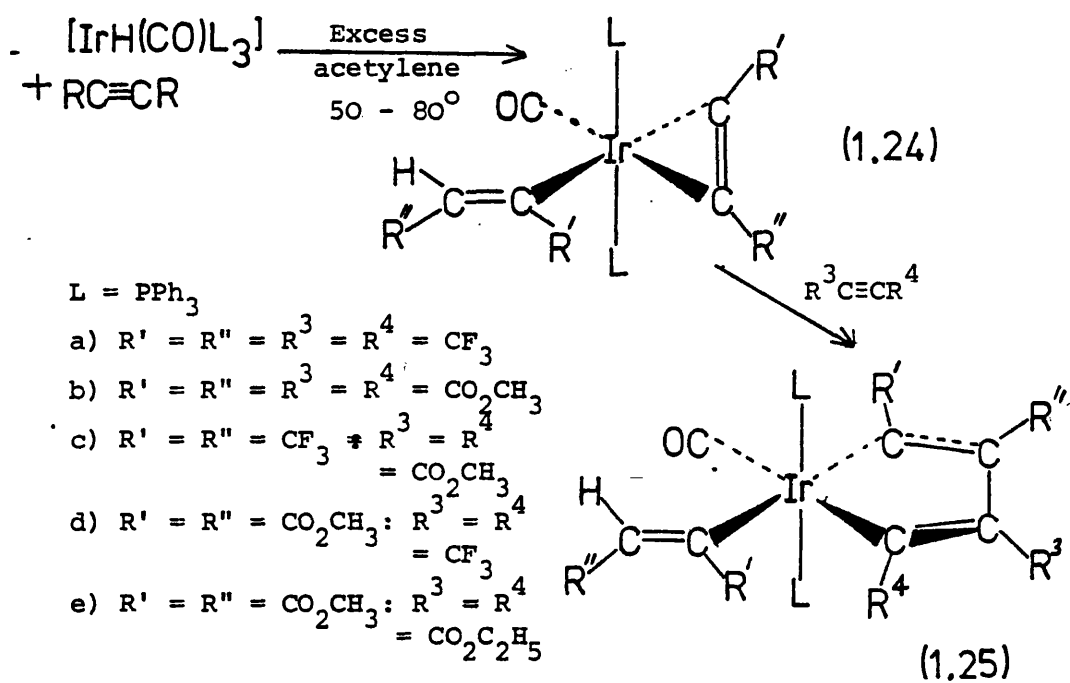
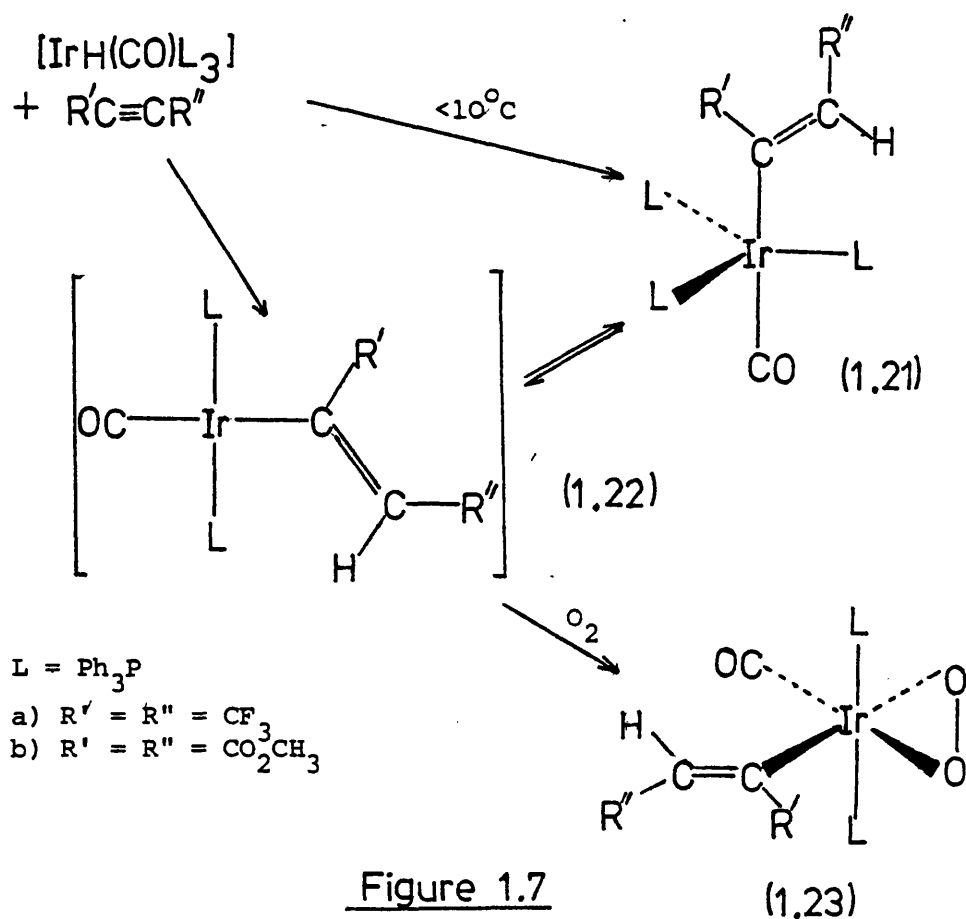
The dicyanoacetylene adduct of Vaska's complex has been prepared by Bruce and Iqbal,⁵⁴ and shows a decrease of 413 cm^{-1} in the $\text{C}\equiv\text{C}$ stretching frequency on coordination, as would be expected for this highly electrophilic acetylene. A fuller report on this system has been published by McClure and Baddley,⁵⁵ who prepared a whole series of complexes of the type $(\text{IrX}(\text{CO})(\text{EPh}_3)_2(\text{NCC}\equiv\text{CCN}))$ ($\text{E}=\text{As}$, $\text{X}=\text{Cl}$; $\text{E}=\text{P}$, $\text{X}=\text{Cl}, \text{Br}, \text{I}, \text{NCS}$) as well as an interesting

product derived from $(\text{IrH}(\text{CO})_2(\text{PPh}_3)_2)$ and dicyanoacetylene (1.20).



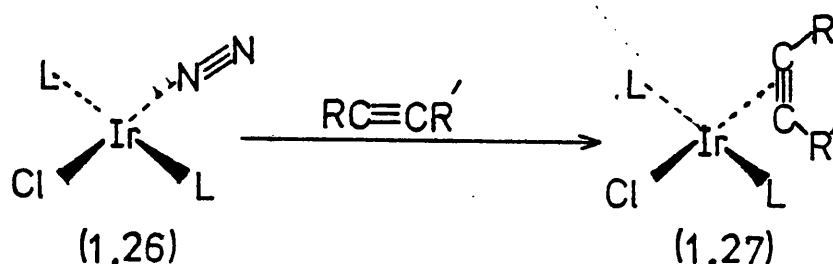
In this complex, one mole of dicyanoacetylene has become π -bonded to the iridium, and a further mole has inserted into the Ir-H bond. Similar products can be isolated⁵⁶ from the reactions of $\text{F}_3\text{CC}\equiv\text{CCF}_3$ and $\text{H}_3\text{CO}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3$ with $(\text{IrH}(\text{CO})(\text{PPh}_3)_3)$. Further work has been done on these latter two systems, including the preparation of some more alkenyl complexes, as well as interesting mixed metalocyclopentadienes. Reaction of $(\text{IrH}(\text{CO})(\text{PPh}_3)_3)$ with either $\text{F}_3\text{CC}\equiv\text{CCF}_3$ or $\text{H}_3\text{CO}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3$ at temperatures below 10°C gives complexes (1.21) which isomerise to (1.22) in benzene solution at room temperature.⁵⁷ The complexes (1.22) easily pick up dioxygen, giving (1.23), (Figure 1.7).

At temperatures between 50 and 80°C , however, in the presence of excess of the acetylene, the σ -alkenyl- π -acetylene compounds (1.24) are formed. These react further with disubstituted acetylenes to give the metalocyclopentadienes (1.25). The unsymmetrical iridia-cyclopentadiene complexes (1.25c,d,e) are effective catalysts for the cyclotrimerisation of disubstituted acetylenes (Figure 1.8).



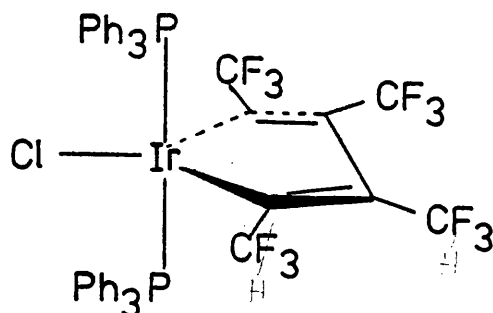
An analogous system to Vaska's complex is trans-(Ir(C≡CCH₃)(CO)(PPh₃)₂) and an adduct of this with H₃CO₂CC≡CCO₂CH₃ is easily prepared.⁵⁸ The reaction with F₃CC≡CCF₃ also yields the acetylene-adduct, but in addition, polymerisation of the acetylene to (C₄F₆)_n occurs. This type of iridium-acetylide complex is quite effective in polymerising terminal acetylenes, and, for example, phenylacetylene is polymerised by (Ir(C≡CPh)(CO)(PPh₃)₃) to polyphenylacetylene, and HC≡CCO₂C₂H₅ is polymerised in a similar way by (Ir(C≡CC₂H₅)(CO)(PPh₃)₃).

Another closely related class of iridium(I)-acetylene compounds can be prepared⁴² from the dinitrogen complex (1.26): some of these are depicted below.



- | | | |
|----------------------|---|---|
| L = PPh ₃ | a) R = R' = CO ₂ CH ₃ | d) R = Ph, R' = CO ₂ C ₂ H ₅ |
| | b) R = R' = COPh | e) R = <u>p</u> -NO ₂ Ph, R' = CO ₂ C ₂ H ₅ |
| | c) R = R' = Ph | |

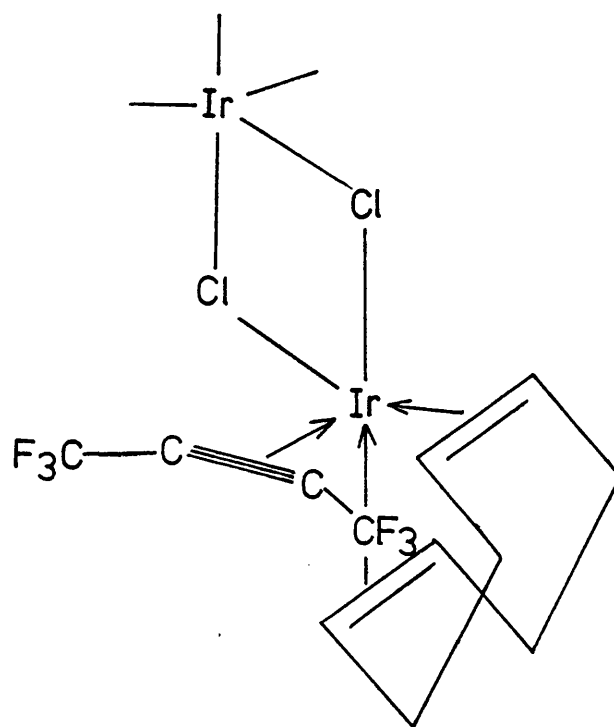
It is interesting that bulky acetylenes such as diphenylacetylene form complexes like (1.27), but do not form isolable compounds with Vaska's complex. Also of interest is the fact that compounds such as (1.27a) easily lose the coordinated acetylene on reaction with carbon monoxide, giving trans-(IrCl(CO)(PPh₃)₂). Not surprisingly the hexafluorobut-2-yne derivative of (1.26) has also been prepared, and further reaction of the adduct so obtained, with but-2-yne, gives the iridiacyclopentadiene (1.28)⁵⁹. (see over)



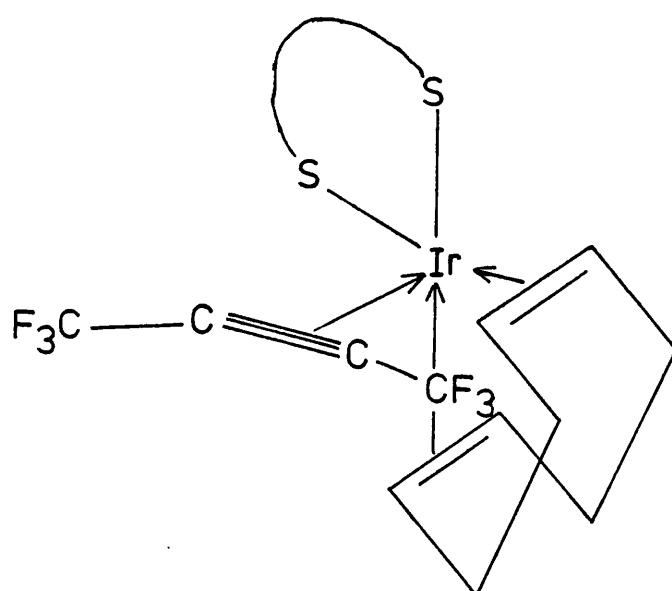
(1.28)

Fluoro-olefin and fluoro-acetylene adducts would be expected to be stabilised by increased electron density on the metal atom, and this is confirmed by comparing the reactions of trans-(IrCl(CO)(PPh₂CH₃)₂) with those of trans-(IrCl(CO)(PPh₃)₂), when the former is found to give more stable complexes with hexafluoropropene and bromotrifluoroethylene.⁵⁹ In the course of these studies with the methyldiphenylphosphine derivative of Vaska's complex, a C₄F₆ adduct and an iridiacyclopentadiene incorporating two moles of C₄F₆ were isolated.

A series of iridium(I)-acetylene complexes containing both a coordinated cycloocta-1,5-diene moiety, and a hexafluorobut-2-yne ligand have been prepared,^{6,22} these being the first compounds to contain both a π -bonded diene and a π -bonded acetylene to the same metal atom. Reaction of (IrCl(cod))₂ with F₃CC \equiv CCF₃ at room temperature gives the compound (1.29): similar reaction of (Ir(dmdtc)(cod)), (Ir(dtc)(cod)), (Ir(dpdtc)(cod)) and (Ir(dtp)(cod)) gives complexes of the type (1.30).

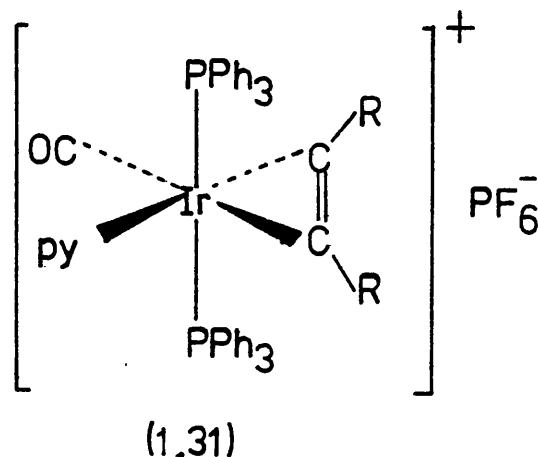


(1.29)



(1.30)

As with rhodium(I), cationic acetylene complexes are known for iridium(I). Dimethyl acetylenedicarboxylate reacts with the cationic five-coordinate complex $(\text{IrL}_2(\text{CO})_3)(\text{BPh}_4^-)$ ($\text{L}=\text{PPh}_3$, PPh_2CH_3 , $\text{P}(\text{C}_2\text{H}_5)_3$ and $\text{P}(\text{C}_6\text{H}_{11})_3$) with displacement of a carbonyl ligand to form simple mono-acetylene compounds, and with $(\text{Ir}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_2(\text{PPh}_3)_3)(\text{ClO}_4^-)$, resulting in loss of a phosphine ligand, and formation of a similar mono-acetylene complex.⁶¹ Surprisingly, the complex $(\text{Ir}(\text{CO})(\text{acetone})(\text{PPh}_3)_2)(\text{PF}_6^-)$ does not give stable complexes on reaction with hexafluorobut-2-yne or dimethyl acetylenedicarboxylate, but if pyridine is introduced into the mixture before the acetylene, the compounds (1.31) are formed.⁶² It seems likely that the pyridine blocks one of the coordination sites, preventing the formation of intermediates involving more than one acetylene.

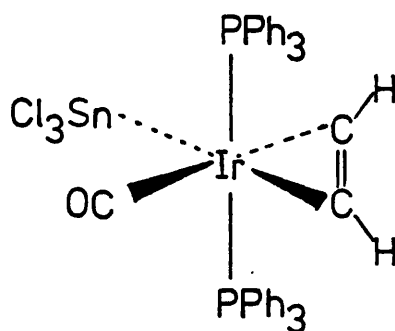


$\text{R}=\text{CO}_2\text{CH}_3, \text{CF}_3$; py=pyridine

The reaction of $(\text{Ir}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2)$ with $\text{F}_5\text{C}_6\text{C}\equiv\text{CC}_6\text{F}_5$ in refluxing mesitylene has been studied,⁴⁵ with isolation of similar mono-acetylene complexes to those derived from the analogous reactions between $(\text{Rh}(\pi\text{-C}_5\text{H}_5)(\text{CO})_2)$ and acetylenes.^{44,45} Thus, complexes similar to (1.10), (1.12a) and (1.14) are obtained, the

differences being that the metal is iridium, and the acetylene is dipentafluorophenylacetylene.

Finally, an interesting complex which makes use of the π -accepting ability of the SnCl_3^- ligand has been obtained,⁶³ by reacting acetylene with $(\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{SnCl}_2)_3(\text{C}_6\text{H}_6))$, prepared in situ. Complex (1.32) has a $\text{C}\equiv\text{C}$ stretching frequency at 1682 cm^{-1} , and an n.m.r. peak due to the acetylene protons at $\tau 5.40$, the region for olefinic protons, signifying a considerable reduction in bond-order.



(1.32)

1.4 Palladium(O) complexes

Relatively few acetylene complexes of palladium(O) have been prepared thus showing a marked difference from platinum(O)-acetylene complexes, of which many are now known. The acetylene compounds which have been prepared with palladium(O) are largely those of the very electrophilic acetylenes hexafluorobut-2-yne and dimethyl acetylenedicarboxylate, and this reflects the importance of the back-bonding contribution to the metal-acetylene bond in compounds involving a very electron-rich central metal atom. The difference in stability between palladium(O)-acetylene complexes and those of platinum(O) is more marked than that between the rhodium(I) and iridium(I) systems, indicating the difficulty for a second-row d^{10} system of releasing sufficient electron density to form a stable π -bond to an acetylene, or indeed an olefin ligand.

The first mono-acetylene complexes of palladium(O) were prepared^{16, 64} by displacement of two triphenylphosphine ligands from $(\text{Pd}(\text{PPh}_3)_4)$ using $\text{F}_3\text{CC}\equiv\text{CCF}_3$ or $\text{H}_3\text{CO}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3$. Attempts to prepare similar compounds with less electrophilic acetylenes such as $\text{PhC}\equiv\text{CCH}_3$ and $\text{PhC}\equiv\text{CPh}$ were unsuccessful. Similar compounds, of the form $(\text{Pd}(\text{PR}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$ ($\text{R}_3=\text{n-Bu}_3, \text{Ph}(\text{CH}_3)_2$) can be prepared by addition of C_4F_6 to the hydrazine reduction product of $(\text{PdCl}_2(\text{PR}_3)_2)$. This reduction method is a useful way of preparing platinum(O)-acetylene compounds, but has not been as profitable with palladium(O). Table 1.7 lists the reduction in $\text{C}\equiv\text{C}$ stretching frequency of $\text{F}_3\text{CC}\equiv\text{CCF}_3$ on coordination in various nickel(O), platinum(O) and palladium(O) systems. Two interesting trends are apparent from these results: taking the decrease in $\text{C}\equiv\text{C}$ stretching-frequency as a measure of the metal-acetylene bond-strength, for the series $(\text{M}(\text{PPh}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$, the

bond-strength increases in the order $\text{Pd} < \text{Ni} < \text{Pt}$, and for the series $(\text{M}(\text{PR}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$, where $\text{M} = \text{Pt}$ or Pd , the bond-strength increases in the order $\text{PPh}_3 < \text{PPh}_2 < \text{Pn-Bu}_3$. The second phenomenon is a result of increased electron-density on the metal causing greater back-bonding to the acetylene, but the first trend is surprising, since the expected order, based on back-bonding theories, would be $\text{Ni} < \text{Pd} < \text{Pt}$. A similar result has been found for some Group IVb complexes⁶⁵, where a stability order $\text{Mo} < \text{Cr} < \text{W}$ was observed.

Table 1.7 Infra-red data for some metal(O)-acetylene complexes¹⁶

<u>Complex</u>	<u>$\nu(\text{C}\equiv\text{C}) \text{ cm}^{-1}$</u>	<u>Decrease in $\nu(\text{C}\equiv\text{C}) \text{ cm}^{-1}$</u>
$(\text{Ni}(\text{PPh}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$	1790	510
$(\text{Pd}(\text{PPh}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$	1811, 1838	475
$(\text{Pt}(\text{PPh}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$	1775	525
$(\text{Pd}(\text{PPh}(\text{CH}_3)_2)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$	1800, 1837	482
$(\text{Pd}(\text{Pn-Bu}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$	1795, 1837	484
$(\text{Pt}(\text{PPh}(\text{CH}_3)_2)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$	1767	533
$(\text{Pt}(\text{Pn-Bu}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$	1758	542
$(\text{Pd}(\text{PPh}_3)_2(\text{H}_3\text{CO}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3))$	1830, 1845	410

For the palladium complexes, the $\text{C}\equiv\text{C}$ band appears as a doublet, even in solution. The reasons for this are not understood, but in such cases, the figure in the third column is a mean value.

The crystal structure of $(\text{Pd}(\text{PPh}_3)_2(\text{H}_3\text{CO}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3))$ has been determined⁶⁶, and shows a lengthening of the $\text{C}\equiv\text{C}$ bond on coordination to $1.28(1)\text{\AA}$, a value between those of free olefins and free acetylenes. It also shows a bend-back angle for the acetylene substituents of 35° .

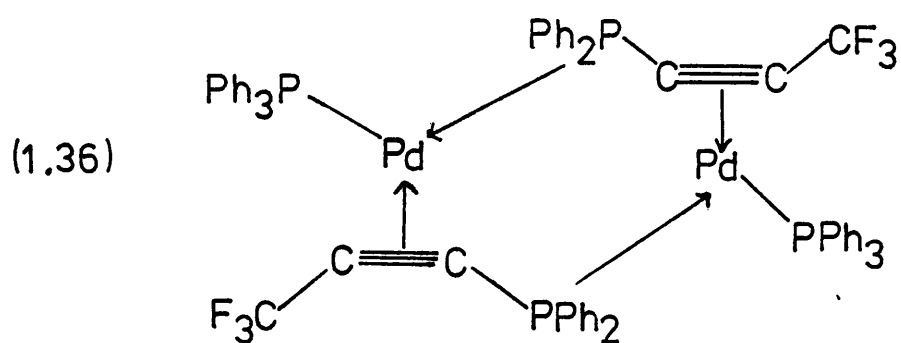
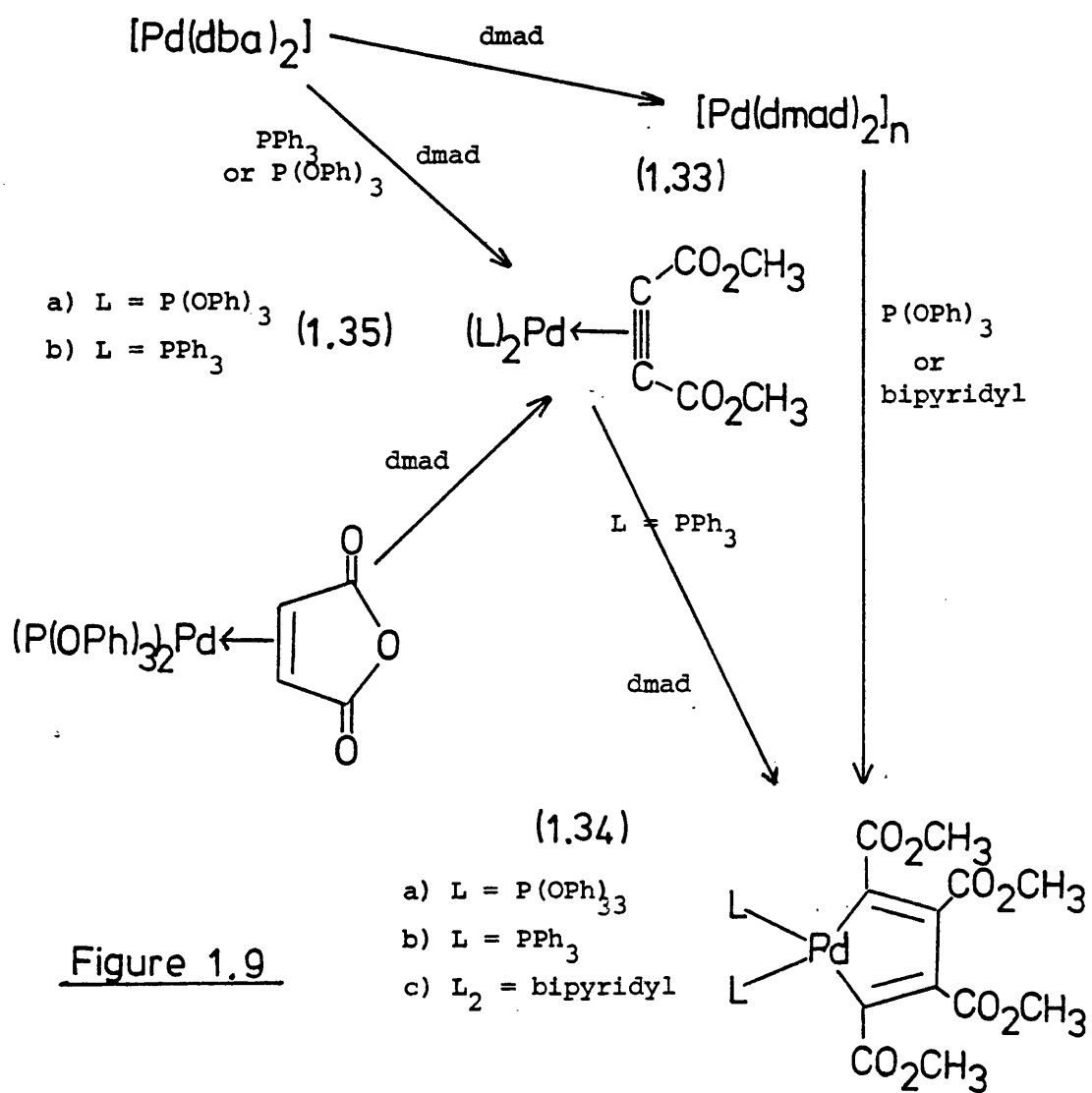
The complex $(\text{Pd}(\text{PPh}_3)_2(\text{NCC}\equiv\text{CCN}))$ has also been prepared,⁵⁵ but requires a more devious route than simple substitution in

$[\text{Pd}(\text{PPh}_3)_4]$. It is prepared instead by displacement of fumaronitrile from the compound $(\text{Pd}(\text{PPh}_3)_2(\text{trans-HC}(\text{CN})=\text{C}(\text{CN})\text{H}))$.

Two fairly labile palladium(0)-acetylene compounds have been prepared⁶⁷ from the binuclear compound " $(\text{Pd}(\text{t-BuNC})_2)$ ". Reactions of acetylenes with this yield $(\text{Pd}(\text{t-BuNC})_2(\text{acetylene}))$ complexes - the acetylene is either $\text{PhC}\equiv\text{CPh}$ or $\text{H}_3\text{CO}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3$. The diphenylacetylene derivative is particularly labile and reacts with molecular oxygen below -40°C to give $(\text{Pd}(\text{t-BuNC})_2(\text{O}_2))$.

Another interesting compound which utilises basic ligands on the metal to stabilise the bond to the acetylene is prepared from bis(benzylideneacetone)palladium(0) and dimethyl acetylenedicarboxylate.⁶⁸ If these two compounds are reacted together, a polymeric palladiacyclopentadiene product (1.33) is obtained, which reacts with triphenylphosphite or 2,2'-bipyridyl to give the monomeric compounds (1.34). If, however, the two reactants are mixed in the presence of triphenylphosphite, the mono-acetylene complex (1.35a) is obtained: this does not react with excess of the acetylene to give (1.34a), but the triphenylphosphine derivative (1.35b) does undergo this further reaction. The acetylene complex (1.35a) can also be obtained by displacement of the olefin from $(\text{Pd}(\text{P}(\text{OPh})_3)_2(\text{maleic anhydride}))$.

A novel phosphinoacetylene complex of palladium(0), $(\text{Pd}(\text{Ph}_2\text{PC}\equiv\text{CCF}_3)_2)_2$ has been prepared by the reduction of cis- $(\text{PdCl}_2(\text{Ph}_2\text{PC}\equiv\text{CCF}_3)_2)$ with sodium borohydride in dry tetrahydrofuran⁶⁹. In addition to this, an X-ray crystal-structure determination of the compound (1.36), prepared from $(\text{Pd}(\text{PPh}_3)_4)$ and $\text{Ph}_2\text{PC}\equiv\text{CCF}_3$, has been carried out. The structure of the former compound is similar, except that the triphenylphosphine group is replaced by another molecule of the phosphinoacetylene. The platinum analogues of both these compounds have also been made.

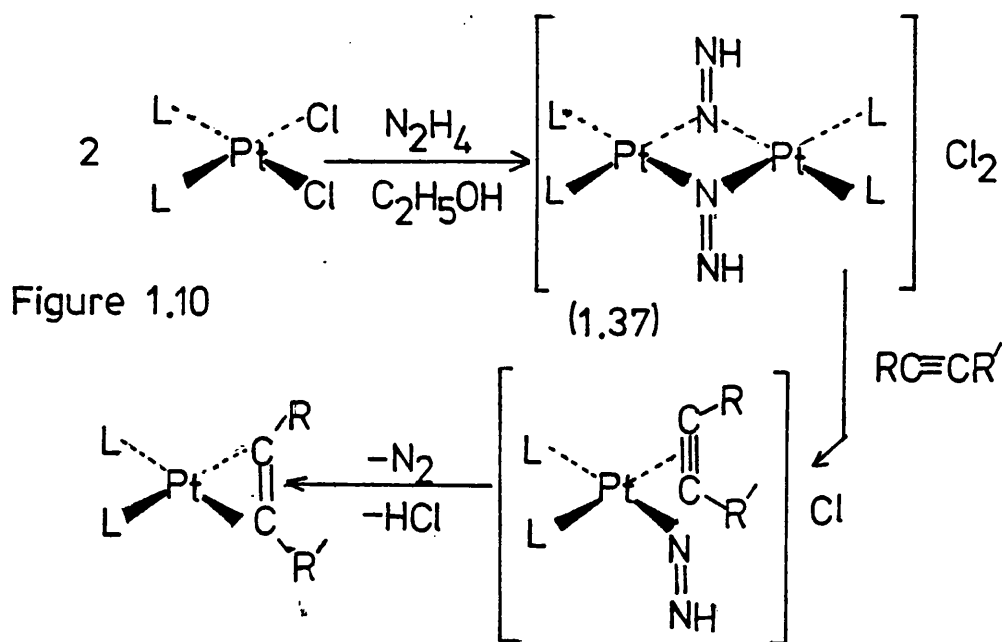


1.5 Platinum(0) complexes

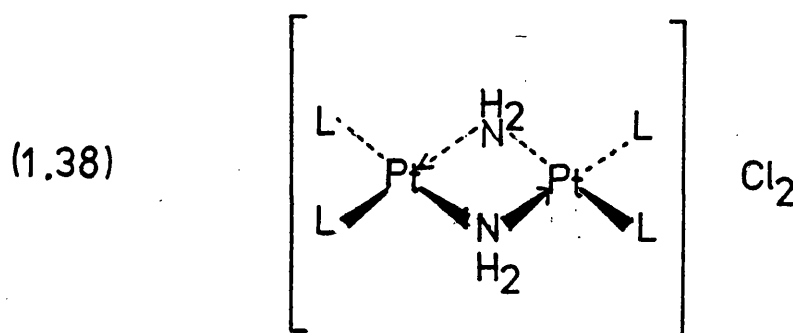
Nearly all the known zerovalent platinum-acetylene complexes contain phosphines as stabilising ligands, and are of the form $(\text{Pt}(\text{PR}_3)_2(\text{acetylene}))$. Two general methods are commonly used in preparing these compounds : a) reduction of platinum(II) compounds, and b) ligand substitution in platinum(0) compounds.

a) Preparation from platinum(II) complexes

Complexes of the type $(\text{Pt}(\text{PR}_3)_2(\text{acetylene}))$ were first prepared by Chatt and co-workers by reduction of an ethanolic suspension of cis-($\text{PtCl}_2(\text{PR}_3)_2$) with hydrazine, in the presence of the acetylene⁷⁰. The most likely mechanism for this reaction is illustrated in Figure 1.10.



The crystal structure of the tetraphenylborate derivate of the bridged species has been determined⁷¹, and shows it to be a mixture of compounds (1.37) and (1.38). The imine-bridged dimer (1.38) does not react with hydroxyacetylenes, although hydroxyacetylene complexes can be prepared by this reduction method, suggesting that (1.37) is the reactive species. The alternative mechanism involves initial reduction of cis-($\text{PtCl}_2(\text{PR}_3)_2$) to $(\text{PtHCl}(\text{PPh}_3)_2)$, followed by further reduction

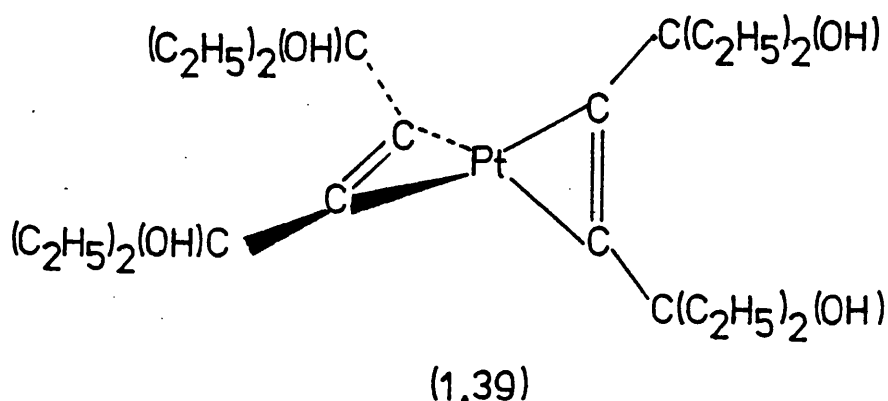


to $(\text{Pt}(\text{PPh}_3)_2)$, which then reacts with the acetylene to give the platinum(0)-acetylene product⁷⁰. Several observations suggest that this is not the correct mechanism: a) no infra-red bands due to Pt-H or Pt-Cl stretching modes are observed in the compound isolated from reduction of cis- $(\text{PtCl}_2(\text{PPh}_3)_2)$ with hydrazine in ethanol⁷¹; b) $(\text{Pt}(\text{PPh}_3)_2)$ has only been prepared from a platinum-hydride under oxidising conditions, rather than the reducing conditions employed here⁷⁵; c) only in a very few cases does the reaction of hydrides with olefins or acetylenes yield olefin or acetylene complexes⁷⁶. More commonly, vinyl complexes result⁷⁷.

This method for making platinum(0)-acetylene compounds can be used for a variety of different acetylenes, e.g.^{70,78,79} but has failed for $(\text{PtCl}_2(\text{PBU}_3)_2)$ and $(\text{PtCl}_2(\text{PPh}_2\text{CH}_3)_2)$ with some acetylenes.¹⁶

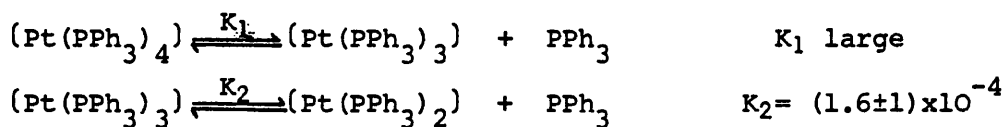
A synthesis of platinum(0)-acetylene compounds starting from a platinum(II) species has also been developed⁸⁰ for the complexes $(\text{Pt}(\text{acetylene})_2)$. The synthesis involves⁸¹ a simple reaction in ethanol/water mixtures of potassium tetrachloroplatinite with acetylenes of the type $\text{R}^1\text{R}^2\text{C}(\text{OH})\text{C}\equiv\text{CC}(\text{OH})\text{R}^1\text{R}^2$ (a, $\text{R}^1=\text{CH}_3$, $\text{R}^2=\text{C}_2\text{H}_5$; b, $\text{R}^1=\text{R}^2=\text{C}_2\text{H}_5$; c, $\text{R}^1=\text{CH}_3$, $\text{R}^2=\text{C}_3\text{H}_7$; d, $\text{R}^1=\text{CH}_3$, $\text{R}^2=\text{C}_5\text{H}_{11}$; e, $\text{R}^1=\text{C}_2\text{H}_5$, $\text{R}^2=\text{C}_4\text{H}_9$; f, acetylene=di(hydroxy-1-cyclohexyl)-1,2,-acetylene). The crystal structure of the compound in which

$R^1=R^2=C_2H_5$ has been determined,⁸² and shows that the two acetylene groups are 180° apart, and perpendicular to each other. (1.39)
 The triple-bond lengths are $1.35(3)\text{\AA}$ and $1.36(2)\text{\AA}$, as compared to an average value of $1.203(3)\text{\AA}$ for free acetylenes, and the bend-back angles for the acetylene substituents are $38.21(85)^\circ$ and $38.95(46)^\circ$.



b) Substitution in platinum(0) complexes

Whilst reporting the synthesis of platinum(0)-acetylene systems from cis-($PtCl_2(PPh_3)_2$), Chatt et al.⁷⁰ also reported that some acetylenes reacted with $(Pt(PPh_3)_4)$, with substitution of two phosphine ligands, again giving $(Pt(PPh_3)_2(\text{acetylene}))$ complexes. These reactions are due to $(Pt(PPh_3)_4)$ becoming coordinatively unsaturated in solution^{83,84}.



Interestingly, hydroxyacetylenes react with $(Pt(PPh_3)_4)$ to give two types of acetylene complexes,⁷² as shown in Figure 1.11.

Complexes of type (1.40) are formed using excess of a bulky terminal acetylene and type (1.41) are formed using less bulky acetylenes.

1-ethynylcyclohexanol forms derivatives of both type (1.40) and type (1.41) and single-crystal X-ray studies have been carried out on both these complexes. The π -bonded acetylene derivative (1.41) shows two independent molecules in the asymmetric unit, these being isomers, with the acetylene group equatorially bonded to the cyclohexane ring in one molecule, and axially bonded in the other⁷³. For the derivative of type (1.40), the X-ray studies confirm that this is a bis-acetylide complex, with the acetylide groups trans to each other, but the hydrogen atoms could not be located⁷⁴. The hydrogen atoms can, however, be seen in the n.m.r. in the region associated with metal-hydride species⁷², so it seems probable that complexes (1.40) are platinum(IV) dihydrides.

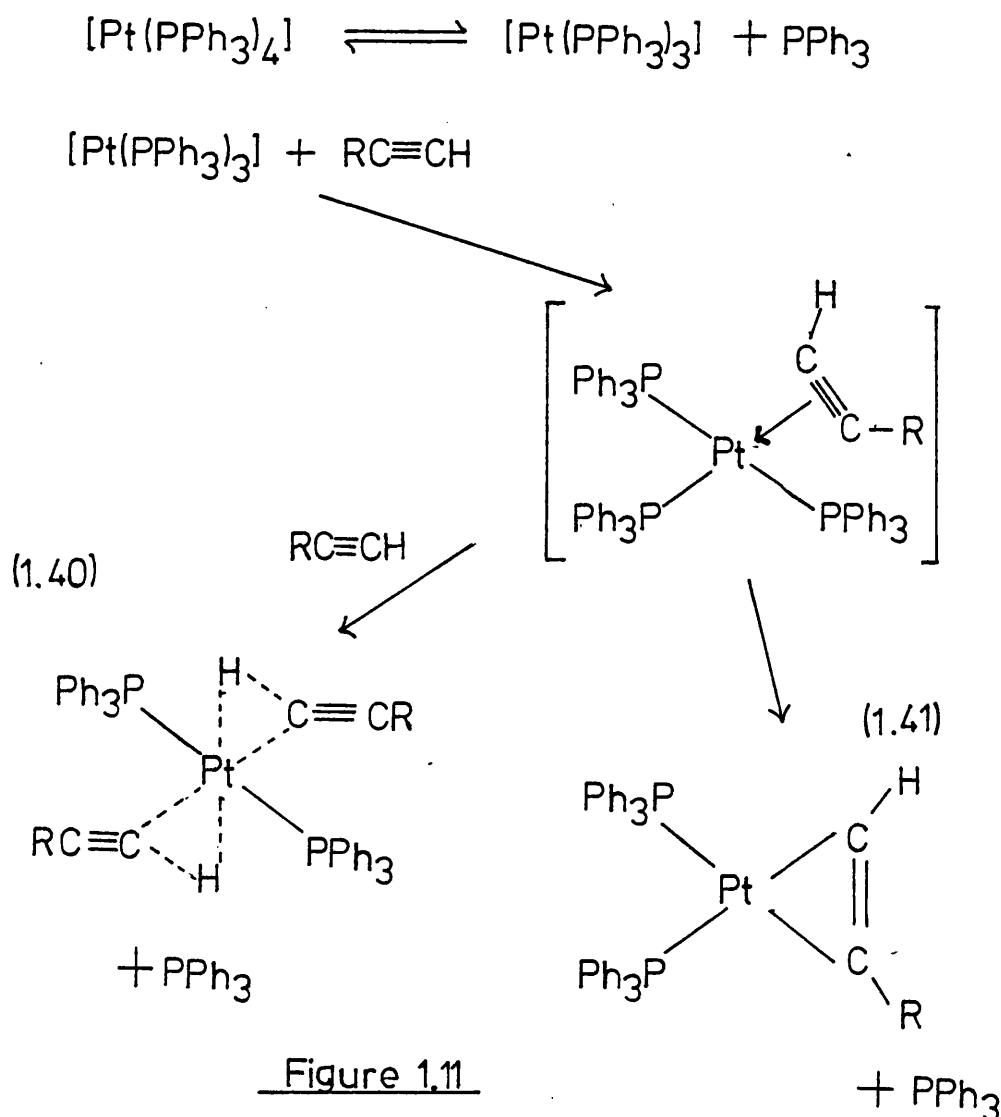
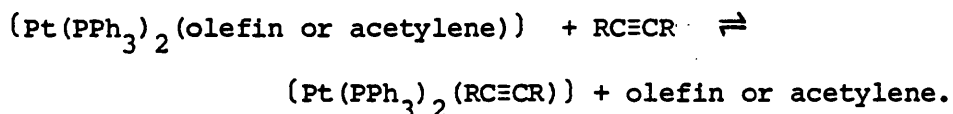
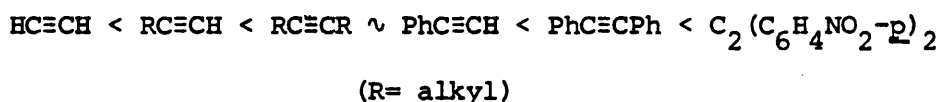


Figure 1.11

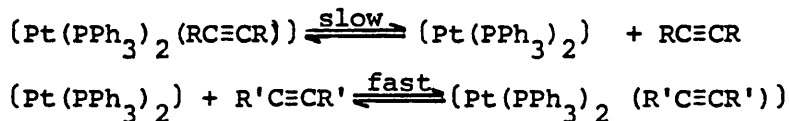
An alternative means of preparation involving substitution in platinum(0) species is reactions of the type:



A series of displacement reactions⁷⁰ show that the stability of the complexes increases in the order:



In general, the stability increases with increasing electronegativity of the substituents on the acetylene, as would be expected. The mechanism originally proposed⁸⁵ for these substitutions involves a rate-determining dissociation of the acetylene, followed by reaction of the incoming ligand with the intermediate $(\text{Pt}(\text{PPh}_3)_2)$.



Isolation⁷⁵ of $(\text{Pt}(\text{PPh}_3)_2)$, followed by the discovery that it reacts with acetylenes to give $(\text{Pt}(\text{PPh}_3)_2(\text{acetylene}))$ complexes⁸⁶, gives much credibility to the dissociative-mechanism theory.

N.m.r. spectroscopy, however, fails to provide evidence for dissociation of the acetylene in $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCH}_3))$ ⁸⁷, and later n.m.r. work on $(\text{Pt}(\text{P}(\text{C}_6\text{D}_5)_3)_2(\text{D}_5\text{C}_6\text{C}\equiv\text{CH}))$ ⁸⁸, as well as complexes having mono-substituted phenylacetylene ligands also shows no indication of acetylene dissociation, or rotation in solution. This leads these workers⁸⁸ to reconsider the mechanism of acetylene substitution, and to propose a reaction pathway involving a rate-determining change in the stereochemistry of the original complex, possibly involving rotation of the acetylene through 90° to give a pseudotetrahedral transition-state. This is followed by coordination of the incoming acetylene, loss of the

original ligand, and rotation back to a planar system. Figure 1.12 illustrates the reaction coordinate/potential energy diagram for this process.

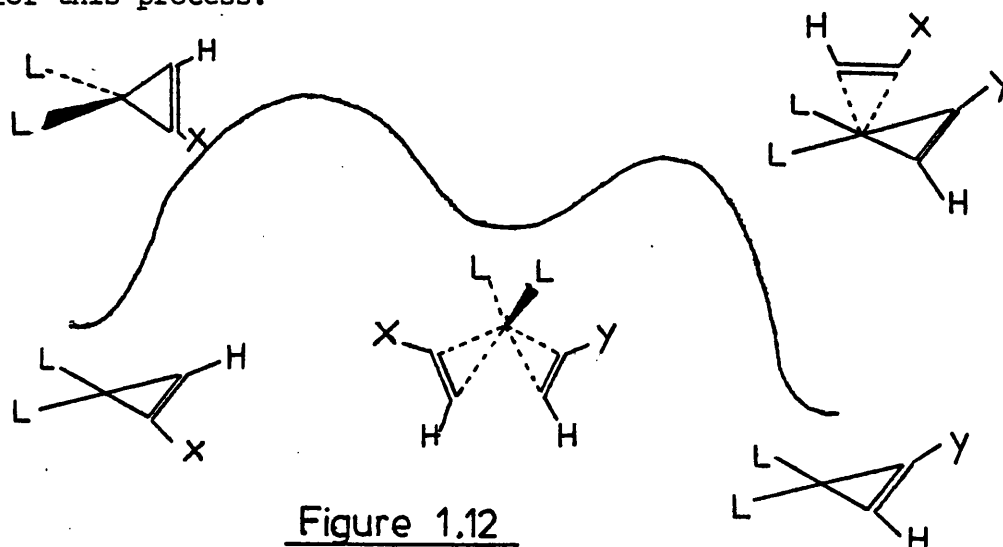


Figure 1.12

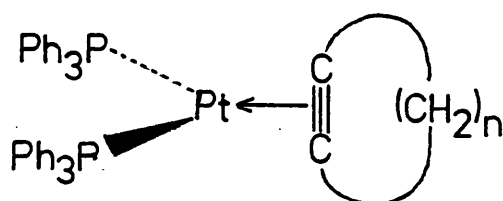
In connection with this ligand-displacement route to platinum(0)-acetylene species, it is interesting to note that the enthalpy of the reaction:

$(\text{Pt}(\text{PPh}_3)_2(\text{H}_2\text{C}=\text{CH}_2)) (\text{cryst}) + \text{PhC}\equiv\text{CPh}(\text{cryst}) \rightarrow$
 $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CPh})) (\text{cryst}) + \text{C}_2\text{H}_4(\text{g})$ has been measured as
 $\Delta H_{298} = -82 \pm 12 \text{ kJ.mol}^{-1}$ from solution calorimetry⁸⁹. This gives an interesting measure of the relative strengths of the platinum-diphenylacetylene and platinum-ethylene bonds, and comparison with earlier results⁹⁰ shows that the platinum-tetracyanoethylene bond is the strongest of the three.

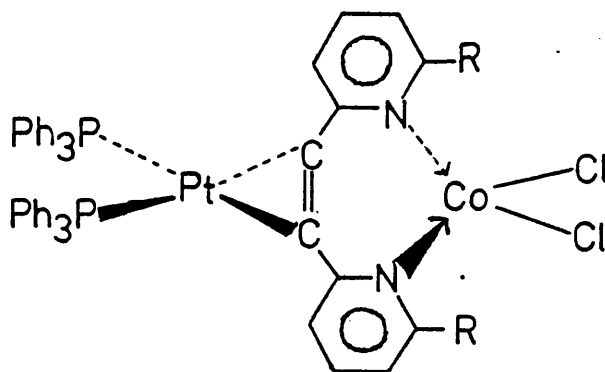
Two interesting compounds which have recently been prepared⁹¹ using the ligand-substitution route are the cyclohexyne and cycloheptyne compounds (1.42a) and (1.42b). They are prepared from the reaction of $(\text{Pt}(\text{PPh}_3)_3)$ with 1,2-dibromocyclohexene and 1,2-dibromocycloheptyne respectively, and both have been the subject of single-crystal X-ray studies⁹². These structural determinations show the $\text{C}\equiv\text{C}$ bond-lengths in the two compounds to be equal within experimental error, and the bond-lengths and bond-angles in the metal atom first coordination spheres

are also almost equal. Cyclohexyne and cycloheptyne have not been isolated in the free state, although there is some evidence for their existence, as short-lived intermediates. Cyclooctyne, however, can be isolated in the free state and a platinum(0) complex (1.42c) of this acetylene has now been prepared,⁹³ although this time via the hydrazine reduction of cis-(PtCl₂(PPh₃)₂) in the presence of cyclooctyne.

(1.42)
a, n=4
b, n=5
c, n=6



A further interesting series of compounds can be derived from (Pt(PPh₃)₄) and several 2-pyridylacetylenes⁹⁴. A clever synthesis, which makes use of the ability of these acetylenes to coordinate via both the acetylene triple-bond and the nitrogen lone-pairs of the pyridine rings, gives the compound (1.43).



(1.43) R=H, CH₃

This synthesis is aided by the bending-back of the acetylene on coordination to platinum leaving the pyridyl groups in a favourable position for chelation to the cobalt atom. Preliminary X-ray data suggest that this compound is flat, or almost so.

Some reactions of platinum(0)-acetylene complexes

Acids such as HCl, HBr, picric, thioacetic and trifluoroacetic acid react with $(\text{Pt}(\text{PPh}_3)_2(\text{acetylene}))$ complexes to give the compounds $(\text{PtX}_2(\text{PPh}_3)_2)$ (where $\text{X}=\text{Cl}, \text{Br}, \text{picrate}, \text{thioacetate}$ and trifluoroacetate), as well as the olefin produced by reduction of the acetylene. The mechanism of this reaction is thought to involve platinum(II) and platinum(IV) hydrides, as well as a vinyl intermediate (Figure 1.13)⁹⁷.

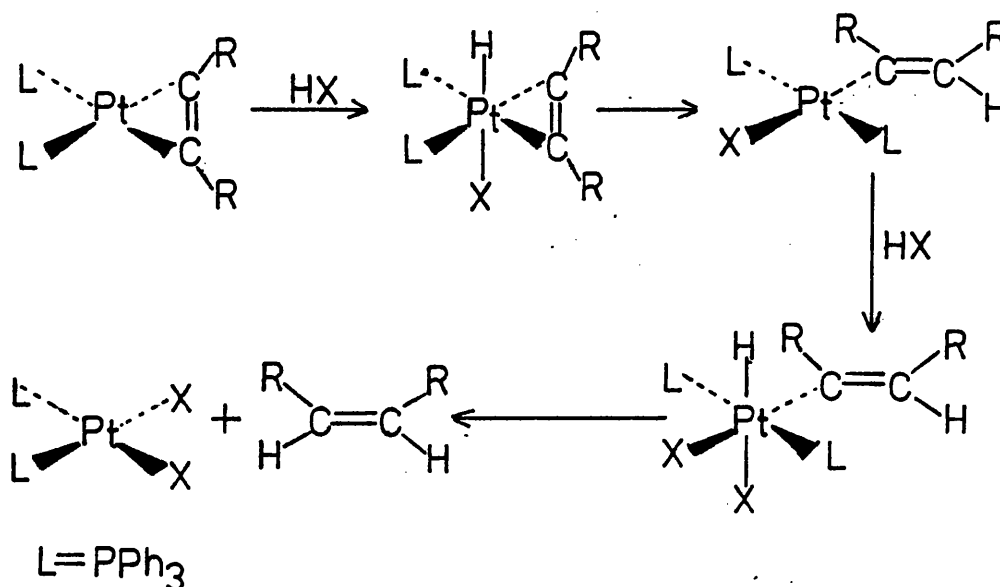
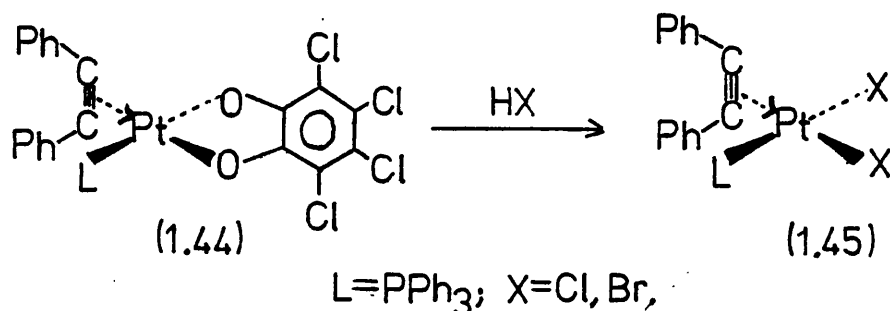


Figure 1.13

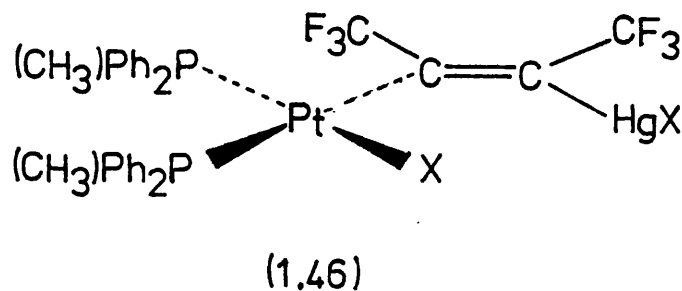
Evidence for the vinyl intermediate is given by the reactions of $(\text{Pt}(\text{PPh}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$ with HCl ⁹⁶ and $\text{F}_3\text{CCO}_2\text{H}$,⁹⁵ which give vinyl complexes which are too stable to decompose to the free olefin in the presence of excess acid. Further, addition of just one mole of acid in reactions such as this causes the isolation of the trans vinyl complexes, where the stereochemistry about the double-bond is cis.⁹⁸ The proportions of cis- and trans- olefins which are obtained from these reactions seem to

vary considerably, depending on the nature of the olefin, and also of the acid.

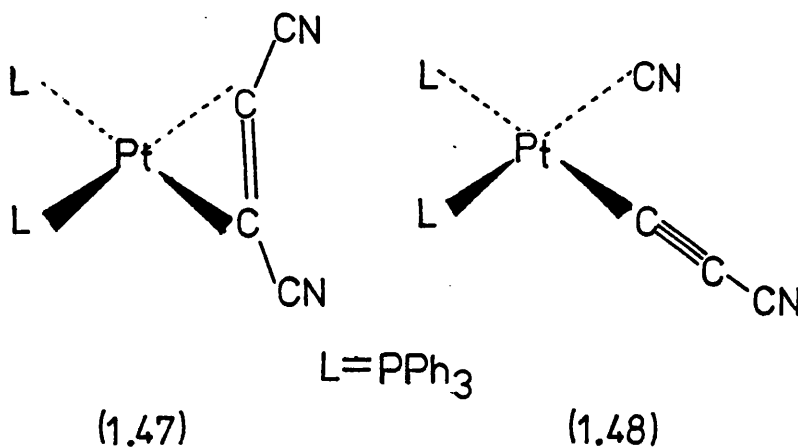
An interesting oxidative-elimination reaction occurs^{95,99} between $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CPh}))$ and tetrachloro-o-benzoquinone, giving compound (1.44). Reaction of this with triphenylphosphine causes elimination of the acetylene, but HCl or HBr give a useful route to the platinum(II)-acetylene complexes (1.45).



Reaction between $(\text{Pt}(\text{PPh}_2\text{CH}_3)_2(\text{F}_3\text{CC}\equiv\text{CCF}_3))$ and HgX_2 ($\text{X}=\text{Cl}$ or Br) gives the cis vinyl complexes (1.46) in which the geometry about the olefinic double-bond is also cis⁹⁵.



Finally, mention is made of two reactions involving isomerisation of a coordinated acetylene to a σ -bonded acetylide group. The platinum(0)-dicyanoacetylene compound (1.47) can be photochemically isomerised to (1.48), the first well defined example of an acetylene to acetylide isomerisation¹⁰⁰. A crystal-structure determination indicates cis geometry about the platinum.



Harbourne and Stone¹⁰¹ have prepared $[\text{Pt}(\text{PPh}_3)_2(\text{F}_3\text{CC}\equiv\text{CH})_2]$ from $(\text{Pt}(\text{PPh}_3)_4)$ and 3,3,3-trifluoropropyne. Some later work by Cullen and Hou¹⁰² shows that using excess of the acetylene over a longer time-period, the product obtained is $(\text{Pt}(\text{PPh}_3)_2(\text{C}\equiv\text{CCF}_3)_2)$. A similar acetylide complex is obtained using $\text{HCC}\equiv\text{CC}_2\text{F}_5$. The geometry of the former compound is assigned as cis, on the basis of i.r. and n.m.r. data, but the geometry of the second compound is less certain. It seems plausible that the mechanism for the formation of these bis-acetylide complexes involves an acetylene to acetylide isomerisation.

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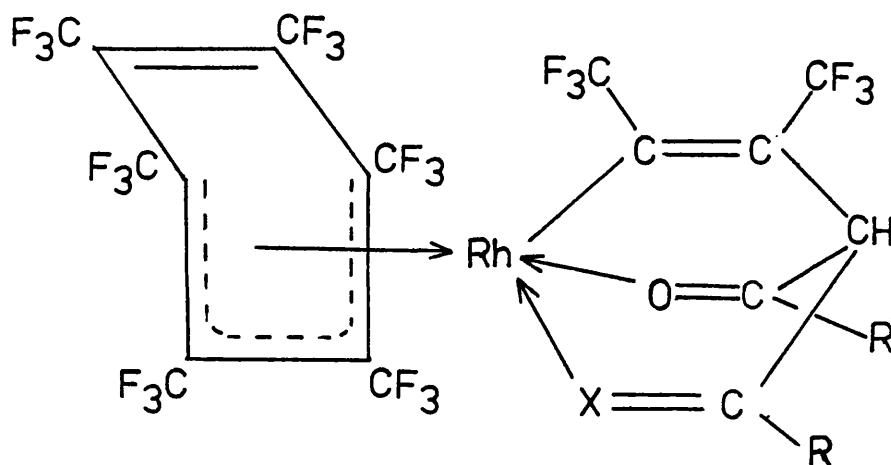
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CHAPTER 2

FURTHER REACTIONS OF OLEFIN-RHODIUM(I)- β -KETOENOLATE AND RELATED COMPLEXES
WITH HEXAFLUOROBUT-2-YNE, AND SOME CHEMISTRY OF THE π -ACETYLENE COMPLEXES
SO FORMED

2.1 Introduction

It has been shown ^{1,2,3}, that the rhodium(I) complexes
 $(\text{Rh}(\beta\text{-ketoenolate})(\text{cod}))$ (β -ketoenolate = acac, dpm, aan, dbm) and
 $(\text{Rh}(\text{apeo})(\text{cod}))$ react with the electrophilic acetylene hexafluorobut-2-yne
 at room temperature to give the adducts (2.1).

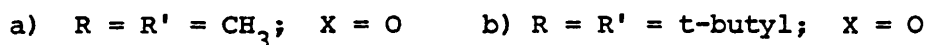
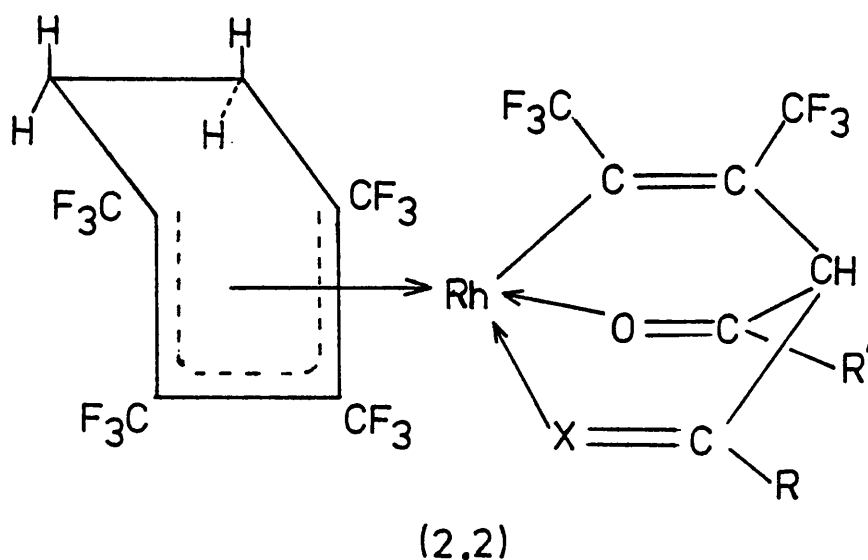


(2.1)

- a) $\text{R} = \text{R}' = \text{CH}_3$; $\text{X} = \text{O}$. b) $\text{R} = \text{R}' = \text{t-butyl}$; $\text{X} = \text{O}$
 c) $\text{R} = \text{CH}_3$, $\text{R}' = \text{NHPh}$; $\text{X} = \text{O}$ d) $\text{R} = \text{R}' = \text{Ph}$; $\text{X} = \text{O}$
 e) $\text{R} = \text{R}' = \text{CH}_3$; $\text{X} = \text{NH}$.

In each case, one mole of the acetylene has added 1,4 across the
 rhodium- β -ketoenolate ring and a further three moles of the acetylene have
 trimerised to a hexakis(trifluoromethyl)benzene ligand which has replaced
 the cyclo-octadiene molecule, and coordinated to the rhodium as a diene.

Similar reaction of the complexes $(\text{Rh}(\beta\text{-ketoenolate})(\text{C}_2\text{H}_4)_2)$ and $(\text{Rh}(\text{apeo})(\text{C}_2\text{H}_4)_2)$ with hexafluorobut-2-yne gives either compounds of type (2.1) in which both ethylene molecules are displaced or (2.2), in which one ethylene molecule has been retained and incorporated into a 1,2,3,4-tetrakis(trifluoromethyl)cyclohexa-1,3,-diene ligand coordinated to the rhodium^{2,3}.

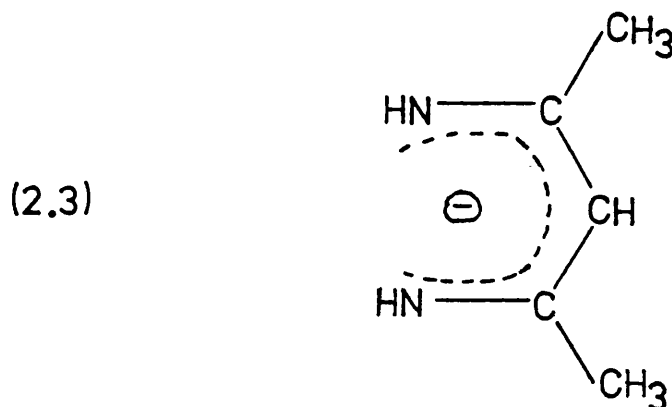


It is clear that the nature of R , R' and X influence the course of this reaction, since for $(\text{Rh}(\text{aan})(\text{C}_2\text{H}_4)_2)$ and $(\text{Rh}(\text{apeo})(\text{C}_2\text{H}_4)_2)$ the product is of type (2.1) rather than (2.2).

In this work, further reactions are carried out to determine factors affecting the formation of complexes of types (2.1) and (2.2). In addition, the reactions of $(\text{Rh}(\beta\text{-ketoenolate})(\text{cod}))$ and $(\text{Rh}(\beta\text{-ketoenolate})(\text{olefin})_2)$ compounds have been studied at low temperature (-78°C) with a view to isolating intermediates in the reactions. Successful isolation of some of these species has allowed a preliminary investigation of their chemistry to be undertaken.

2.2 The preparations of $(\text{Rh}(\text{apemino})(\text{cod}))$ and $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$ and their room temperature reactions with hexafluorobut-2-yne

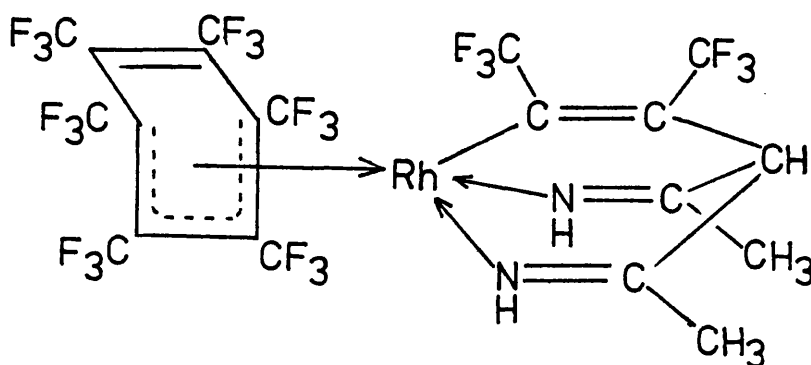
Reactions of $(\text{Rh}(\beta\text{-ketoenolate})(\text{C}_2\text{H}_4)_2)$ and $(\text{Rh}(\text{apeo})(\text{C}_2\text{H}_4)_2)$ with hexafluorobut-2-yne have been shown^{2,3} to give complexes (2.1) or (2.2), depending on the nature of the bidentate anion. Compounds involving a cyclohexa-1,3,-diene ligand are formed when the anion is acac or dpm, whilst a benzene-type ligand is formed when the anion is aan or apeo. These latter two anions are unsymmetrical, which may have some bearing on the course of reaction, but the basicity of the anion may also be influential. In order to clarify this point, the compound $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$ (apemino = 4-aminopent-3-ene-2-iminato) was investigated, since this anion (2.3) is symmetrical but also should be more basic than the anions studied so far.



The synthesis of $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$ was achieved by a modification of the method used by McGeachin⁴ for making $(\text{metal}(\beta\text{-diketimine})_2)$ complexes. $(\text{Rh}(\text{apemino})(\text{cod}))$ was prepared in a similar way. Both complexes have two infra-red absorptions in the region $1540 - 1580\text{cm}^{-1}$, which is characteristic of a conjugated $-\text{N}=\text{C}-\text{C}=\text{C}-$ system⁵. An interesting feature of the ^1H n.m.r. spectra is that the γ -proton of the β -diketimine ring appears as a triplet ($J_{\text{HH}} \approx 3\text{Hz}$) due to coupling with the N-H protons.

Room temperature reaction of $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$ with hexafluorobut-2-yne gave a yellow crystalline solid identified as the complex (2.4), in which both molecules of ethylene have been lost, and the acetylene has

trimerised to give a coordinated hexakis(trifluoromethyl)benzene ligand acting as a diene. 1,4-addition of the acetylene across the rhodium- β -diketimine ring has also occurred.



(2.4)

The ^{19}F spectrum of this compound clearly shows that four molecules of C_4F_6 have been incorporated, and that both molecules of ethylene have been displaced. The three resonances at -12.74 (br, 6F) -10.05 (br, 6F) and -5.68 (br, 6F) relative to α, α, α -trifluorotoluene can be assigned to a hexakis(trifluoromethyl)benzene ligand^{2,6}, whilst those at -12.12 (br, 3F) and -3.07 (q, 3F, $J_{\text{FF}} = 15.6\text{Hz}$) are due to the α and β - CF_3 groups of a $\text{Rh}-\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)-$ system respectively⁷. The coupling constant is consistent with a cis arrangement of the CF_3 groups on the double-bond^{7,8}, the trans systems having values for J_{FF} of 2 - 3Hz⁹.

The infra-red spectrum also indicates that a hexakis(trifluoromethyl)-benzene ligand has been formed, there being an absorption at 1634cm^{-1} assigned to the $\text{C}=\text{C}$ stretch of the uncoordinated double-bond^{2,6}, whilst bands at 1677 and 1605cm^{-1} can be respectively assigned to $\text{C}=\text{N}$ and the $\text{C}=\text{C}$ of the vinylic system.

From this, it is clear that the apemino anion favours the incorporation of four, rather than three, moles of C_4F_6 into the product. This evidence suggests that it is the basicity of the anion which influences the course

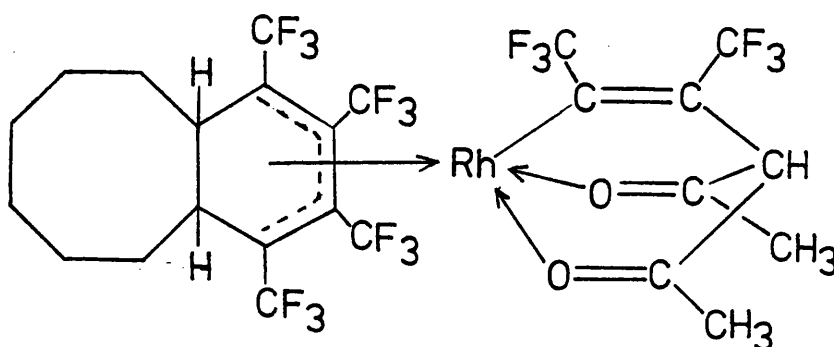
of reaction, since those anions involving donor nitrogen atoms (aan, apeo, apemino) result in the formation of benzene-type ligands, whereas the slightly less basic anions (acac and dpm) lead to cyclohexa-1,3-diene ligands.

Reaction of $(\text{Rh}(\text{apemino})(\text{cod}))$ with hexafluorobut-2-yne at room temperature also gave complex (2.4), this reaction being completely analogous to those of the complexes $(\text{Rh}(\beta\text{-ketoenolate})(\text{cod}))$ and $(\text{Rh}(\text{apeo})(\text{cod}))$ listed in Section 2.1.

2.3 Room temperature reaction of $(\text{Rh}(\text{acac})(\text{cis-C}_8\text{H}_{14})_2)$ with hexafluorobut-2-yne

Following on from the reactions of $(\text{Rh}(\beta\text{-ketoenolate})(\text{C}_2\text{H}_4)_2)$ systems with hexafluorobut-2-yne, in which the anion was varied with interesting results, it was thought to be worthwhile investigating the reaction of a complex involving a different olefin.

Reaction of $(\text{Rh}(\text{acac})(\text{cis-C}_8\text{H}_{14})_2)$ with hexafluorobut-2-yne at room temperature, in diethyl ether, is considerably slower than the reaction of the bis(ethylene) analogue, taking 5 - 6 days to go to completion. The product is the yellow, crystalline complex (2.5).



(2.5)

The conformation of the bicyclododeca-9,11-diene ligand is uncertain, since the cyclo-octene group may adopt either a chair or a boat form, or possibly an intermediate form, in order to minimise steric interactions.

Evidence for the retention of a cyclo-octene ligand, rather than formation of a hexakis(trifluoromethyl)-benzene moiety, is given by the ^{19}F n.m.r. spectrum, which has four resonances at -11.21(br,3F), -8.62(br,6F) -8.16(br,6F) and -2.63(q,3F, $J_{\text{FF}} = 15.5\text{Hz}$) relative to α,α,α -trifluorotoluene. The high-field quartet is assigned to the $\beta\text{-CF}_3$ group of the $\text{Rh-C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{-}$ system, the coupling constant again indicating a cis arrangement of CF_3 groups, whilst the broad signal at -11.21 is due to the $\alpha\text{-CF}_3$. The broad nature of this signal may be due to rhodium coupling, or through-space coupling of the CF_3 groups on the ring system. The remaining two ^{19}F n.m.r. resonances are thus assigned to the CF_3 groups of the bicyclododeca-1,3-diene group.

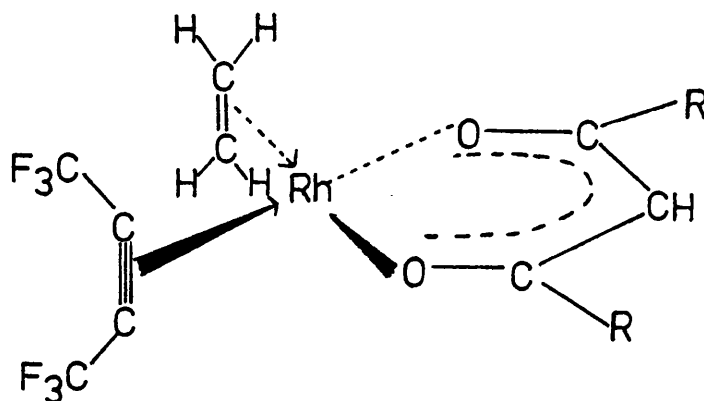
The i.r. spectrum has a strong C=O absorption at 1702cm^{-1} , and a band due to C=C stretching at 1593cm^{-1} , consistent with the proposed structure. The retained cyclo-octene group is also visible as a broad resonance between 8.00 and 8.55 in the ^1H n.m.r.

The product of this reaction is therefore analogous to the complex obtained from room temperature reaction of $(\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2)$ with hexafluorobut-2-yne, involving retention of one olefinic ligand.

In order to investigate further the factors leading to formation of cyclohexa-1,3-diene, bicyclododeca-9,11-diene, and benzene-type ligands in these room temperature reactions, and in the hope of isolating reaction-intermediates, some of the reactions were repeated at low temperature (-78°C).

2.4 Low temperature (-78°C) reactions of hexafluorobut-2-yne with compounds of the type $(\text{Rh}(\beta\text{-ketoenolate})(\text{olefin})_2)$ and with $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$, $(\text{Rh}(\text{apeo})(\text{C}_2\text{H}_4)_2)$, $(\text{Rh}(\text{dpm})(\text{cod}))$ and $(\text{Rh}(\text{dpm})(\text{CO})_2)$

Reaction of the complexes $(\text{Rh}(\beta\text{-ketoenolate})(\text{C}_2\text{H}_4)_2)$ ($\beta\text{-ketoenolate}$ = acac or dpm) with liquid C_4F_6 , in diethyl ether, at -78°C , gave the products $(\text{Rh}(\beta\text{-ketoenolate})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ (2.6) in which one molecule of ethylene in the starting material has been replaced by a molecule of the acetylene.



(2.6)

$\text{R}=\text{CH}_3, \text{C}(\text{CH}_3)_3$

These compounds are air-stable yellow solids, soluble in diethyl ether, even at -78°C , but recrystallisable from ether/methanol at low temperatures. They can be readily sublimed, under vacuum, at temperatures of approximately 50°C , although some decomposition does occur on warming to temperatures just below the melting-points.

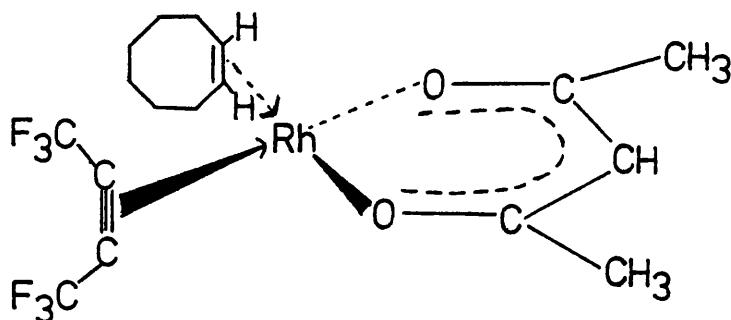
The n.m.r. spectra of the complexes were obtained in d^6 -acetone, since slight decomposition appears to occur in CDCl_3 , the more normal n.m.r. spectral solvent. The ^{19}F n.m.r. spectra show just one resonance, due to coordinated C_4F_6 , at -8.95 ($\text{R} = \text{CH}_3$) and -8.68 ($\text{R} = \text{t-butyl}$), relative to α,α,α -trifluorotoluene. In the complex with $\text{R} = \text{t-butyl}$, the ^{19}F resonance is a doublet ($J_{\text{RhF}} = 2\text{Hz}$), but in the compound with $\text{R} = \text{CH}_3$, this splitting could not be observed.

Both the chemical-shift values, and the coupling-constant, are in excellent agreement with values observed for π -bonded C_4F_6 in the complex $(RhCl(PPh_3)_2(C_4F_6))$ prepared by Mays and Wilkinson¹⁰.

The 1H n.m.r. spectra show, as well as signals due to the bidentate anion, resonances due to coordinated ethylene at 6.33τ for both complexes (free C_2H_4 has a resonance at $4.6 - 4.7\tau(s)$). These resonances are doublets, having J_{RhH} values of 2Hz.

The i.r. spectra both show a strong absorption at $1976cm^{-1}$ due to $C\equiv C$ stretching of the coordinated acetylene, there also being a shoulder on the low-energy side of these bands. The origin of this splitting is not clear, but it has been observed before in π -bonded complexes of C_4F_6 ^{11,12}.

Reaction of $(Rh(acac)(\text{cis-}C_8H_{14})_2)$ with C_4F_6 at $-78^\circ C$ was rather slower than reactions of the ethylene derivatives, but also gave, after 12 hours, an olefin-acetylene complex, $(Rh(acac)(C_8H_{14})(C_4F_6))$ (2.7). Purification of this complex involves the initial removal of the displaced cyclo-octene ligand by warming, under vacuum, since attempted recrystallisation in the presence of cyclo-octene resulted only in the isolation of $(Rh(acac)(C_8H_{14})_2)$. Selected spectroscopic data for complex (2.7), as well as for the other two olefin-acetylene complexes, are listed in Table 2.1.



(2.7)

Table 2.1 Selected spectroscopic data for some rhodium(I)-olefin-acetylene complexes

<u>Infra-red</u> ^a	$\frac{(\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))}{1976, 1960\text{cm}^{-1}}$	$\frac{(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))}{1976, 1962\text{cm}^{-1}}$	$\frac{(\text{Rh}(\text{acac})(\text{cis-C}_6\text{H}_8)(\text{C}_4\text{F}_6))^*}{1958\text{cm}^{-1}}$
$\nu(\text{C}\equiv\text{C})$			
¹⁹ F n.m.r. ^b			
C_4F_6	-8.95 (s)	-8.68 (d, $J_{\text{RhF}}=2\text{Hz}$)	-9.91 (s)
¹ H n.m.r. ^c			
$\text{C}_2\text{H}_4/\text{C}_8\text{H}_{14}$	6.33 (d, $4\text{H}, J_{\text{RhH}}=2\text{Hz}$)	6.33 (d, $4\text{H}, J_{\text{RhH}}=2\text{Hz}$)	6.55 (10 lines, $2\text{H}, J_{\text{HH}}=7\text{Hz}, J_{\text{RhH}}=2\text{Hz}$)
$\text{CH}_3/\text{t-butyl}$	7.94 (s, 6H)	8.86 (s, 18H)	7.69 - 8.73 (br, 12H)
$\gamma\text{-H}$	4.30 (s, 1H)	3.99 (s, 1H)	4.52 (s, 1H)

a. Nujol mulls

b. Measured in $(\text{CD}_3)_2\text{CO}$: chemical shifts relative to α, α -trifluorotoluene.

c. Measured in $(\text{CD}_3)_2\text{CO}$: chemical shifts (τ) relative to internal T.M.S.

* N.m.r. spectra measured in CD_2Cl_2

These are the first examples of complexes having a monodentate olefin and a monodentate acetylene π -bonded to the same metal atom. Several examples of compounds having a diene and an acetylene bonded to the same metal atom are known,^{11,13,14} and a ruthenium complex, $(\text{Ru}_4(\text{CO})_{11}\text{C}_8\text{H}_{10})$ containing a coordinated cyclo-octa-1-ene-5-yne ligand has been made¹⁵. The crystal structure of this latter complex¹⁶ shows that the acetylenic carbon atoms are bonded to four metal atoms.

When the complexes $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ and $(\text{Rh}(\text{acac})(\text{C}_8\text{H}_{14})(\text{C}_4\text{F}_6))$ were reacted further with hexafluorobut-2-yne at room temperature, the products were the same as those isolated from room temperature reactions of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)_2)$ and $(\text{Rh}(\text{acac})(\text{C}_8\text{H}_{14})_2)$ with C_4F_6 -i.e. (2.2b) and (2.7). These observations are consistent with a mechanism for build-up of the cyclohexa-1,3-diene, and bicyclododeca-9,11-diene ligands involving an intermediate metal-olefin-acetylene complex.

Catalytic cyclotrimerisation of two acetylene molecules with an olefin to form cyclohexa-1,3-diene derivatives has been the subject of several investigations^{17,18,19} as also has the catalytic cyclotrimerisation of three acetylene molecules to form benzene derivatives^{20,21}. Schrauzer²² has suggested that hexakis(trifluoromethyl)-benzene nickel complexes are formed by coordination of three molecules of the acetylene onto the metal, followed by concerted ring closure, but several workers^{20,21,23} have shown that benzene derivatives can be built up from metalocyclopentadiene complexes. Both metalocyclopentadienes¹⁸ and metalocyclopentenes¹⁷ have been postulated as intermediates in catalytic formation of cyclohexa-1,3-diene ligands.

Two possible mechanisms for the formation of cyclohexa-1,3-diene ligands in the reactions of $(\text{Rh}(\text{olefin})_2(\beta\text{-ketoenolate}))$ with hexafluorobut-2-yne are shown in Figure 2.1.

A piece of evidence supporting the metalocyclopentadiene, rather than the metalocyclopentene, mechanism is the formation of benzene-type

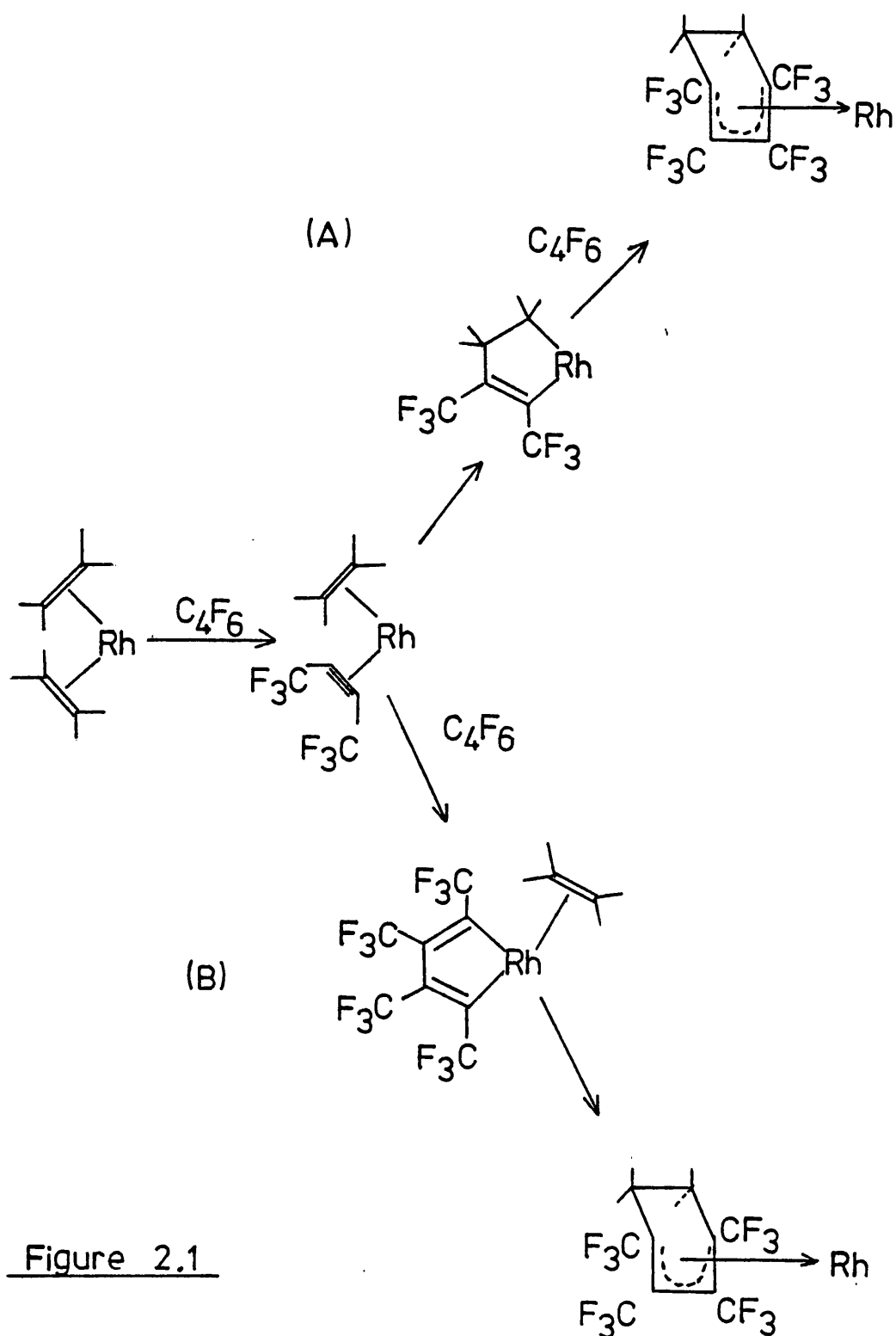


Figure 2.1

ligands, rather than cyclohexa-1,3-dienes, in the cases when the anion coordinated to the rhodium is apeo, apemino, or aan. The formation of benzene derivatives is harder to envisage from a metalocyclopentene

intermediate. If a metallocyclopentadiene is involved, however, it is possible that competition occurs between the olefin and C_4F_6 for reaction with the intermediate, and that the result of this competition is influenced by the anion (figure 2.2). Evidence for this

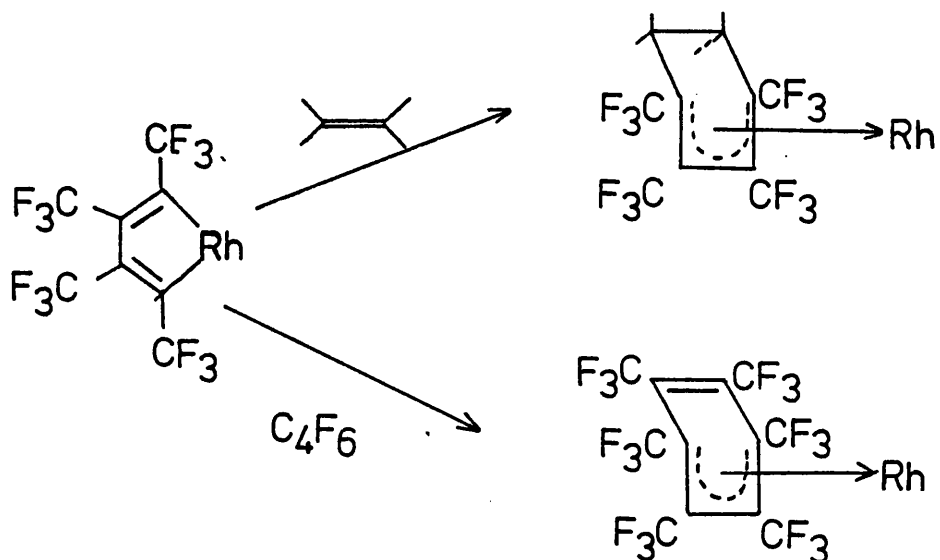


Figure 2.2

type of competition has been presented for a reaction involving the formation of benzene derivatives and cyclohexa-1,3-dienes using a palladiacyclopentadiene catalyst¹⁸.

It is, however, possible that mechanism A is operating when cyclohexa-1,3-diene derivatives are formed, whilst the formation of benzene derivatives involves mechanism B. The results obtained so far do not permit the assignment of one particular mechanism to these reactions.

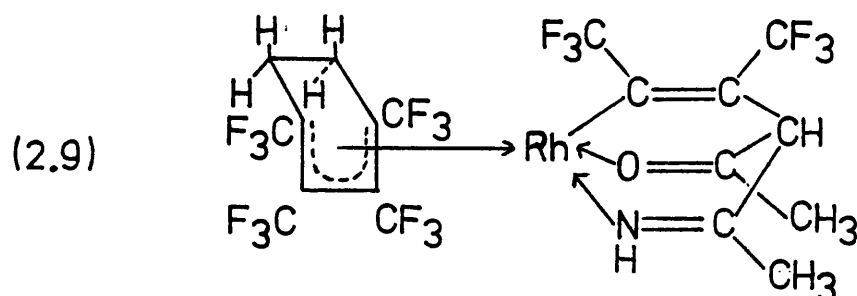
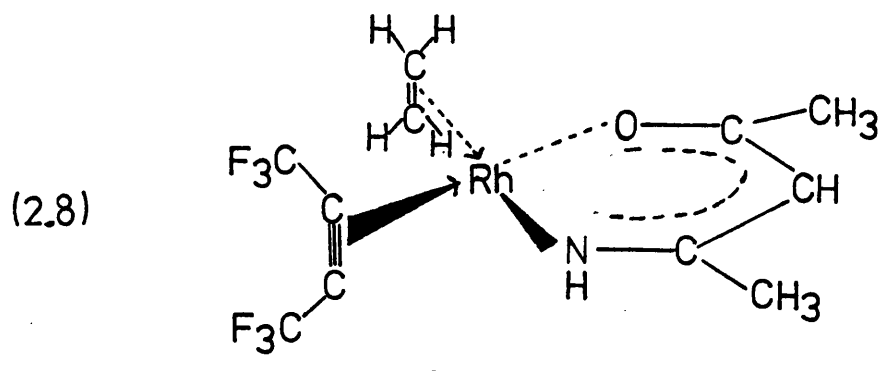
The 1,4 addition of hexafluorobut-2-yne across the rhodium- β -ketoenolate rings, which constitutes the other novel feature of the room temperature reactions, has been postulated² to involve either a concerted addition of the acetylene across the rhodium and the γ -carbon atom of the β -ketoenolate system, or alternatively, formation of a carbon bonded β -ketoenolate complex, followed by insertion of the

acetylene into the rhodium-carbon bond.

Low temperature reactions were also carried out using $(\text{Rh}(\text{apeo})(\text{C}_2\text{H}_4)_2)$ and $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$ with hexafluorobut-2-yne. The former complex gave, after 1 hour, a mixture of a compound having a π -bonded C_4F_6 ligand, and a compound in which 1,4 addition of C_4F_6 across the β -ketoamine ligand has occurred. These two types of complex were identified from the i.r. spectrum, which has a strong absorption at 1944cm^{-1} ($\text{C}\equiv\text{C}$ stretch), and a band at 1692cm^{-1} ($\text{C}=\text{O}$ stretch). When the reaction mixture was left for a longer time (6 hours), the i.r. spectrum of the product no longer showed π -bonded C_4F_6 , but still had an absorption at 1692cm^{-1} , and a further one at 1618cm^{-1} . Regrettably, this compound could not be crystallised, so that no analytical figures were obtained, and only a very poor ^1H n.m.r. spectrum was observed. The ^{19}F n.m.r. spectrum, however, clearly shows four resonances at -9.62 (br, 3F), -6.96 (br, 6F), -6.69 (br, 6F) and -3.69 (q, 3F, $J_{\text{FF}} = 16.92\text{Hz}$) relative to α,α,α -trifluorotoluene. This pattern is characteristic of complexes having a 1,2,3,4-tetrakis-(trifluoromethyl)cyclohexa-1,3-diene ligand, as well as 1,4 addition of C_4F_6 across a rhodium- β -ketoenolate ring^{2,3}, so that this complex is tentatively assigned structure (2.9). It seems probable that the compound having a π -bonded C_4F_6 ligand is the olefin-acetylene complex (2.8), which can exist in two isomers, having either the acetylene or the olefin trans to the oxygen atom.

The room temperature product from reaction of $(\text{Rh}(\text{apeo})(\text{C}_2\text{H}_4)_2)$ involves loss of both ethylene molecules, so that if structure (2.9) is correct, it indicates that only one ethylene molecule is lost in the low temperature reaction.

Similar difficulty was experienced in obtaining a crystalline product from $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$ and C_4F_6 at -78°C , and in this case no evidence of a metal-olefin-acetylene complex was obtained. No



n.m.r. spectra could be obtained of the product, although the i.r. (1684cm^{-1} (C=N ?) and 1610cm^{-1} (C=C ?)) suggests a cyclohexa-1,3-diene type complex. The main conclusion to be drawn from the low-temperature reactions of the β -diketimine and β -ketoamine complexes is that any metal-olefin-acetylene complexes are destabilised relative to further reaction with hexafluorobut-2-yne. One possible factor affecting the stability of these metal-olefin-acetylene complexes is the basicity of the chelating anion.

Although $(\text{Rh}(\text{dpm})(\text{cod}))^2$ and $(\text{Rh}(\text{dpm})(\text{CO})_2)^3$ have both been found to react with hexafluorobut-2-yne at room temperature, no reactions were observed at -78°C , over periods of up to 12 hours.

2.5 Structures of the complexes $(\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ and $(\text{Rh}(\text{acac})(\text{C}_8\text{H}_{14})(\text{C}_4\text{F}_6))$

Because of the novel nature of the metal-olefin-acetylene complexes, the crystal structures of two of them were investigated.

Crystals of (2.6), $\text{RhC}_{11}\text{H}_{11}\text{F}_6\text{O}_2$ (mol.wt. = 392.159) are triclinic,

space group $P\bar{1}$, with $a = 7.88(6)$, $b = 12.63(7)$, $c = 8.57(5)$ $\alpha = 95.89(3)^\circ$, $\beta = 121.08(1)^\circ$, $\gamma = 94.79(8)^\circ$, $u = 718.57\text{\AA}^3$, and $z = 2$.

The structure is shown in Figure 2.3. As expected, the Rh(acac) unit is almost planar, and both the ethylene and the hexafluorobut-2-yne ligands are approximately perpendicular to this plane (87.89° and 93.08°).

Comparison of the rhodium-acetylenic carbon bond-lengths ($2.046(11)\text{\AA}$ and $2.017(10)\text{\AA}$) with the rhodium-olefinic carbon bond-lengths ($2.154(16)\text{\AA}$ and $2.183(19)\text{\AA}$) shows that the bond to the acetylene is shorter. Comparison of these values with those for $(\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2)^{25}$ ($2.13(2)\text{\AA}$ and $2.14(2)\text{\AA}$) shows that in the C_4F_6 complex, C_2H_4 is less strongly bound, and C_4F_6 more strongly bound than the C_2H_4 ligands in the bis-ethylene complex. This is in accordance with the expected π -acceptor properties of C_4F_6 and C_2H_4 , but contrary to their σ -donor properties, again showing that π -bonding is the dominant factor in this type of bond. Further comparison with the compound $(\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4))^{25}$ suggests that the π -bonding capacity of these ligands is in the order $\text{C}_2\text{F}_4 > \text{C}_4\text{F}_6 > \text{C}_2\text{H}_4$, since the rhodium-ethylene bond is longer in the C_2F_4 complex, and the Rh- C_2F_4 bond is shorter than the Rh- C_4F_6 bond.

The C=C and C \equiv C bonds of the ligands are lengthened on coordination to the metal as expected. The ethylene double-bond has a mean value of $1.36(3)\text{\AA}$, compared with 1.336\AA in the free-olefin²⁴, whilst the hexafluorobut-2-yne triple-bond measures $1.23(3)\text{\AA}$ —slightly longer than an average value²⁶ for free acetylenes of $1.204(2)\text{\AA}$. It should be noted that some difficulties have been encountered in obtaining the coordinated C=C bond length, since refinement of the structure in the absence of the hydrogen atoms gives a value of $1.39(3)\text{\AA}$, whereas inclusion of the hydrogen atoms gives $1.33(3)\text{\AA}$ as the bond length.

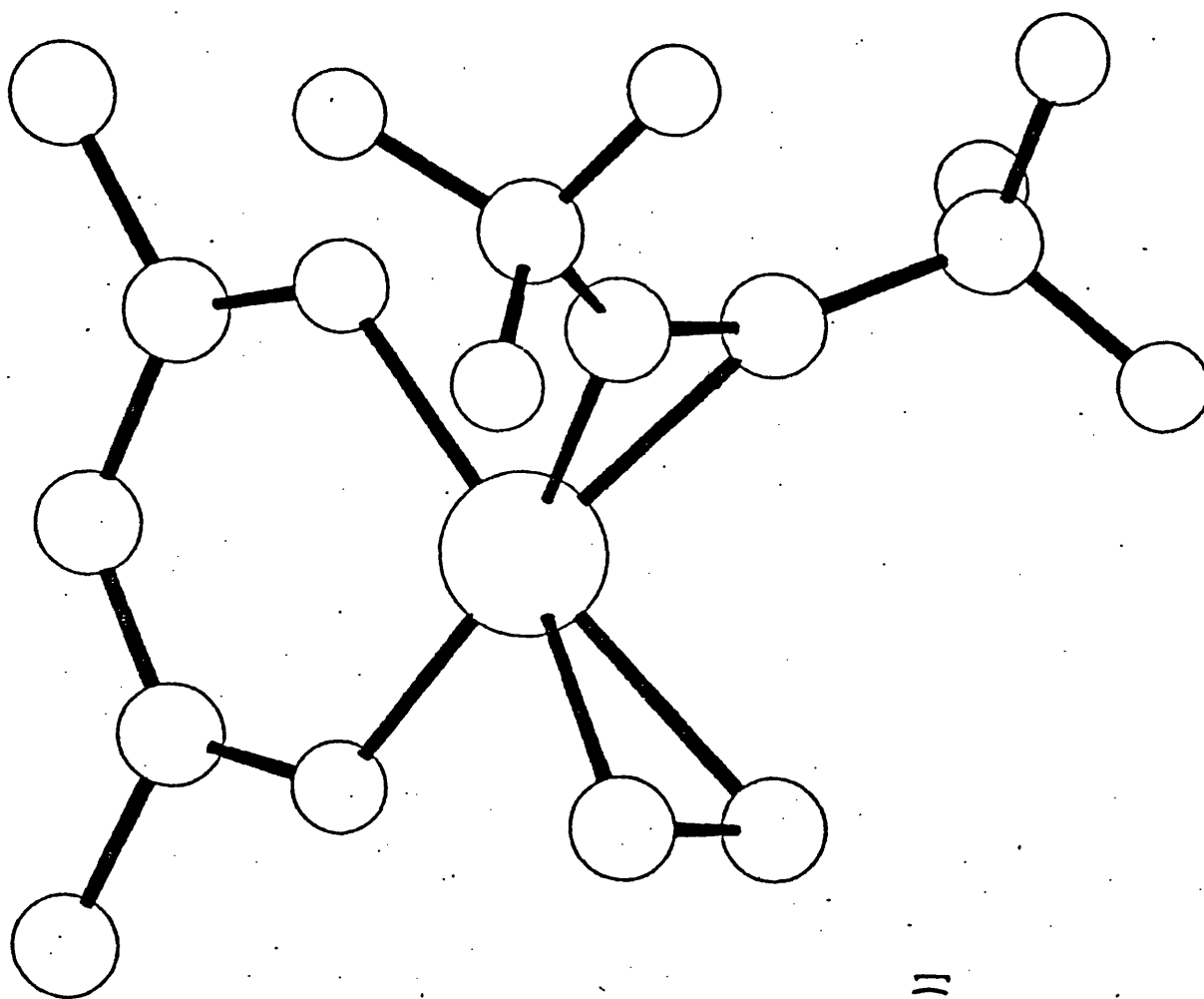
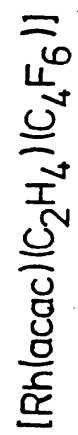
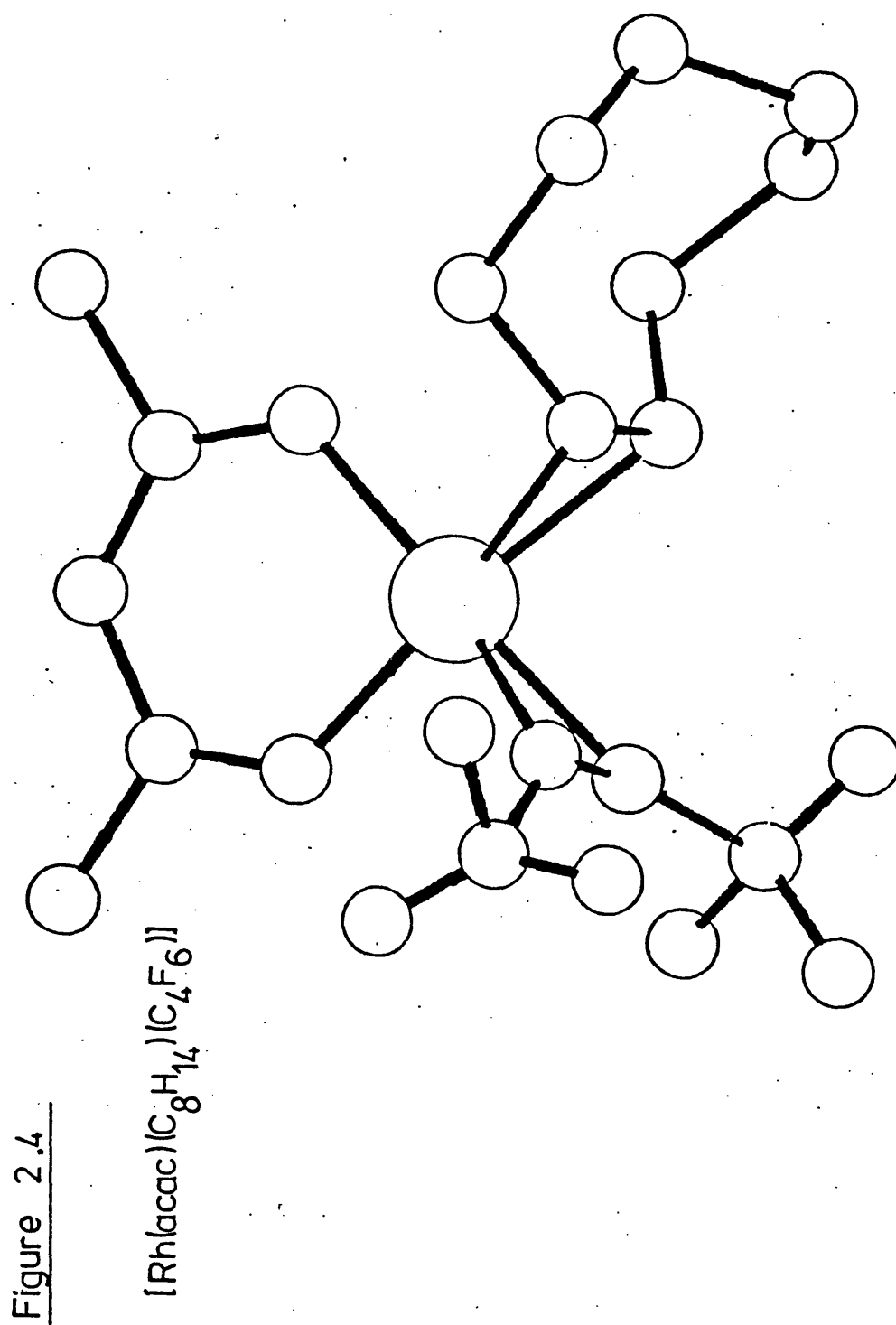


Figure 2.3





Another change occurring in the acetylene on coordination, also believed to result from increased population of the $\text{C}\equiv\text{C}$ π^* orbitals, is a distortion from planarity. In this case, the CF_3 groups are bent back through $27(1)^\circ$ and $33(1)^\circ$, away from the metal - comparable with the value of $34.4(4)^\circ$ observed in $(\text{Pt}(\text{CH}_3)(\text{HB}(\text{N}_2\text{C}_3\text{H}_3)_3)(\text{C}_4\text{F}_6))^{27}$.

Crystals of (2.7), $(\text{RhC}_{17}\text{H}_{21}\text{F}_6\text{O}_2)$ (mol.wt. = 474.305) are monoclinic, space group B21/C, with $a = 14.16(3)$, $b = 17.89(3)$, $c = 15.71(3)$, $\beta = 97.5(2)^\circ$, $u = 3945.65\text{\AA}^3$, and $z = 8$.

The structure is shown in Figure 2.4. The $\text{Rh}(\text{acac})$ unit is again found to be virtually planar, with the cyclo-octene double-bond and the acetylenic triple-bond lying almost perpendicular to the plane (91.15° and 88.52°).

The bond to the acetylene is similar to that in the ethylene analogue, the $\text{Rh}-\text{C}$ bond lengths being $2.059(10)\text{\AA}$ and $2.034(10)\text{\AA}$. As expected, the rhodium-olefin bond is again found to be longer, having $\text{Rh}-\text{C}$ bond-lengths of $2.196(11)\text{\AA}$ and $2.163(13)\text{\AA}$.

Changes occurring to the acetylene are also similar to those taking place in the ethylene complex, the $\text{C}\equiv\text{C}$ bond-length having undergone a slight increase to $1.241(15)\text{\AA}$, and the bend-back angles of the CF_3 groups being $31(1)^\circ$ and $29(1)^\circ$.

2.6 Some reactions of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$

Reaction of an ether solution of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ with carbon monoxide resulted in rapid displacement of both the olefin and the acetylene ligands, and the isolation of $(\text{Rh}(\text{dpm})(\text{CO})_2)$. With weaker π -accepting ligands, however, the hexafluorobut-2-yne ligand is retained, although the ethylene molecule is lost.

Thus, for example, triphenylphosphine, triphenylarsine and triphenylstibine all react rapidly with ether solutions of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ to give good yields of the crystalline complexes

(Rh(dpm)(EPh₃)₂(C₄F₆)) (E = P, As or Sb). The i.r. spectra of these complexes all show two absorptions in the region 1780-1830cm⁻¹ due to C≡C stretching of the coordinated C₄F₆. The ¹H n.m.r. spectra indicate that two molecules of the ligands EPh₃ have become coordinated to the metal, and also show that the two t-butyl groups of the dipivaloylmethanato group are in different chemical environments, thus providing a clue to the geometries of the complexes.

The ¹⁹F n.m.r. spectra are, however rather more surprising. At room temperature, each compound exhibits a doublet (J_{RhF} = 2Hz) in the region associated with π-hexafluorobut-2-yne complexes of rhodium. On cooling the solutions down, however, the spectra show two resonances, separated by up to 2.5ppm. These results are listed in Table 2.2.

Table 2.2 ¹⁹F n.m.r.* spectra of the complexes (Rh(dpm)(EPh₃)₂(C₄F₆))

<u>Complex</u>	<u>Room temperature</u>	<u>-58°C</u>
(Rh(dpm)(PPh ₃) ₂ (C ₄ F ₆))	-12.04 (d, J _{RhF} =2Hz)	-12.08 (d, 3F, J _{PF} =16.8Hz) -11.29 (s, 3F)
(Rh(dpm)(AsPh ₃) ₂ (C ₄ F ₆))	-11.04 (d, J _{RhF} =2Hz)	-12.67 (s, 3F) -11.22 (s, 3F)
(Rh(dpm)(SbPh ₃) ₂ (C ₄ F ₆))	-10.73 (d, J _{RhF} =2Hz)	-12.08 (s, 3F) -9.60 (s, 3F)

*Measured in CDCl₃ solution: chemical shifts are relative to α,α,α-trifluorotoluene.

It is, at first, tempting to interpret these observations in terms of rotation of the hexafluorobut-2-yne ligand about the rhodium-acetylene bond, similar to that found in other metal-acetylene complexes²⁸⁻³¹.

(Figure 2.5a.) (See Section 1.1.) The absence of any ³¹P-¹⁹F coupling in the room temperature spectrum of the triphenylphosphine derivative, however, suggests that an equilibrium process involving ligand

dissociation may be taking place (Figure 2.5b). Dissociation of a ligand would remove the inequivalence of the CF_3 groups of the C_4F_6 ligand, and therefore have similar effects to acetylene rotation on the ^{19}F n.m.r. spectrum.

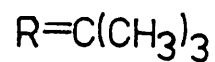
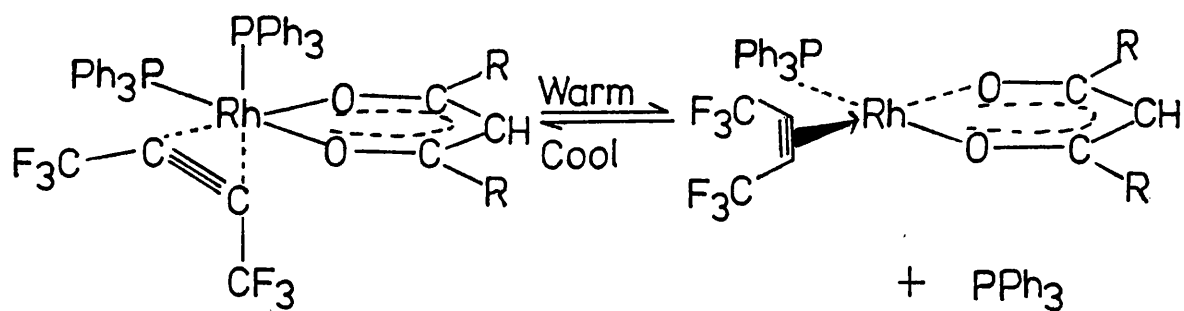
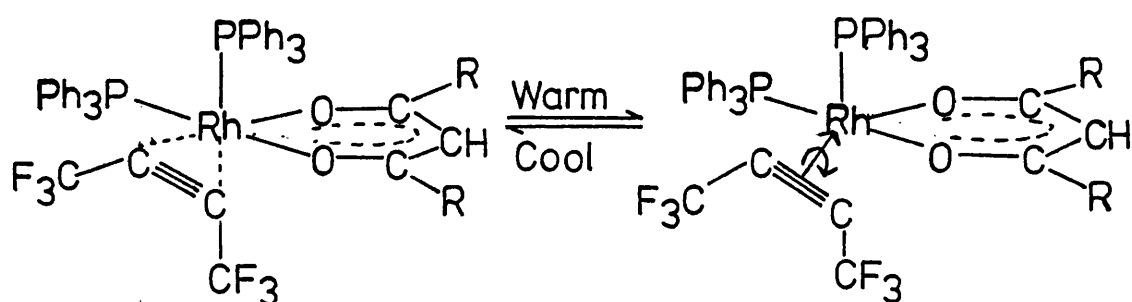


Figure 2.5

In order to decide between the two possibilities, attempts were made to disturb the equilibrium illustrated in Figure 2.5b by saturating the solutions with the potentially dissociating ligand. This should not have any effect on an acetylene-rotation process, but would disturb a ligand-dissociation equilibrium to the left - i.e. a greater temperature would be required to get equivalence of the CF_3 groups in the ^{19}F n.m.r. spectrum.

Variable temperature ^{19}F n.m.r. studies permit the measurement of coalescence temperatures, at which the two distinct CF_3 resonances of the low temperature spectra become a single peak, due to the CF_3 groups becoming equivalent on the n.m.r. time scale. These coalescence temperatures are listed in Table 2.3, along with the coalescence points when the solutions are saturated with the appropriate ligand.

Table 2.3 Variable temperature ^{19}F n.m.r. of the compounds
 $(\text{Rh}(\text{dpm})(\text{EPh}_3)_2(\text{C}_4\text{F}_6))$

<u>Complex</u>	<u>Coalescence Temperatures ($^{\circ}\text{C}$)</u>	
	<u>a</u>	<u>b</u>
$(\text{Rh}(\text{dpm})(\text{PPh}_3)_2(\text{C}_4\text{F}_6))$	-19	-10
$(\text{Rh}(\text{dpm})(\text{AsPh}_3)_2(\text{C}_4\text{F}_6))$	-44	-37
$(\text{Rh}(\text{dpm})(\text{SbPh}_3)_2(\text{C}_4\text{F}_6))$	-21	-10

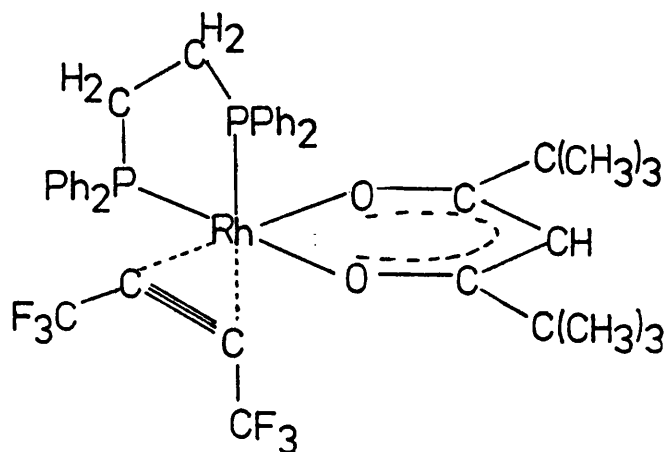
a In CDCl_3 solution

b In CDCl_3 solution saturated with Ph_3P , Ph_3As and Ph_3Sb respectively.

The observed increase in coalescence temperatures on saturating the solutions with the appropriate ligand is consistent with displacement of the ligand-dissociation equilibrium (Figure 2.5b) to the left, necessitating an increase in temperature to produce the same degree of dissociation.

Although these results show that ligand-dissociation is affecting the ^{19}F n.m.r. spectra of these complexes, they do not remove the possibility of acetylene-rotation occurring as well. In order to test further for acetylene-rotation in this type of complex, $(\text{Rh}(\text{dpm})(\text{diphos})(\text{C}_4\text{F}_6))$ (diphos = 1,2-bis-(diphenylphosphino)ethane) was prepared, and its n.m.r. spectra investigated. Ligand-dissociation is expected to be unfavourable for this compound involving a chelating phosphine ligand, so that any change in the ^{19}F n.m.r. spectrum on varying the temperature can be attributed to another process.

The room temperature ^{19}F n.m.r. of $(\text{Rh}(\text{dpm})(\text{diphos})(\text{C}_4\text{F}_6))$ has two resonances, at -11.90 (4 lines, $3\text{F}, J_{\text{PF}}=17.4\text{Hz}$, $J_{\text{RhF}}=4.5\text{Hz}$) and -10.28 (d, $3\text{F}, J_{\text{RhF}}=3\text{Hz}$) relative to α,α,α -trifluorotoluene. This spectrum is fully consistent with a rigidly bound hexafluorobut-2-yne molecule, and also with a non-dissociating diphos. ligand. Observation of this spectrum suggests that the variable temperature effects in the ^{19}F n.m.r. spectra are due to ligand-dissociation, and not to acetylene rotation. The spectra of $(\text{Rh}(\text{dpm})(\text{diphos})(\text{C}_4\text{F}_6))$ are consistent with the geometry shown (2.10), and comparison with the low-temperature limiting spectra of the complexes $(\text{Rh}(\text{dpm})(\text{EPh}_3)_2(\text{C}_4\text{F}_6))$



shows that these compounds all have the EPh_3 ligands cis to each other.

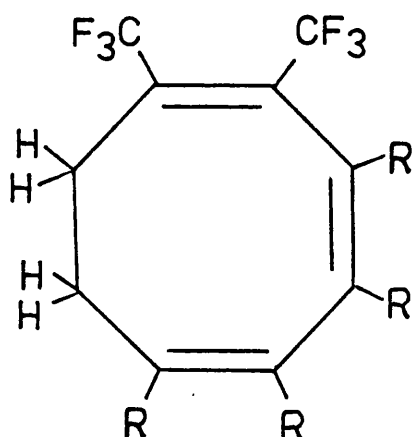
Reactions of acetylenes other than C_4F_6 with $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ were also thought to be worthy of investigation. 2,5-dimethylhex-3-yne-2,5-diol reacted with an ether solution of the metal-olefin-acetylene complex, over 3 days, to give a low yield of an orange, crystalline solid, identified from analytical data as having the stoichiometry $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6)) \left\{ (\text{H}_3\text{C})_2\text{C}(\text{OH})\text{C}\equiv\text{CC}(\text{OH})(\text{CH}_3)_2 \right\}_2$

The infra-red spectrum of this complex has no absorptions in the region $1600\text{--}2000\text{cm}^{-1}$, but shows normal dpm bands at 1551 and 1534cm^{-1} . The O-H stretching region has two bands at 3312 and 3210cm^{-1} .

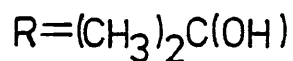
The ^1H n.m.r. spectrum is complex, having a large number of resonances between 8 and 9 τ , as well as resonances due to the dpm ligand at 8.83(s,18H) and 3.99(s,1H), and hydroxyl proton peaks at 2.16 and 2.66. These latter two peaks appear to integrate for a total of 3 hydrogen atoms. The ^{19}F n.m.r. spectrum has two signals at -20.16 (q,3F, $J_{\text{FF}}=15.0\text{Hz}$) and -11.3 (vbr,3F) relative to α,α,α -trifluorotoluene. No change occurred in the ^{19}F n.m.r. on cooling the solution to -45°C , although slight precipitation of the complex made observations difficult, but warming a solution to 70°C (in *o*-dichlorobenzene) resulted in sharpening of the very broad signal at -11.3 . Further heating only produced decomposition of the compound.

A possible explanation for these spectroscopic observations is that one molecule of hexafluorobut-2-yne, two molecules of 2,5-dimethylhex-3-yne-2,5-diol, and one molecule of ethylene have combined to form a cyclo-octa-1,3,5-triene ring, (2.11) which is coordinated to the rhodium atom.

Failure to observe a C=C i.r. absorption suggests either that the ligand is fluxional or that it is tridentate, giving pentacoordinate

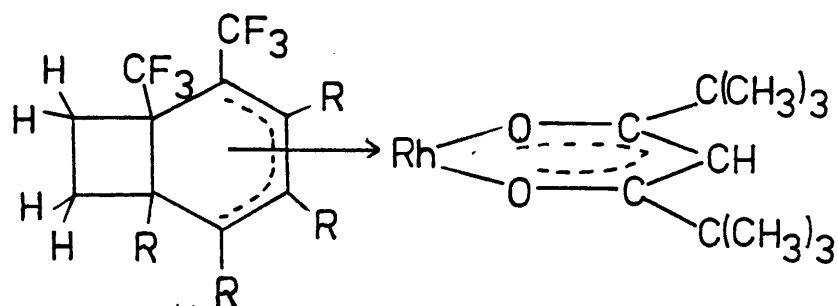


(2.11)

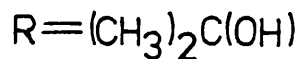


rhodium(I). Neither explanation appears to fit the ^{19}F n.m.r. spectrum.

A second possibility is that the triene ligand has rearranged to a bicyclo(4,2,0)octadiene (2.12). This type of rearrangement is well



(2.12)



known³²⁻³⁴, and in the case of $(\text{Fe}(\text{CO})_3(\text{C}_8\text{H}_{10}))$ an equilibrium has been shown to exist, with the bicyclo-diene complex being the more stable³³. A compound (2.12) appears to be more in accordance with the ^{19}F n.m.r., since the olefinic CF_3 and the bridgehead CF_3 groups would be expected to have a considerable difference in chemical shift. Possible explanations for the broad signal observed for one of

the CF_3 groups include: a) hindered rotation of a CF_3 group due to steric interaction with $-\text{C}(\text{CH}_3)_2(\text{OH})$ groups; b) hydrogen-bonding to hydroxyl protons, which is broken at higher temperatures; c) fluxionality about the C-C bridge - this is unlikely, since a change in the ^{19}F n.m.r would be expected, but is not observed, on cooling.

It seems probable that a crystal-structure determination will be necessary to finally identify this compound. Step-wise formation of a cyclo-octa-1,3,5-triene, followed by rearrangement to a bicyclo(4,2,0)octadiene, would, however, be a novel process.

The reaction of dimethylacetylene with $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ was also carried out. A yellow-brown solid was obtained, which was found to contain hexamethylbenzene impurity, but an attempt to separate the two components of the mixture by column chromatography gave only a red, intractable oil. The i.r. spectrum of the impure solid has bands due to carbon-fluorine stretching between 1100 and 1250cm^{-1} , and a medium intensity band at 2040cm^{-1} , two medium absorptions at 1596 and 1567cm^{-1} , and bands due to the dpm group. The ^{19}F n.m.r. has just one resonance at $-10.46(\text{s})$ relative to α,α,α -trifluorotoluene, whilst the ^1H n.m.r. spectrum, in addition to signals due to the dpm ligand, has a group of resonances between 7.1 and 8.0τ , partially obscured by the hexamethylbenzene signal at 7.88τ .

Clearly, no definite structural assignment can be made on the basis of these results, although it is certain that the dpm ligand is retained. A π -bonded acetylene ligand also seems probable, but although the ^{19}F n.m.r. resonance is in the normal position for π -bonded C_4F_6 , the i.r. absorption is exceptionally high for this class of compound, and π -bonded dimethylacetylene remains a possibility.

2.7 Summary

Further studies have been undertaken on the reactions of the highly electrophilic acetylene hexafluorobut-2-yne with rhodium(I)- β -ketoenolate complexes. In particular, factors leading to the formation of cyclohexa-1,3-diene, bicyclododeca-9,11-diene, and benzene-type ligands have been investigated. Low temperature reactions of hexafluorobut-2-yne with compounds of the type $(\text{Rh}(\beta\text{-ketoenolate})(\text{olefin})_2)$ have led to the formation of a new class of compounds, $(\text{Rh}(\beta\text{-ketoenolate})(\text{olefin})(\text{C}_4\text{F}_6))$, containing a π -bonded olefin and a π -bonded acetylene ligand. The crystal structures of two of these complexes have been obtained, and a preliminary investigation of their chemistry has been made.

2.8 Experimental

This section includes melting points, microanalytical results, and infra-red and n.m.r. spectroscopic data for all new compounds. Microanalyses were carried out by D. Butterworth, The Butterworth Microanalytical Consultancy Ltd., 41, High Street, Teddington, Middlesex, or by C.H.N. Analysis Ltd., Alpha House, South Wigston, Leicester. 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.

^1H n.m.r. spectra were recorded on a Jeol JNM-PS-100 spectrometer, operating at 100MHz, chemical shifts (τ) being reported relative to internal T.M.S. ^{19}F n.m.r. spectra were recorded on a Jeol JNM-PS-100 spectrometer, operating at 94.1 MHz., chemical shifts (p.p.m.) being reported relative to external α,α,α -trifluorotoluene.

Reactions carried out in Carius tubes (150cm^3) were done in $\sim 15\text{cm}^3$ of the appropriate solvent. All solvents were dried and degassed before use.

Ligands and Reagents

The following materials were purchased:

cyclo-octa-1,5-diene	Koch Light Labs. Ltd.
<u>cis</u> -cyclo-octene	Koch Light Labs Ltd.
ethylene	B.O.C.Ltd.
carbon monoxide	B.O.C.Ltd.
acetylacetone	Fisons Ltd.
dipivaloylmethane	Eastman Kodak Ltd.
hexafluorobut-2-yne	Bristol Organics Ltd.
but-2-yne	B.A.S.F.
2,5-dimethylhex-3-yne-2,5-diol	Fluka A.G.

Rhodium trichloride (hydrated) was obtained on loan from Johnson Matthey Ltd.

The following were prepared as described in the literature:

$(\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2)$, $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)_2)$, $(\text{Rh}(\text{apeo})(\text{C}_2\text{H}_4)_2)$, $(\text{Rh}(\text{dpm})(\text{cod}))$ and $(\text{Rh}(\text{dpm})(\text{CO})_2)^3$.

chlorobis(ethylene)rhodium(I) dimer³⁵.

chlorobis(cyclo-octene)rhodium(I) dimer³⁶.

acetylacetonatobis(cyclo-octene)rhodium(I)³⁷.

4-aminopent-3-ene-2-one³⁸.

4-aminopent-3-ene-2-immonium fluoborate⁴.

A The preparations of $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$ and $(\text{Rh}(\text{apemino})(\text{cod}))$ and their reactions with hexafluorobut-2-yne at room temperature

i 4-aminopent-3-ene-2-iminatobis(ethylene)rhodium(I)

To a stirred suspension of $(\text{RhCl}(\text{C}_2\text{H}_4)_2)_2$ (0.15g, 0.38mmol) in anhydrous methanol was added a solution of 0.14g (0.76mmol) of 4-aminopent-3-ene-2-immonium fluoborate in 3.5cm³ of anhydrous 0.5N sodium methoxide in methanol. The resulting orange suspension was stirred at room temperature under an atmosphere of dry nitrogen, for 1 hour, after which the solvent was removed under reduced pressure. The residue was extracted with benzene, evaporation of which left an orange-yellow solid, which was recrystallised from dichloromethane/methanol to give yellow crystals of $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$. Yield = 0.15g, 75%.

M. Pt. 124 - 125°C.

Analysis Calculated: C, 42.2; H, 6.6%

Found: C, 42.2; H, 6.5%

Infra-red 3290m 1572m,sh 1556s 1536w 1333m 1262w 1236w 1227m
1188w 1182w 1025m 966m 938m,br 783m,sh 780s 773s 669w 650w
638w 606w 477w 468w.

N.m.r. (in CDCl_3): 3.0 - 3.9(br,2H); 5.10(t,1H, $J_{\text{HH}} = 3\text{Hz}$); 7.24(s,8H); 7.83(s,6H).

ii 4-aminopent-3-ene-2-iminato(cyclo-octa-1,5-diene)rhodium(I)

To a stirred suspension of 0.3g (0.6mmol) of $(\text{RhCl}(\text{cod}))_2$ in 10cm³ of anhydrous methanol was added a solution of 0.23g(1.2mmol) of 4-aminopent-3-ene-2-immonium fluoborate in 5cm³ of anhydrous 0.5N sodium methoxide in methanol. The resulting pale-yellow suspension was stirred at room temperature, under an atmosphere of dry nitrogen, for 30 minutes, after which the solvent was removed under reduced

pressure. The residue was extracted with benzene, evaporation of which left a yellow solid, which was recrystallised from dichloromethane/ethanol to give yellow crystals of $(\text{Rh}(\text{apemino})(\text{cod}))$. Yield = 0.32g, 85%.

M. Pt. 167 - 169°C (sublimes ~ 164°C)

Analysis Calculated: C, 50.7 H, 6.9%

Found: C, 50.5 H, 7.1%

Infra-red 3310m 1568m 1549s 1329m 1303w 1234w 1216w 1196w

1172w,br 1024w,br 992w 954m 863w 818w 795w,br 768s 727w 678w

667w 642w 487w 477w.

N.m.r. (in CDCl_3): 3.2-3.9 (br, 2H); 5.22(t, 1H, $J_{\text{HH}} = 2.5\text{Hz}$);

6.03(br, 4H); 7.1-8.5 (br, 8H); 7.90(s, 6H).

iii Reaction of $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$ with hexafluorobut-2-yne at room temperature

An excess of hexafluorobut-2-yne (1.0cm^3) was condensed (-196°C) onto a solution of $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$ (0.15g, 0.58mmol) in diethyl ether contained in a Carius tube. The tube was sealed and shaken at room temperature. After 15 minutes, the solution had turned red, and an orange-yellow solid was present. The tube was shaken for a total of 48 hours, after which it was opened, volatile material removed, and the yellow solid filtered. Concentration of the red solution gave a further sample of the yellow solid which was purified by recrystallisation from acetone/ethanol, and identified as $(\text{Rh}(\text{apemino} \text{C}_4\text{F}_6)(\text{C}_6(\text{CF}_3)_6))$. Yield = 0.3g, 70%.

M. Pt. $>320^\circ\text{C}$

Analysis Calculated: C, 29.7; H, 1.1%

Found: C, 29.9; H, 1.2%

Infra-red 3380m 3370m 1677s 1634s 1605s 1443s 1428s 1394s

1342s 1322s 1296m 1288m 1269s 1260s 1239m,sh 1229s 1194vs,br

1181s 1171s 1157s 1149s 1125s 1105m,sh 1081w 1070w 1018w 937m

909m 893w 866m 842s,br 824s 811s 799w,sh 779s 765w 752s

746s 741m 717w 711m,sh 703s 695m 688m 665vs,br 642s 633s
605m,sh 561m 525s 503s 475m.

^1H n.m.r. (in $(\text{CD}_3)_2\text{CO}$): -0.24(br,2H); 4.39(s,1H); 7.31(s,6H).

^{19}F n.m.r. (in $(\text{CD}_3)_2\text{CO}$): -12.74(br,6F); -12.12(br,3F); -10.05(br,6F);
-5.68(br,6F); -3.07(q,3F, $J_{\text{FF}} = 15.6\text{Hz}$).

iv Reaction of $[\text{Rh}(\text{apemino})(\text{cod})]$ with hexafluorobut-2-yne at room temperature

An excess of hexafluorobut-2-yne (1.0cm^3) was condensed (-196°C) onto a suspension of $[\text{Rh}(\text{apemino})(\text{cod})]$ (0.28g, 0.9mmol) in diethyl ether contained in a Carius tube. The tube was sealed, and shaken at room temperature for 48 hours, after which it was opened and volatile material removed. Concentration of the orange solution to about 2cm^3 gave yellow crystals of $[\text{Rh}(\text{apeminoC}_4\text{F}_6)(\text{C}_6(\text{CF}_3)_6)]$, identified by its melting point and infra-red spectrum. Yield = 0.43g, 65%.

B Reaction of acetylacetonatobis(cyclo-octene)rhodium(I) with hexafluorobut-2-yne at room temperature

An excess of hexafluorobut-2-yne (1.0cm^3) was condensed (-196°C) onto a solution of $[\text{Rh}(\text{acac})(\text{C}_8\text{H}_{14})_2]$ (0.43g, 1.02mmol) in diethyl ether contained in a Carius tube. The tube was sealed and shaken at room temperature for 6 days. After opening the tube, and removing volatile material, the solution was slowly concentrated to about 2cm^3 , to yield yellow crystals of $[\text{Rh}(\text{acac.C}_4\text{F}_6)\{(\text{C}_8\text{H}_{14})(\text{C}_4\text{F}_6)_2\}]$.

Yield = 0.26g, 34%

M. Pt. 218 - 222°C (decomp)

Analysis Calculated: C, 37.6; H, 2.7%

Found: C, 37.8; H, 2.6%

Infra-red 1702s 1672w 1526vw 1488m 1420m 1293s 1267w 1259w
1228vs 1208s 1194s 1170s,sh 1161vs 1138m 1115vs 1093m 1059vw

1034w 1027w,sh 1014m 998m 971m,sh 967m 925m 870w 841m 822m
 813w 773w 755w,sh 751w 743m 726m 710w 688m,sh 680s 664s 656m
 634s 618w 588w 540w 519m 507w 487m

^1H n.m.r. (in $(\text{CD}_3)_2\text{CO}$): 3.47(s,1H); 7.25(s,6H); 7.47(m,2H);

8.00-8.55(br,12H).

^{19}F n.m.r. (in $(\text{CD}_3)_2\text{CO}$): -11.21(br,3F); -8.62(br,6F); -8.16(br,6F);

-2.63(q,3F, $J_{\text{FF}} = 15.5\text{Hz}$).

C The reactions of hexafluorobut-2-yne with compounds of the type

$(\text{Rh}(\beta\text{-ketoenolate})(\text{olefin})_2)$, and with $(\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2)$, $(\text{Rh}(\text{apeo})(\text{C}_2\text{H}_4)_2)$
 $(\text{Rh}(\text{dpm})(\text{cod}))$ and $(\text{Rh}(\text{dpm})(\text{CO})_2)$ at -78°C

i Reaction of dipivaloylmethanatobis(ethylene)rhodium(I) with hexafluorobut-2-yne at -78°C

An excess of hexafluorobut-2-yne (1.0cm^3) was condensed (-196°C) onto a solution of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)_2)$ (0.39g, 1.14mmol) in diethyl ether contained in a 50cm^3 'Quickfit' flask. The flask was allowed to warm to -78°C and the solution was stirred at this temperature, under an atmosphere of dry nitrogen. The colour of the solution slowly changed to pale yellow, and a small amount of a purple, oily solid was present in the upper part of the flask. After 2 hours, the solvent, and other volatile material were removed rapidly using a rotary evaporator, to give a yellow solid (no purple colour was apparent), identified as $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$. Yield = 0.50g, 93%. The compound is pure by M.Pt. in this state, but can be recrystallised from ether/methanol at -78°C , or sublimed onto an ice-cooled probe at $50-70^\circ\text{C}$ (0.2mm Hg).

M. Pt. $84-86^\circ\text{C}$ (decomp.)

Analysis Calculated: C, 42.9; H, 4.9%

Found: C, 43.1; H, 4.9%

Infra-red 1976s 1962m,sh 1548s 1538s 1521w 1505s 1426w 1374s
 1356s 1266s 1259s,sh 1250m,sh 1240vw 1223s 1203vw 1182w,sh 1163m,sh
 1150vs 1145s,sh 1136s,sh 978w 960w 938vw 920vw 900m 811m 786w
 751vw 724vw 704w 662m 646m 601vw 530w 512w 493w.

^1H n.m.r. (in $(\text{CD}_3)_2\text{CO}$): 3.99(s,1H); 6.33(d,4H, $J_{\text{RhH}} = 2\text{Hz}$); 8.86(s,18H).

^{19}F n.m.r. (in $(\text{CD}_3)_2\text{CO}$): -8.68(d, $J_{\text{RhF}} = 2\text{Hz}$).

ii Reaction of acetylacetonatobis(ethylene)rhodium(I) with hexafluorobut-2-yne at -78°C

An excess of hexafluorobut-2-yne (1.0cm^3) was condensed (-196°C) onto a solution of $(\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2)$ (0.25g, 0.97mmol) in diethyl ether contained in a 50cm^3 'Quickfit' flask. The flask was allowed to warm to -78°C , at which temperature the $(\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2)$ was in suspension. The suspension was stirred at this temperature under an atmosphere of dry nitrogen for 2 hours, after which the product was a clear yellow solution. Rapid removal of the solvent and of volatile material on a rotary evaporator gave a yellow solid, identified as $(\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$. Yield = 0.32g, 85%. The complex could be purified by recrystallisation from ether/methanol at -78°C , or by sublimation onto an ice-cooled probe at $<40^\circ\text{C}$ (0.2mm Hg).

M. Pt. 57-59 $^\circ\text{C}$.

Analysis Calculated: C, 33.7; H, 2.8%

Found: C, 33.4; H, 3.0%

Infra-red 1976s 1960s 1566s 1527s 1430w 1268s 1242w 1227s 1201w
 1165s 1150vs 1026m 995w,sh 984w 967vw 936w 922vw 900m 796m
 789m 728w 708m 692m 664m 647m 627m 601w 522m 458m 426w.

^1H n.m.r. (in $(\text{CD}_3)_2\text{CO}$): 4.30(s,1H); 6.33(d,4H, $J_{\text{RhH}} = 2\text{Hz}$); 7.94(s,6H).

^{19}F n.m.r. (in $(\text{CD}_3)_2\text{CO}$): -8.95(s)

iii Reaction of acetylacetonatobis(cyclo-octene)rhodium(I) with hexafluorobut-2-yne at -78°C

An excess of hexafluorobut-2-yne was condensed (-196°C) onto a solution of $[\text{Rh}(\text{acac}(\text{C}_8\text{H}_{14})_2)]$ (0.52g, 1.23mmol) in diethyl ether contained in a 50cm^3 'Quickfit' flask. The flask was allowed to warm to -78°C and the yellow suspension was stirred at this temperature under an atmosphere of dry nitrogen. After 12 hours the solvent and volatile materials were rapidly removed to give a yellow solid, identified as impure $[\text{Rh}(\text{acac})(\text{C}_8\text{H}_{14})(\text{C}_4\text{F}_6)]$. Yield = 0.53g, 91%. Recrystallisation of this solid from ether/ethanol resulted only in the isolation of $[\text{Rh}(\text{acac})(\text{C}_8\text{H}_{14})_2]$, due to the presence of displaced cyclo-octene in the solution. The compound could, however, be purified by removing the cyclo-octene at 35°C , under vacuum (0.2mm Hg), followed by recrystallisation from ether/ethanol, or by sublimation onto an ice-cooled probe at $55-70^{\circ}\text{C}$ (0.2mm Hg).

M.Pt. $113 - 114^{\circ}\text{C}$ (decomp.)

Analysis Calculated: C, 43.1; H, 3.6%

Found: C, 43.3; H, 4.0%

Infra-red 1958s 1584s 1568s 1525s 1355m 1339w 1323m 1277s 1263vs 1241m 1227s 1197w 1170m,sh 1159s 1149vs, 1141s 1125m,sh 1022m 976w 967vw 932w 919vw 900m 857w 849w 818vw 791s 766w 723w 706m 688w 673m 644m 623m (spectrum not obtained below 600cm^{-1})

^1H n.m.r. (in CD_2Cl_2): 4.52(s, 1H); 6.55(q x d, 2H, $J_{\text{HH}} = 7\text{Hz}$, $J_{\text{RhH}} = 2\text{Hz}$) 7.97(s, 6H); 7.69-8.73(br, 12H).

^{19}F n.m.r. (in CD_2Cl_2): -9.91(s)

iv Reaction of 4-aminopent-3-ene-2-iminatobis(ethylene)rhodium(I) with hexafluorobut-2-yne at -78°C

An excess of hexafluorobut-2-yne (0.5cm^3) was condensed (-196°C) onto a solution of 0.1g (0.39mmol) of $[\text{Rh}(\text{apemino})(\text{C}_2\text{H}_4)_2]$ in diethyl

ether, contained in a 50cm³ 'Quickfit' flask. The flask was allowed to warm to -78°C, and the solution was stirred at this temperature for 2 hours, under an atmosphere of dry nitrogen. Rapid removal of the solvent and other volatile material, on a rotary evaporator, gave a red oily solid. All attempts to crystallise the product were unsuccessful. Only very poor ¹H n.m.r. and ¹⁹F spectra could be obtained, but the i.r. spectrum has bands at 1684s and 1610m, as well as strong absorptions at 1263, 1231, 1193, 1158, 1137 and 1099cm⁻¹ in the C-F stretching region.

v Reaction of 4-aminopent-3-ene-2-onatobis(ethylene)rhodium(I) with hexafluorobut-2-yne at -78°C

An excess of hexafluorobut-2-yne (1.0cm³) was condensed (-196°C) onto a solution of [Rh(apeo)(C₂H₄)₂] (0.3g, 1.17mmol) in diethyl ether contained in a 50cm³ 'Quickfit' flask. The flask was allowed to warm to -78°C, and the orange solution was stirred at this temperature for 2 hours under an atmosphere of dry nitrogen. Rapid removal of the solvent and volatile material gave an orange oily solid, the i.r. spectrum of which included strong absorptions at 1944 and 1692cm⁻¹, as well as a complex set of bands between 1500 and 1600cm⁻¹. Repetition of the reaction over a period of 6 hours gave a red oily solid, which could not be crystallised. The i.r. spectrum of this product included strong absorptions at 1692 and 1618cm⁻¹, as well as bands at 1265, 1227, 1189 and 1136cm⁻¹ in the C-F stretching region. The ¹H n.m.r. spectrum was very poor, but the ¹⁹F n.m.r. (measured in d⁶ acetone) had signals at -9.62(br, 3F), -6.96(br, 6F), -6.69(br, 6F) and -3.69(q, 3F, J_{FF} = 16.92Hz).

vi Reaction of dipivaloylmethanato(cyclo-octa-1,5-diene)rhodium(I) with hexafluorobutyne at -78°C

An excess of hexafluorobut-2-yne (1.0cm³) was condensed (-196°C)

onto $(\text{Rh}(\text{dpm})(\text{cod}))$ (0.53g, 1.34mmol) in diethyl ether solution, contained in a 50cm³ 'Quickfit' flask. The flask was allowed to warm to -78°C and the solution was then stirred at this temperature, under an atmosphere of dry nitrogen, for 12 hours. Rapid removal of the solvent and volatile material gave a yellow solid, identified as unreacted $(\text{Rh}(\text{dpm})(\text{cod}))$ by i.r. and M. Pt.

vii Reaction of dipivaloylmethanatodicarbonylrhodium(I) with hexafluorobut-2-yne at -78°C

An excess of hexafluorobut-2-yne (1.0cm³) was condensed (-196°C) onto a solution of $(\text{Rh}(\text{dpm})(\text{CO})_2)$ (0.45g, 1.32mmol) in diethyl ether, contained in a 50cm³ 'Quickfit' flask. The flask was allowed to warm to -78°C , and the suspension was stirred at this temperature, under an atmosphere of dry nitrogen. After 8 hours the suspended solid was filtered, and identified as unreacted $(\text{Rh}(\text{dpm})(\text{CO})_2)$ by i.r. and M.Pt. Removal of the solvent, and volatile material, also gave unreacted $(\text{Rh}(\text{dpm})(\text{CO})_2)$.

D The reactions of the compounds $(\text{Rh}(\beta\text{-ketoenolate})(\text{olefin})(\text{C}_4\text{F}_6))$ with hexafluorobut-2-yne at room temperature

i Reaction of dipivaloylmethanato(ethylene) (hexafluorobut-2-yne)rhodium(I) with hexafluorobut-2-yne at room temperature

An excess of hexafluorobut-2-yne (1.0cm³) was condensed (-196°C) onto $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ (0.65g, 1.37mmol) dissolved in diethyl ether contained in a Carius tube. The tube was sealed and shaken at room temperature for 48 hours, after which it was opened, and volatile material removed. Slow concentration of the solution to about 2cm³ gave yellow crystals of $(\text{Rh}(\text{dpm} \text{C}_4\text{F}_6)(\text{C}_6(\text{CF}_3)_4\text{H}_4))$ identified by i.r. M. Pt., ¹H n.m.r. and ¹⁹F n.m.r. Yield = 0.66g, 55%.

ii Reaction of acetylacetonato(cyclo-octene)(hexafluorobut-2-yne)rhodium(I) with hexafluorobut-2-yne at room temperature

An excess of hexafluorobut-2-yne (1.0cm^3) was condensed (-196°C) onto a solution of $(\text{Rh}(\text{acac})(\text{C}_8\text{H}_{14})(\text{C}_4\text{F}_6))$ (0.1g , 0.2mmol) in diethyl ether contained in a Carius tube. The tube was sealed and shaken at room temperature for 6 days, after which it was opened and volatile material removed. Evaporation of the solvent gave a yellow solid identified as $(\text{Rh}(\text{acac}(\text{C}_4\text{F}_6))((\text{C}_8\text{H}_{14})(\text{C}_4\text{F}_6)_2))$ by i.r. and M. Pt. Yield = 0.11g , 65%.

E Some reactions of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$

i With carbon monoxide

Carbon monoxide was passed slowly through a stirred solution of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ (0.3g , 0.63mmol) in diethyl ether. A red colouration was instantly visible on the side of the flask. After 5 minutes, the reaction was stopped, and the solvent evaporated to give a green-red solid, identified as the known complex $(\text{Rh}(\text{dpm})(\text{CO})_2)$ by i.r. and M. Pt. Yield = 0.16g , 73%.

ii With triphenylphosphine

Triphenylphosphine (0.45g , 1.7mmol) was added to a solution of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ (0.41g , 0.85mmol) in diethyl ether. The solution immediately changed colour from yellow to orange. It was stirred at room temperature, under an atmosphere of dry nitrogen, for 1 hour, after which methanol was added, and the solution was slowly concentrated to give yellow crystals of $(\text{Rh}(\text{dpm})(\text{PPh}_3)_2(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$. Yield = 0.72g , 85%.
M. Pt. $129-130^\circ\text{C}$

Analysis Calculated: C, 63.0; H, 5.1%

Found: C, 63.0; H, 5.2%

Infra-red 1815s 1787s 1583s 1562s 1548s 1527s 1496s 1484s

1436s 1396s 1319w 1307w 1251s 1242s 1225vs 1188s 1160w 1137s
 1126s 1116s 1108vs 1101s,sh 1093s, 1031w 1003w 990w 981vw 973vw
 965w 932w 924w,sh 902w 873m 849w 825w 810m 790m 766w,sh 758m
 746s 732w 706s,sh 696vs 678s 644w 619w 600vw 535s 521s 504s
 462w 455w 432m 417w.

^1H n.m.r. (in CDCl_3): 2.63(br,3OH); 4.29(s,1H); 9.02(s,9H); 9.20(s,9H).

^{19}F n.m.r. (in CDCl_3): room temperature: $-12.04(\text{d}, J_{\text{RhF}} = 2\text{Hz})$
 at -58°C : $-12.08(\text{d}, 3\text{F}, J_{\text{PF}} = 16.8\text{Hz})$;
 $-11.29(\text{s}, 3\text{F})$.

iii With triphenylarsine

0.26g (0.85mmol) of triphenylarsine was added to 0.2g (0.42mmol) of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ dissolved in diethyl ether. The solution immediately changed colour from yellow to orange. It was stirred at room temperature, under an atmosphere of dry nitrogen for 30 minutes, after which methanol was added, and the solution slowly concentrated to give orange crystals of $(\text{Rh}(\text{dpm})(\text{AsPh}_3)_2(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$. Yield = 0.35g, 80%.

M. Pt. $152-154^\circ\text{C}$

Analysis Calculated: C, 57.3; H, 4.7%

Found: C, 57.5; H, 4.9%

Infra-red 1821s 1790s 1584s 1559s 1550s 1526s 1492s 1484s 1438s
 1395s 1312w 1305w,sh 1252s 1242s 1221vs,br 1186s 1158m 1139s,sh
 1127s 1118s 1109vw 1086m,sh 1079s 1027m 1001m 989vw 977vw 972vs
 953w 931w,br 901m 872m 849w 824w 807m 790m 767w 748s 737vs
 694vs 680s 670m,sh 644m 624w 618w 603vw 495m,sh 486s 472s 458m
 437w.

^1H n.m.r. (in CDCl_3): 2.73(br,3OH); 4.27(s,1H), 9.00(s,9H); 9.14(s,9H).

^{19}F n.m.r. (in CDCl_3): room temperature: $-11.04(\text{d}, J_{\text{RhF}} = 2\text{Hz})$
 at -58°C : $-12.67(\text{s}, 3\text{F})$; $-11.22(\text{s}, 3\text{F})$

iv With triphenylstilbine.

0.32g (0.90mmol) of triphenylstilbine was added to a solution of 0.21g (0.45mmol) of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ in diethyl ether. The solution immediately changed from yellow to red. It was stirred at room temperature under an atmosphere of dry nitrogen, for 20 minutes, after which methanol was added, and the solution concentrated to give orange-red crystals of $(\text{Rh}(\text{dpm})(\text{SbPh}_3)_2(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$. Yield = 0.40g, 75%.

M. Pt. 144-146°C (decomp.)

Analysis Calculated: C, 53.1; H, 4.3%

Found: C, 53.3; H, 4.4%

Infra-red 1829s 1790m 1583s 1560s 1549s 1526s 1491s 1480s 1432s
1396s 1336m 1308w 1300w 1276w,sh 1253s 1241s 1220vs,br 1186s
1159m 1139s,sh 1123vs,br 1111s 1070s 1023m 1000s 990vw 972w 951w
931w 920vw 900m 871m 853w 824w 803w 791m 768w 731vs,br 696s
678s 659w 643m 624w 607w 537w 496m 483w 463s 452s 441m.

¹H n.m.r. (in CDCl_3): 2.74(br, 3OH); 4.34(s, 1H); 8.95(s, 9H); 9.14(s, 9H).

¹⁹F n.m.r. (in CDCl_3): room temperature: -10.73(d, $J_{\text{RhF}} = 1.5\text{Hz}$)

at -58°C: -12.08(s, 3F); -9.60(s, 3F).

v With 1,2-bis(diphenylphosphino)ethane

0.125g (0.31mmol) of 1,2-bis(diphenylphosphino)ethane was added to a solution of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ (0.15g, 0.31mmol) in diethyl ether. A yellow suspension formed immediately. The mixture was stirred overnight at room temperature under an atmosphere of dry nitrogen, after which there was an almost clear solution. Filtration of the solution and evaporation of the solvent under vacuum, followed by addition of a small amount of methanol gave a yellow solid, identified as $(\text{Rh}(\text{dpm})(\text{diphos})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$. Yield = 0.04g, 15%. The compound can be recrystallised from dichloromethane/petrol (B.Pt 40-60°C).

M. Pt. 128-129°C

Analysis Calculated: C, 58.2 H, 5.1%

Found: C, 59.1 H, 5.4%

Infra-red 1829s 1794m 1580s 1563s 1540w,sh 1525s 1493s 1483m,sh
1437s 1313vw 1307vw 1257s 1246s 1220s,br 1187m 1161w 1135s 1115s,br
1105s,br 1030w 1001w 954w 932w 903m 873m 846vw 815m 799m 786w
753m 744m 711s 706s 694s 675s 654m 645m 620w,br 524s 500s 481m
455w 431m

¹H n.m.r. (in CDCl₃): 2.3-3.0(br, 2OH); 4.70(s, 1H); 8.65(br, 4H)
9.03(s, 9H); 9.30(s, 9H).

¹⁹F n.m.r. (in CDCl₃): -11.90(d x d, 3F, J_{PF} = 17.4Hz, J_{RhF} = 4.5Hz);
-10.28(d, 3F, J_{RhF} = 3Hz).

vi With 2,5-dimethylhex-3-yne-2,5-diol

0.135g (0.95mmol) of 2,5-dimethylhex-3-yne-2,5-diol was added to a solution of (Rh(dpm)(C₂H₄)(C₄F₆)) (0.45g, 0.95mmol) in diethyl ether. The yellow solution was stirred at room temperature, under an atmosphere of dry nitrogen for 3 days, after which the solution had turned orange. Addition of methanol, followed by slow concentration (room temp., atmospheric pressure) of the solution gave orange crystals, which were dried in vacuo for several days, and identified as (Rh(dpm){ (C₂H₄)(C₄F₆)((H₃C)₂C(OH)C≡CC(OH)(CH₃)₂)₂ }) from microanalytical data. Yield = 0.12g, 17%.

M. Pt. 129-133°C.

Analysis Calculated: C, 52.1; H, 6.8%

Found: C, 52.0; H, 6.8%

Infra-red 3312m 3210m 1612vw 1551s 1534s 1529m,sh 1503s 1350s
1328m 1290m 1278m,sh 1248m 1217s,br 1191s 1180s,sh 1171s 1158w,sh
1143s 1113m 1098m 1052m 1007m,sh 1004m 974m 966m 955m 938w
859vw 844vw 834vw 825w 806m 786m,br 778m,sh 769w 757w 746w

729w 701w 690w 663w 644vw 634w 571w 548w 526w,br 505w 494vw.

^1H n.m.r. (in CD_2Cl_2): 2.16(br) and 2.66(br,) (total of $\sim 3\text{H}$); 3.99(s,1H);

7.96-8.88 (complex, $\sim 32\text{H}$); 8.83(s,18H).

^{19}F n.m.r. (in CH_2Cl_2): -20.16(q,3F, $J_{\text{FF}} = 15.0\text{Hz}$); -11.3(br,3F).

vii With dimethylacetylene

An excess of dimethylacetylene (1.0cm^3) was condensed (196°C) onto a solution of $(\text{Rh}(\text{dpm})(\text{C}_2\text{H}_4)(\text{C}_4\text{F}_6))$ (0.6g, 1.25mmol) in diethyl ether, contained in a Carius tube. The tube was sealed and shaken at room temperature for 16 hours, during which reaction occurred, giving a dark red solution. The tube was opened, and the solution concentrated slowly, under reduced pressure, to give a yellow-brown solid (0.3g). The i.r., ^{19}F n.m.r. and ^1H n.m.r. spectra of the solid were obtained, and suggested the presence of a coordinated acetylene, but the solid also appeared to contain some hexamethylbenzene. Attempted purification on an alumina column, using diethyl ether eluant, gave only an intractable oil, which gave a very poorly defined ^1H n.m.r. spectrum. Yellow-brown solid: i.r. spectrum includes 2035m, 1596m, 1567m, 1553s, 1545s, 1501s, 1249m 1227m,sh, 1221s, 1208m, 1189m, 1167m, 1142s, 1023s.

^1H n.m.r. (in $(\text{CD}_3)_2\text{CO}$): 4.28(s,1H); 7.1-8.0 (complex, integration uncertain, since $\text{C}_6(\text{CH}_3)_6$ may be in this region); 8.91(s,18H).

^{19}F n.m.r. (in $(\text{CD}_3)_2\text{CO}$): -10.46(s).

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CHAPTER 3

AN INVESTIGATION OF THE REACTIONS OF PHENYLHALOACETYLENES WITH
COMPLEXES OF PLATINUM(O), PALLADIUM(O), RHODIUM(I) AND IRIDIUM(I)

The reactions of halo-olefins with compounds of platinum(O),¹⁻⁵ palladium(O),^{6,7} rhodium(I),⁸⁻¹⁰ and iridium(I)¹¹⁻¹² have been thoroughly investigated, but very little work using haloacetylenes has so far been reported²⁹. Consequently, it was considered interesting to investigate the reactions of a series of acetylenes, $\text{PhC}\equiv\text{CX}$, ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with complexes of these metals, with a view to comparing the chemistry of the two systems. This chapter is sub-divided according to the metal complex used, and then further divided for the reactions with each acetylene; experimental details and infra-red spectroscopic data are in Section 3.6.

3.1 Platinum

Reactions were carried out in three different ways:

1) addition of the acetylene to a solution of $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ in benzene; 2) addition of the acetylene to a suspension of $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ in ether; 3) reduction of $\text{cis}-(\text{PtCl}_2(\text{PPh}_3)_2)$ by hydrazine in ethanol, followed by addition of the acetylene. This latter method is based on the work of Chatt et al.¹³.

(i) Phenylchloroacetylene

Reaction of phenylchloroacetylene with $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ in benzene solution at room temperature afforded a pale-yellow complex, which was identified as $\text{trans}-(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, by its infra-red spectrum and analytical data. The i.r. band due to the acetylide group is at 2125cm^{-1} , considerably higher than

the C≡C stretching frequencies of π -bonded acetylene compounds of platinum(0)¹⁴, which are commonly as low as 1700cm^{-1} , but slightly lower than the value in the free acetylene, of 2225cm^{-1} . This decrease in i.r. absorption frequency is due to partial occupation of the acetylide π^* -antibonding orbitals, caused by some transfer of d-electron density from the platinum, and is a well characterised phenomenon¹⁵. The complex was identified as the trans isomer by examination of the i.r. spectrum in the region $540\text{--}560\text{cm}^{-1}$, since the intensity of a band at $550 \pm 5\text{cm}^{-1}$ in compounds of the type $(\text{Pt}(\text{PPh}_3)_2 \text{XY})$ is believed to be related to complex stereochemistry¹⁶. This absorption may be a weak band of triphenylphosphine, which has undergone a slight shift to higher frequency on coordination. In the case of cis complexes, the band is strong, whereas in trans complexes it is weak, and consequently the stereochemistry of $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ formed in this reaction is assigned as trans, since the i.r. shows only a weak absorption at 549cm^{-1} .

The complex trans- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ has been reported before¹⁷, having been prepared by reaction of hydrogen chloride with trans- $(\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_3)_2)$, and also from cis- $(\text{PtCl}_2(\text{PPh}_3)_2)$ and sodium phenylacetylide: there is a slight discrepancy in the melting point of the compound obtained by these workers, and that of the compound prepared in this work, but the u.v. and i.r. spectra are consistent, as are the analytical data. trans- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ is believed to be an active species in the polymerisation of phenylacetylene by various platinum(II) complexes including cis and trans- $(\text{PtCl}_2(\text{PPh}_3)_2)$, and trans- $(\text{PtHCl}(\text{PPh}_3)_2)$ ¹⁸. The compounds trans- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PR}_3)_2)$ ($\text{R}_3 = \text{Ph}(\text{C}_2\text{H}_5)_2$ or Ph_2CH_3) have also recently been prepared by reaction of $(\text{Sn}(\text{C}\equiv\text{CPh})(\text{CH}_3)_3)$

with $\text{cis}-(\text{PtCl}_2(\text{PPh}_3)_2)^{19}$.

The mechanism for formation of $\text{trans}-(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ from $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ and phenylchloroacetylene is probably as shown in Figure 3.1.

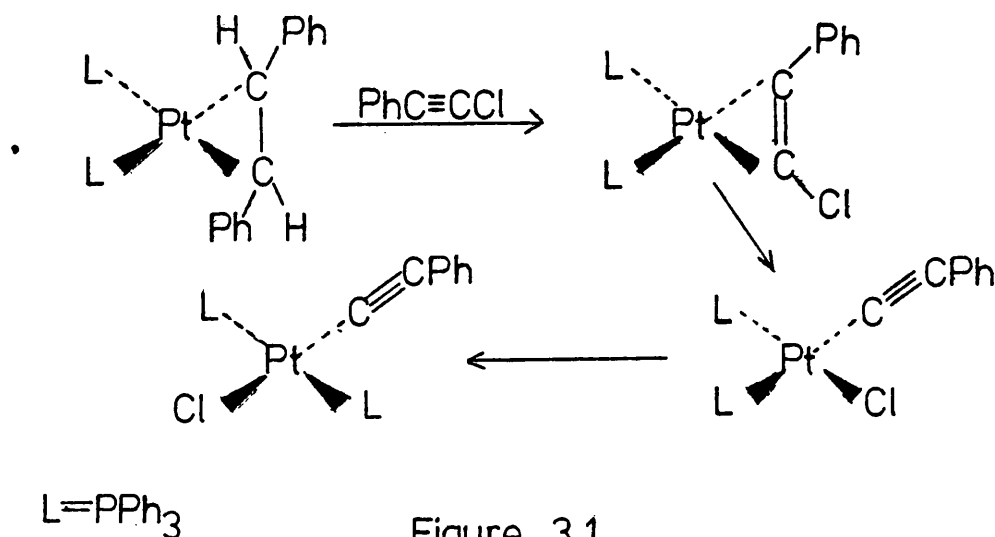


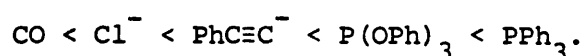
Figure 3.1

Substitution of trans-stilbene by other olefins or acetylenes is a well known process⁴; in the case of halo-olefins, isomerisation of the π -bonded complexes to cis and trans halovinyl compounds is also well documented,¹⁻⁵ and the cis-trans isomerisation of $(\text{Pt}(\text{PPh}_3)_2\text{XY})$ complexes has been the subject of a considerable amount of investigation^{20,21,22}. A parallel reaction is that of $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ with trans- $\text{CF}_3(\text{CN})\text{C}=\text{C}(\text{CN})\text{CF}_3$, which does not yield an olefin complex, but goes directly to a platinum-vinyl compound, probably having trans geometry about the platinum¹³.

Repetition of the reaction of phenylchloroacetylene with $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ in ether suspension, rather than in benzene solution, provides evidence in support of the postulated mechanism, since the product is the previously unknown $\text{cis}-(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, the i.r. spectrum of which shows a strong band at 544cm^{-1} , indicating cis stereochemistry. It therefore appears that it is essential for the reaction to be carried out in solution for the cis-trans isomerisation to occur, and in accordance with

this it was found that stirring the cis isomer in benzene solution for several hours caused it to rearrange to the trans species. A suggested mechanism²² for this type of cis-trans rearrangement involves solvent catalysis - a process which is assisted by the complex being in solution, and thus having greater interaction with the solvent.

An interesting comparison is given by the Pt-Cl i.r. stretching frequencies for these compounds. For the trans compound, in which the chlorine is trans to the acetylide, the band due to Pt-Cl is at 320cm^{-1} , whereas in the cis compound, with the chlorine trans to triphenylphosphine, the absorption is at 306cm^{-1} , signifying a stronger Pt-Cl bond in the trans derivative. The extent to which a ligand weakens the bond trans to itself in the equilibrium state of a complex has been termed its "trans-influence"²⁴ and this ligand property has been the subject of a considerable amount of study (e.g. a review of the field by Clark et al.²⁵). Metal-halogen stretching frequencies have been used as a measure of trans-influence, e.g.²⁶, and Clark²⁵ lists the platinum-chlorine stretching frequencies of a series of compounds trans-(PtXClL₂) (L = P(C₂H₅)₃ or PPh(CH₃)₂), thus formulating a tentative trans-influence order for the ligands X. Comparison of these frequencies with the value of 320cm^{-1} for the platinum-chlorine stretch in trans-(PtCl(C≡CPh)(PPh₃)₂) observed in this work suggests that the phenylacetylide group should be placed as follows (order of increasing trans-influence):



A greater trans-influence for triphenylphosphine than for phenylacetylide is also suggested by the lower value of the platinum-chlorine stretching frequency in cis-(PtCl(C≡CPh)(PPh₃)₂)

than in the trans isomer.

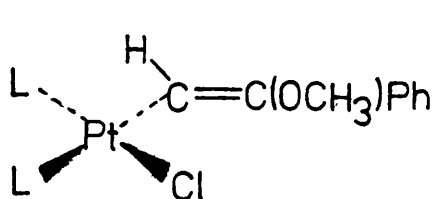
The third method employed to study the chemistry of the platinum/phenylchloroacetylene system - i.e. hydrazine hydrate reduction of cis-(PtCl₂(PPh₃)₂), followed by addition of the acetylene - did not give an acetylide complex, but the π -bonded acetylene complex, (Pt(PPh₃)₂(PhC \equiv CCl)). The i.r. of this compound has no absorptions in the regions associated with acetylide groups or Pt-Cl bonds, but instead has an absorption at 1698cm⁻¹, due to the C \equiv C bond of the coordinated acetylene. Formation of this compound, rather than a metal-acetylide, is probably a result of the completely different reaction conditions involved, since this reaction involves bridge cleavage of the hydrazine-reduction product of cis-(PtCl₂(PPh₃)₂) (see Section 1.5), whereas the other two methods employed both involve displacement of trans-stilbene by the acetylene.

As a further test of the scheme outlined in Figure 3.1, the π -bonded acetylene complex was warmed in methanol at 35°C for several hours, upon which it underwent isomerisation to trans-(PtCl(C \equiv CPh)-(PPh₃)₂). This rearrangement was also observed in benzene solution. Acetylene-acetylide isomerisation has been observed before, e.g.²⁷, and is believed to be involved in the polymerisation of monosubstituted acetylenes by (Ni(CO)₂(PPh₃)₂)²⁸, but in the isomerisation of (Pt(PPh₃)₂(PhC \equiv CCl)), the formation of the trans, rather than the cis acetylide, is interesting. The kinetics of this reaction are described in Chapter 4, which includes a more detailed discussion of the postulated mechanism. These preliminary results seem to vindicate the reaction path shown in Figure 3.1, however, since it has proved possible to isolate both the expected intermediates in the reaction, and to isomerise these to the final product.

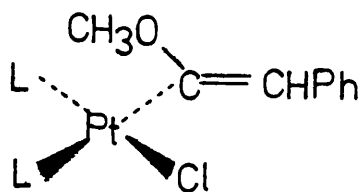
In view of this observed preference for trans geometry, it was thought that an attempt to prepare $(\text{Pt}(\text{diphos})(\text{PhC}\equiv\text{CCl}))$ (diphos = 1,2-bis(diphenylphosphino)ethane) and to isomerise this to an acetylide complex, would be interesting, since the chelating phosphine ligand would force any isomerisation product into a cis configuration. The synthesis was achieved by reduction of $(\text{PtCl}_2(\text{diphos}))$ with sodium borohydride, in the presence of phenylchloroacetylene, to give a white solid, having a $\text{C}\equiv\text{C}$ i.r. absorption at 1667cm^{-1} . An attempt to isomerise this by warming in methanol at 40°C for several hours, resulted only in the recovery of the π -bonded complex, and a small amount of decomposition product. This may in part be due to a change in basicity of the phosphine, but since such an effect would only be slight, it is quite possibly a consequence of the inability to achieve trans stereochemistry.

Since the mechanism for isomerisation of $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ in methanol is proposed to involve cis- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ as an intermediate, isolation of the cis isomer, followed by warming with methanol, might be expected to produce the trans compound. As has already been pointed out, this change does occur in benzene solution at room temperature, but strangely, a methanol suspension at room temperature changed from white to yellow over several hours, and gave a yellow solid having interesting i.r. absorptions at 1618 and 295cm^{-1} , as well as bands at 2125 and 320cm^{-1} associated with a trans acetylide complex. The band at 544cm^{-1} , indicating cis geometry in the starting material, is lower in intensity (relative to the bands due to the triphenylphosphine ligands at 526 , 510 and 496cm^{-1}) in the product. Additional stirring of the suspension for several days did not produce any further changes in the i.r. spectrum,

indicating that the reaction occurring was complete. These changes also occurred when attempts were made to recrystallise the cis complex from dichloromethane/methanol solutions. A possible explanation for these observations is that two competing reactions are taking place: i) cis-trans isomerisation as expected, resulting in the i.r. bands at 2125 and 320cm^{-1} , and the observed weakening of the 544cm^{-1} absorption: ii) nucleophilic attack of methanol at the acetylide triple-bond, giving a compound (3.1a or b) which gives rise to a C=C absorption at 1618cm^{-1} , and a new Pt-Cl band at 295cm^{-1} .



(a)



(b)



(3.1)

Attempted purification by preparative T.L.C. gave trans-(PtCl(C≡CPh)(PPh₃)₂) and a yellow compound analysing approximately as a 1:1 adduct between (PtCl(C≡CPh)(PPh₃)₂) and CH₃OH. Unfortunately, insufficient of the compound was obtained for a ¹H n.m.r. spectrum to be observed, and only a weak infra-red spectrum was obtained. The i.r. indicates cis stereochemistry and has an absorption at 295cm^{-1} , but not at 320cm^{-1} . In addition, the medium intensity band at 2125cm^{-1} is no longer present, but unfortunately the weak band at 1618cm^{-1} , postulated as being due to the vinylic double-bond, is not visible. This may be due to the weak nature of the spectrum, but dictates that the assignment of structure (3.1) to this yellow compound can be only tentative at this stage.

It is interesting that none of the yellow compound is obtained when $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ is isomerised in methanol, nor when trans- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ is stirred in methanol, or recrystallised from dichloromethane/methanol. Reactivity in the case of the cis isomer is probably aided by the presence of the π -acid triphenylphosphine ligand trans to the acetylide group, pulling d and π electron density away from it, and facilitating the approach of an incoming nucleophile, whereas in the trans isomer, the ligand trans to the acetylide is chloride, and this will exercise no similar π -acid effect. Failure to isolate any of the yellow compound during isomerisation of $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ in methanol, which is thought to go via the cis-acetylide, may be due to the reaction being carried out at $35-40^\circ\text{C}$, making isomerisation through to the trans isomer a preferred reaction.

(ii) Phenylbromoacetylene and phenyliodoacetylene

Reaction of these two acetylenes with benzene solutions of $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ yielded the trans acetylide products $(\text{PtX}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, ($\text{X} = \text{Br}, \text{I}$) as expected. For $\text{X} = \text{Br}$, the compound has already been prepared by reaction of phenylbromoacetylene with a benzene solution of $(\text{Pt}(\text{PPh}_3)_4)$, although no stereochemistry was specified²⁹. It can now be concluded that the geometry is trans, since the melting points of the compound prepared from $(\text{Pt}(\text{PPh}_3)_4)$, and the compound prepared from $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ are in agreement, and the infra-red spectrum shows no absorptions at all in the region $540-560\text{cm}^{-1}$, where a band would be expected for a cis compound. Both the iodo- and the bromo-derivatives have infra-red bands due to the acetylide group around 2125cm^{-1} , although in the case of the bromo-compound, the band is split, for reasons which are not clear.

When the reactions were repeated in ether suspension, rather than in benzene solution, the previously unknown cis-isomers of $(\text{PtX}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ ($\text{X} = \text{Br}, \text{I}$) were obtained, thus directly paralleling the reactions of phenylchloroacetylene. Both compounds have i.r. bands due to the acetylide group at 2125cm^{-1} , and absorptions at 541cm^{-1} ($\text{X} = \text{Br}$) and 540cm^{-1} ($\text{X} = \text{I}$) indicative of cis-geometry. Attempts to recrystallise these complexes from dichloromethane/methanol mixtures, however, resulted in isomerisation and isolation of the trans-isomers. These trans-isomers were also obtained when the cis-isomers were stirred in benzene solution for several hours. As with the chloro-derivative, the bromo- and iodo-compounds are seen, therefore, to undergo facile cis-trans isomerisations in solution, although it is interesting that methanol does not react with these derivatives in the way that it does with the chloro-analogue.

Attempts to prepare π -bonded complexes of these acetylenes by hydrazine reduction of cis-($\text{PtCl}_2(\text{PPh}_3)_2$), followed by reaction with the acetylene, as was seen to work for phenylchloroacetylene, were unsuccessful. It is apparent that the π -complexes of these acetylenes are unstable relative to isomerisation to acetylide complexes, since the products of these two reactions were the trans-acetylides, $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$. That the trans, rather than the cis-isomers should be obtained is not surprising, since this method of reaction involves heating a solution of reduced cis-($\text{PtCl}_2(\text{PPh}_3)_2$) with the acetylene, in ethanol, to 60°C until crystallisation occurs, and such a process would be expected to facilitate cis-trans isomerisation.

A combination of several factors probably causes the isolation of acetylide, rather than acetylene, complexes from these reactions:

(i) platinum(0)-acetylene compounds are known to be stabilised by electron-withdrawing substituents on the acetylene, since this enhances the π -back-bonding to the ligand. For the series of acetylenes $\text{PhC}\equiv\text{CX}$, the most electrophilic acetylene has $\text{X}=\text{Cl}$; therefore this derivative would be most expected to form a π -complex;

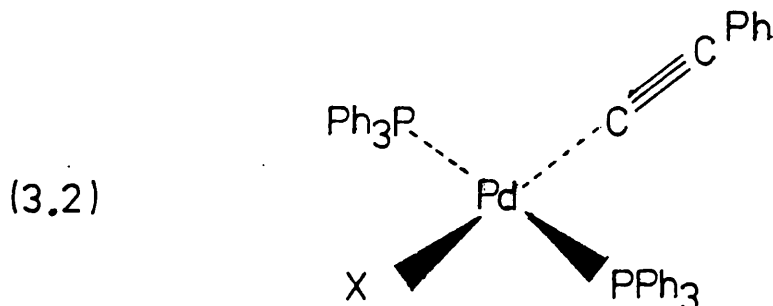
(ii) the formation of the platinum(II)-acetylide compounds involves cleavage of a carbon-halogen bond. The energy required to do this decreases in the order $\text{C-Cl} > \text{C-Br} > \text{C-I}$, so that for $\text{X} = \text{Br}$ or I , acetylide complexes should be formed more easily than for $\text{X} = \text{Cl}$;

(iii) formation of the platinum(II)-acetylides also involves formation of a platinum-halogen bond. Platinum is a 'soft' acid^{30,31}, and as such, its affinity for halide ions decreases in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$, so that again the formation of acetylide complexes is more likely with I^- or Br^- than with Cl^- .

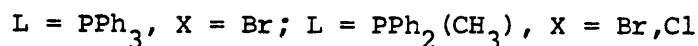
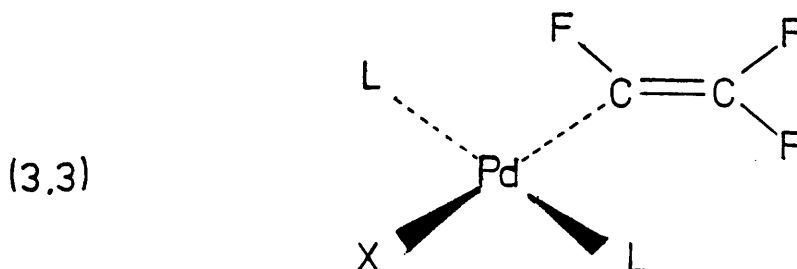
3.2 Palladium

(i) Phenylchloroacetylene and phenylbromoacetylene

Reaction of ether suspensions of $(\text{Pd}(\text{PPh}_3)_4)$ with the acetylenes $\text{PhC}\equiv\text{CX}$ ($\text{X} = \text{Cl}, \text{Br}$) yielded compounds having i.r. bands at 2125cm^{-1} ($\text{X} = \text{Cl}$) and 2120cm^{-1} ($\text{X} = \text{Br}$), and analysing as the acetylide complexes (3.2).



This reaction is therefore an example of the common oxidative-addition reactions of molecules RX ($\text{X} = \text{halogen}$; $\text{R} = \text{e.g. alkyl, vinyl, acetyl}$) to palladium(0), leading to square-planar palladium(II) compounds. A parallel case with these reactions of haloacetylenes is the reaction of halo-olefins, leading to trans vinyl complexes⁷ (3.3).



Trans geometry was assigned to these vinyl complexes on the basis of values for J_{PF} in the ^{19}F n.m.r., and the appearance of the methyl signals as a triplet in the ^1H n.m.r. (for $\text{L} = \text{PPh}_2(\text{CH}_3)$). Similarly,

the vinyl complexes formed from $(\text{Pd}(\text{PPh}_3)_4)$ and chloro-olefins are formulated as trans, on the basis of systematic variations in the Pd-Cl i.r. stretching frequencies⁶.

No such n.m.r. or i.r. studies are possible with the products from the phenylhaloacetylene reactions, but it seems probable that the trans isomers are being formed. Cis-trans rearrangement should be aided in these reactions by the liberation of two moles of triphenylphosphine per mole of $(\text{Pd}(\text{PPh}_3)_4)$, since phosphines are known to catalyse this type of isomerisation^{23,32}. Pieces of evidence which may suggest trans structures are: i) the absence of any i.r. bands in the region $540\text{--}560\text{cm}^{-1}$ which is known to indicate trans geometry for platinum compounds of this type although no systematic study has been undertaken for palladium; ii) in the derivative having $\text{X} = \text{Cl}$, the Pd-Cl stretching-vibration is at 331cm^{-1} , which is comparable with the values obtained for the vinyl complexes⁶; iii) the compounds can be recovered unchanged after several days in benzene solution, indicating that no cis-trans isomerisation can occur. In addition to these pieces of evidence, other work does show that a trans configuration is preferred by many square-planar palladium(II) complexes, e.g.³³.

It seems probable that these compounds are being formed via a π -bonded acetylene complex of palladium(0), which very rapidly isomerises, probably via a cis compound to the trans-palladium(II)-acetylides (Figure 3.2). The failure to isolate a compound $(\text{Pd}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CX}))$ even with phenylchloroacetylene is not surprising in view of the smaller number of stable palladium(0)-acetylene complexes known compared with platinum(0) (see Section 1.4). This difference in ability to form π -complexes between platinum and palladium also has an analogue in metal-olefin chemistry, since, as mentioned earlier, $\text{F}_2\text{C}=\text{CFBr}$ reacts with $(\text{Pd}(\text{PPh}_3)_4)$ to give the vinyl species

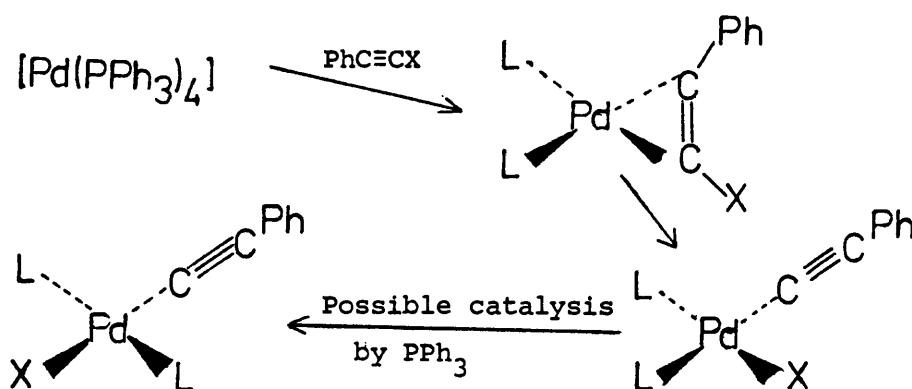


Figure 3.2

$(\text{PdBr}(\text{FC}=\text{CF}_2)(\text{PPh}_3)_2)$ directly⁷, whereas reaction with $(\text{Pt}(\text{PPh}_3)_4)$ leads to the olefin complex $(\text{Pt}(\text{PPh}_3)_2(\text{F}_2\text{C}=\text{CFBr}))$, which is only isomerised to a vinyl on refluxing in n-butanol³.

(ii) Phenyliodoacetylene

This acetylene does not give an acetylide complex on reaction with $(\text{Pd}(\text{PPh}_3)_4)$ in ether, but rather, the known compound trans- $(\text{PdI}_2(\text{PPh}_3)_2)$, identified by comparison with an authentic sample. The reason for the formation of this compound, rather than an acetylide complex, may lie in the higher affinity of palladium for I^- than for Br^- or Cl^- , which may prevent formation of a palladium-carbon bond as would occur in a metal-acetylide product. Platinum, however, does form an acetylide complex with phenyliodoacetylene, this probably being a reflection of the greater strength of the Pt-C bond, and the greater ability of platinum to π -bond to the acetylide, compared with palladium.

3.3 Rhodium

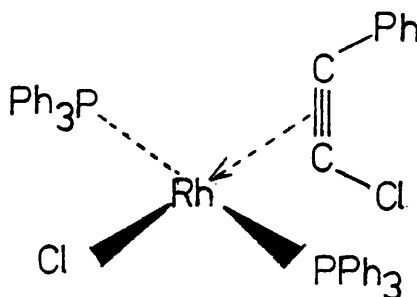
Reactions were carried out using the well known "Wilkinson's catalyst" ($\text{RhCl}(\text{PPh}_3)_3$); monoacetylene complexes of this compound involving displacement of one triphenylphosphine ligand by an acetylene molecule, are quite well known, and are discussed in Section 1.2.

(i) Phenylchloroacetylene

Reaction of a benzene solution of ($\text{RhCl}(\text{PPh}_3)_3$) with phenylchloroacetylene resulted in a change in colour from deep red to bright orange, over a period of one hour. Concentration of this solution, followed by addition of ether, gave an orange solid: it was found, however, that the compound could be obtained in a purer form by stirring the reactants in the dark, in ether suspension, for approximately 24 hours. This solid is air-stable, but undergoes decomposition by light, resulting in a brownish product having i.r. bands at 1883, 1968 and 2125cm^{-1} , suggesting partial isomerisation to an acetylide complex, although the significance of the absorption at 1968cm^{-1} is not clear.

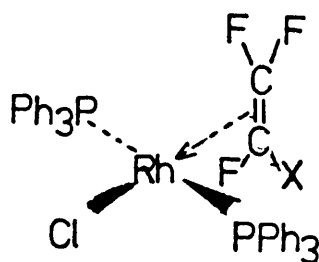
The i.r. spectrum of the orange solid shows a medium intensity band at 1883cm^{-1} , in the region commonly associated with π -bonded acetylene ligands; it also has an absorption due to Rh-Cl stretching at 289cm^{-1} . These observations, combined with analytical data, suggest that the compound is 3.4.

(3.4)



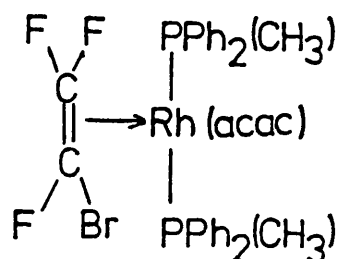
trans geometry is proposed by analogy with the olefin complex $(\text{RhCl}(\text{PPh}_3)_2(\text{F}_2\text{C}=\text{CF}_2))$, which has been shown to be trans by X-ray crystallography³⁴.

Halo-olefin complexes of rhodium(I) are not as well known as those of platinum(0), although (3.5a,b,c) and (3.6) have been made^{8,9,10}. No isomerisation processes have been noted for any of these species.



(3.5)

a) X=F b) X=Cl c) X=Br



(3.6)

It was found, however, that warming a suspension of $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ in methanol at 40°C , for 12 hours, in the dark, caused a change in colour of the solid from bright-orange to dark-orange. The i.r. spectrum of the product has a very weak band at 2125cm^{-1} , which suggests the presence of an acetylide group: in addition, the band due to the π -bonded acetylene at 1883cm^{-1} is no longer present, and the Rh-Cl stretch has moved up to 309cm^{-1} , consistent with a change in oxidation-state to rhodium(III).

It appears, therefore, that the compound has undergone isomerisation, with oxidative-addition, to give a rhodium(III)-acetylide. Unfortunately, analytical data consistent with the most probable formulation, $(\text{RhCl}_2(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, could not be obtained; nor could the data be fitted to any other structure in agreement with the i.r. spectrum. Difficulty in obtaining analytically pure samples

of both rhodium(I) and rhodium(III)-acetylides has been noted before in the literature³⁵; in the case of $(\text{RhCl}_2(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, the analytical impurity may in part be due to the compound being formulated as a five-coordinate rhodium(III) complex. Rhodium(III) is almost invariably octahedral, and although the crystal-structure of a five-coordinate complex, $(\text{RhI}_2(\text{CH}_3)(\text{PPh}_3)_2)$, has been obtained³⁶, and shown it to be a square-based pyramid, the series of dihydrido-complexes $(\text{RhXH}_2(\text{PPh}_3)_2)$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)³⁷ appear to contain a solvent molecule in the sixth position in solution, and also to contain some coordinated solvent in the solid state (in the case of dichloromethane, a dimeric species containing bridging dichloromethane can be isolated). Other pentacoordinate rhodium(III) compounds having coordinated solvent molecules include $(\text{RhClH}(\text{SiCl}_2\text{X})(\text{PPh}_3)_2)$ ($\text{X} = \text{Cl}, \text{CH}_3$)³⁸, and $(\text{RhClH}(\text{GeR}_3)(\text{EPh}_3)_2)$ ($\text{E} = \text{P or As}; \text{R} = \text{CH}_3, \text{C}_2\text{H}_5 \text{ or Cl}$)³⁹. For these latter complexes, in several cases only low analytical purity was observed.

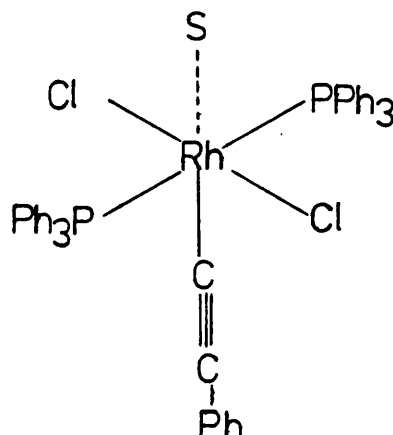
Thus it seems probable that the compound obtained after warming $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ in methanol is the impure pentacoordinate rhodium(III)-acetylide, partially solvated by methanol in the sixth position. The presence of only one rhodium-chloride stretching frequency in the i.r. spectrum of this compound suggests that the chlorine atoms are mutually trans, and it seems probable that the phosphine ligands will remain trans, so that (3.7) is the likely structure adopted by the compound. The presence of the acetylide group in the apical position is also suggested by the occupation of such a position by the methyl group in $(\text{RhI}_2(\text{CH}_3)(\text{PPh}_3)_2)$ ³⁶.

(ii) Phenylbromoacetylene and phenyliodoacetylene

Reaction of phenylbromoacetylene with $(\text{RhCl}(\text{PPh}_3)_2)$ in ether suspension, in the dark, resulted, after 24 hours, in a dark-orange solid, rather than a bright orange product as was obtained from

S=solvent

(3.7)



phenylchloroacetylene. Examination of the i.r. spectrum indicates that this is an acetylide complex, there being a band at 2125cm^{-1} , and no bands in the region $1600 - 2000\text{cm}^{-1}$: the Rh-Cl stretch is at 320cm^{-1} , as expected for a rhodium(III) complex.

It seems, therefore, that this compound is $(\text{RhBrCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, analogous to the product obtained from isomerisation of $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$, and that no π -bonded product can be isolated using phenylbromoacetylene. This is in keeping with the results obtained for the platinum system, and is due to similar factors (see Section 3.1): the formation of an intermediate $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CBr}))$ which rapidly isomerises to the rhodium-acetylide species, is the likely course followed by this reaction.

Analytical data for this complex are, as with the chloro-derivative, not consistent with a pentacoordinate rhodium(III) complex. This may be due, in part, to decomposition of the potentially unstable compound, and may also be caused by the presence of solvent in the sixth coordination-site. In the case of phenyliodoacetylene, a chocolate-brown solid, having an acetylide i.r. absorption at 2120cm^{-1} , was obtained, but again satisfactory microanalytical data could not be obtained.

Attempts to obtain purer compounds, by using other reaction

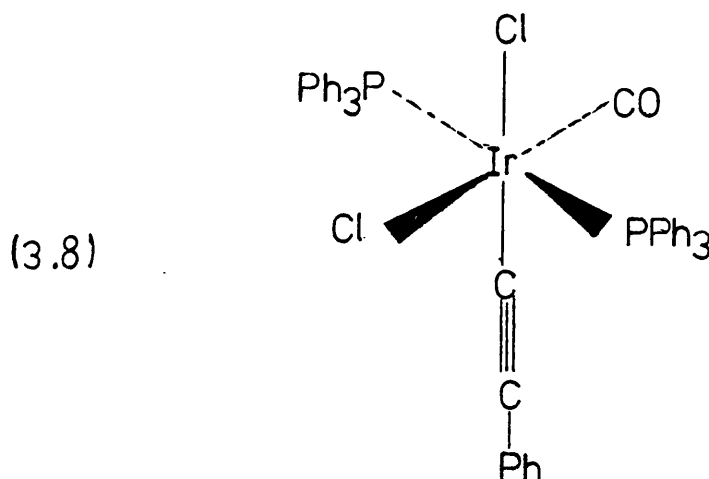
methods (e.g. reactions in chloroform, acetone, or benzene solution, and also mixing hot benzene solutions of the reactants, followed by boiling for two minutes and then cooling⁴⁰) all gave compounds which could be identified as acetylides on the basis of their i.r. spectra, but which did not analyse accurately for five-coordinate species. It does, therefore, seem likely that the instability of pentacoordinate rhodium(III) is playing an important part in these reactions, and in view of this it would be interesting to try some isomerisation reactions leading to octahedral rhodium(III)-acetylides, since in such reactions the possibility of decomposition or solvent-coordination would be considerably less.

3.4 Iridium

An investigation was made of the reactions of "Vaska's complex", $\text{trans}-(\text{IrCl}(\text{CO})(\text{PPh}_3)_2)$, since π -bonded acetylene complexes of this compound are well known (see Section 1.3), and oxidative-addition - the other process likely to occur with the acetylenes being used - has also been the subject of several studies involving "Vaska's complex", e.g.^{41 - 43}.

(i) Phenylchloroacetylene, phenylbromoacetylene and phenyliodoacetylene.

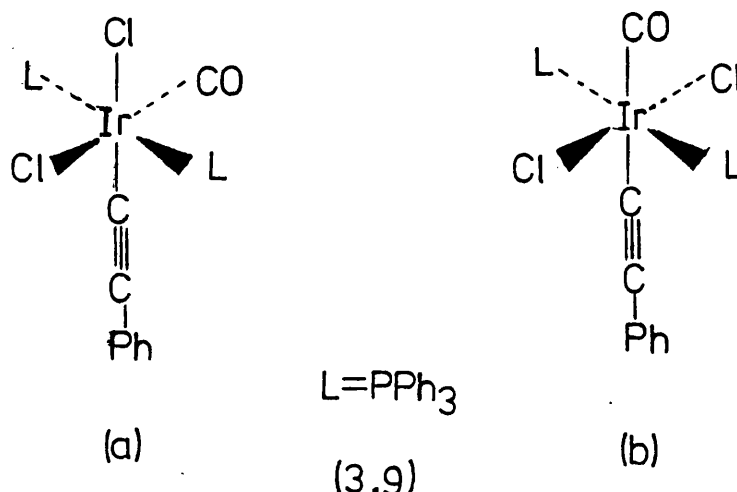
Stirring a solution of $\text{trans}-(\text{IrCl}(\text{CO})(\text{PPh}_3)_2)$ with phenylchloroacetylene in benzene for several hours resulted in the separation of a white precipitate. Reaction was probably complete in 48 hours, but was continued for a further 48 hours, whereupon the solid was examined. The infra-red spectrum shows the disappearance of the band at 1960cm^{-1} due to the carbonyl group of the starting material, and the appearance of a strong band at 2070cm^{-1} and a medium intensity band at 2142cm^{-1} . The iridium-chlorine region of the spectrum has two absorptions at 312 and 285cm^{-1} . Analytical data are consistent with a 1:1 addition product of the iridium complex and the acetylene. From this evidence it is apparent that the product of the reaction is the iridium(III)-acetylide compound (3.8).



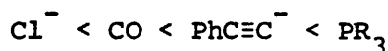
The strong i.r. absorption at 2070cm^{-1} is characteristic of a carbonyl group bonded to iridium(III), the shift to higher energy relative to the position in iridium(I) being due to a decrease in metal-ligand back-bonding. The acetylide absorption is at 2142cm^{-1} and correlates well with other iridium(III)-acetylides⁴⁴. The stereochemistry of the product is revealed by an examination of the iridium-chlorine stretching frequencies. Jenkins and Shaw⁴⁵ have shown that these stretching frequencies depend largely on the ligand trans to the chlorine, and are largely independent of the cis ligands. This work was followed by an investigation by Collman and Sears⁴⁶, based on ^1H n.m.r. and examination of iridium-chlorine stretching frequencies, into the mode of oxidative addition to "Vaska's complex", during which they assigned absorptions at $\sim 310\text{cm}^{-1}$ to iridium-chlorine bonds trans to carbonyl groups. The iridium-chlorine stretch in "Vaska's complex" itself is at 317cm^{-1} , which is higher than the values for iridium-chlorine bonds having trans phosphines⁴⁵, where the absorptions are in the region $262\text{--}278\text{cm}^{-1}$. This is in agreement with the order of trans-influence established using, as an indicator, platinum-chlorine stretching frequencies in trans-(PtXClL₂) complexes²⁵.

It has been established, by ^1H n.m.r. studies, that the phosphine ligands in trans-(IrCl(CO)(PPh₂(CH₃))₂) always remain trans during oxidative-addition reactions⁴⁶, and by analogy one would expect this to be the case when the phosphine is the triphenyl derivative. For the reaction under consideration - i.e. with phenylchloroacetylene - the product can therefore have two possible geometries (3.9a and b).

Structure (3.9b), having mutually trans chlorines, should have one iridium-chlorine stretching frequency⁴⁶, probably around 330cm^{-1} . This is not observed, but instead two bands, at 312cm^{-1} and 285cm^{-1} are seen: the former may be assigned to chlorine trans to a carbonyl



group, and the latter to chlorine trans to the acetylide group. The structure is therefore (3.9a), although this does not reveal whether the mode of addition is cis or trans. These values for the iridium-chlorine stretching frequencies suggest, by comparison with values obtained by Collman and Sears⁴⁶, and by Jenkins and Shaw⁴⁵, that the position of phenylacetylide in the trans-influence series is (order of increasing influence):



Although this order is slightly different from that obtained using platinum-chlorine stretching frequencies as an indicator (Section 3.1), the position of phenylacetylide is seen to be essentially the same.

Further information is revealed by the reactions of phenylbromoacetylene and phenyliodoacetylene, both of which give iridium(III)-acetylide complexes analogous to (3.8). Relevant i.r. data for all three compounds are shown in Table 3.1.

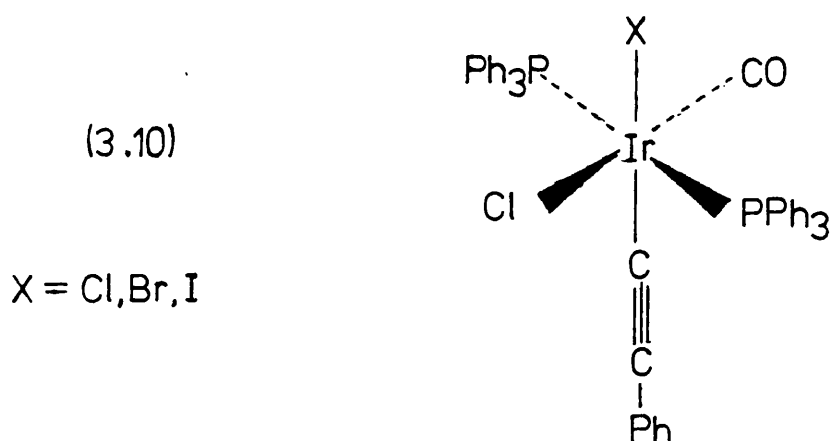
The bands at 300cm^{-1} (X = Br) and 309cm^{-1} (X = I) can be assigned to iridium-chlorine bonds trans to a carbonyl group, so it becomes apparent that the acetylenes are adding across the square-plane - i.e. trans addition, to give compounds (3.10). This mode of addition has also been found to be favoured by several alkyl

Table 3.1 Infra-red^a data for the compounds (IrClX(C≡CPh)(CO)(PPh₃)₂)
(X = Cl, Br, I)

<u>Compound</u>	<u>$\nu(\text{CO}) \text{ cm}^{-1}$</u>	<u>$\nu(\text{C}\equiv\text{C}) \text{ cm}^{-1}$</u>	<u>$\nu(\text{Ir}-\text{Cl}) \text{ cm}^{-1}$</u>
(IrCl ₂ (C≡CPh)(CO)(PPh ₃) ₂)	2070	2142	312, 285
(IrBrCl(C≡CPh)(CO)(PPh ₃) ₂)	2070	2140	300
(IrClI(C≡CPh)(CO)(PPh ₃) ₂)	2070	2140	309

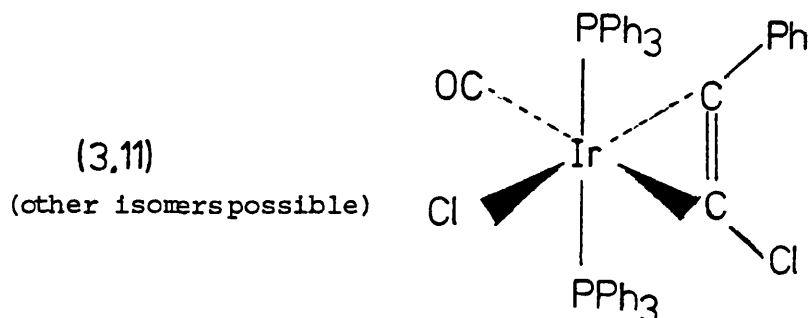
^a Measured as Nujol mulls, on CsI plates, and recorded on a Perkin-Elmer Model 580 grating spectrophotometer.

halides and acetyl halides and by halogens themselves⁴⁶, whereas the geometry of hydrogen-halide addition has been found to be solvent dependent⁴⁷.



It is interesting that phenylchloroacetylene fails to give an acetylene compound with "Vaska's complex", but does give one with (RhCl(PPh₃)₃). Octahedral iridium(III) is a very stable state, however, and will encourage isomerisation of any intermediate iridium(I)-acetylene complexes formed. Further, oxidative addition to trans-(IrCl(CO)(PPh₃)₂) is known in many cases, to be an S_N² process, involving nucleophilic attack by the electron-rich metal centre on the incoming group^{41,42}. For this type of reaction an iridium(I) centre should be more reactive than rhodium(I), since it is more nucleophilic, and indeed iridium(I) is found to be more susceptible to oxidative addition than rhodium(I)⁴⁸.

An interesting observation was made if the reaction with phenylchloroacetylene was stopped after twelve hours, before any precipitation had occurred. Removal of the solvent gave a yellow solid, the i.r. spectrum of which showed bands due to the iridium(III)-acetylide complex at 2142 and 2070cm^{-1} , but in addition, strong absorptions at 1964 and 1700cm^{-1} . The former band is due to a carbonyl group attached to iridium(I), whilst the latter is a typical value for the triple-bond of an acetylene π -bonded to iridium(I)⁴⁴. This result confirms the belief that an intermediate in the formation of the acetylide compound is a π -bonded complex (3.11) although attempts to isolate (3.11) by crystallisation or chromatography resulted only in complete isomerisation through to the acetylide.



A similar mechanism - i.e. coordination of the acetylene, followed by rapid isomerisation - almost certainly operates in the reactions of "Vaska's complex" with the ligands $\text{HC}\equiv\text{CCR}_2\text{Cl}$ which oxidatively add to give σ -allenyl complexes⁴⁹.

3.5 Summary

Prior to this investigation, very little work had been carried out on the reactions of haloacetylenes with transition metal complexes. The analogous halo-olefin reactions had, however, been the subject of a considerable amount of study, which had shown the principal products of the reactions to be metal-olefin or metal-vinyl complexes.

In the case of phenylhaloacetylenes, it has been possible to isolate only two π -complexes - $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ and $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$. Most of the other reactions carried out give metal-acetylide complexes, the stereochemistries of which have been investigated, largely using i.r. spectroscopy. Suggestions have been put forward as to the mechanisms of formation of the various products, and this aspect is also the subject of Chapter 4.

3.6 Experimental

This section is subdivided according to the metal complex involved, and then further divided for reaction with the appropriate acetylene. Melting points are given for all compounds, and analytical data and infra-red spectra are presented for all new complexes, as well as for some which have been made before, but whose structures have previously been in doubt.

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

Infra-red spectra were recorded on a Perkin Elmer 580 spectrophotometer, using Nujol mulls, between CsI plates, and were calibrated using a polystyrene film. Values quoted are in cm^{-1} .

Microanalytical data were obtained by D Butterworth, The Butterworth Microanalytical Consultancy Ltd., 41 High Street, Teddington, Middlesex, or by C H N Analysis Ltd., Alpha House, South Wigston, Leicester.

Solvents

Analar benzene and diethyl ether were dried by standing over sodium wire, and were filtered before use. They were then 'pump-freeze' degassed under high vacuum before use.

All other solvents used were normal reagent grade, and were used without further purification, unless otherwise stated.

Ligand and reagents

The following materials were purchased:

- Triphenylphosphine - British Drug Houses
- Trans-stilbene - Koch-Light Laboratories Ltd
- Hydrazine hydrate - British Drug Houses
- Phenylacetylene - Ralph N Emmanuel Ltd
- 1,2-bis(diphenylphosphino)ethane
- British Drug Houses.

Palladium dichloride, potassium tetrachloroplatinite, hydrated

rhodium trichloride, and iridium trichloride trihydrate were obtained on loan from Johnson Matthey Ltd.

The following were prepared by literature methods:

cis-dichlorobis(triphenylphosphine)platinum(II)⁵⁰
bis(triphenylphosphine)trans-stilbene platinum(O)⁵¹
tetrakis(triphenylphosphine)palladium(O)⁵²
trans-chloro(carbonyl)bis(triphenylphosphine)iridium(I)⁴⁴
chlorotris(triphenylphosphine)rhodium(I)³⁷
dichloro-1,2-bis(diphenylphosphino)ethaneplatinum(II)⁵³
phenylbromoacetylene⁵⁴
phenylchloroacetylene⁵⁵
phenyliodoacetylene⁵⁶

A Reactions of phenylhaloacetylenes with $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$

i Phenylchloroacetylene in benzene

0.3g (0.33mmol) of $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ and 0.05g (0.36mmol) of phenylchloroacetylene were stirred in benzene solution at room temperature under an atmosphere of dry nitrogen. After 24 hours, the solution was reduced to small volume under partial vacuum, and diethyl ether was then added. The resulting pale yellow solid was collected, dried in vacuo, and identified as the known compound trans- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, by infra-red spectroscopy. Yield 0.15g, 53%. M. Pt. 228 -232°C (previously reported¹⁷ as 212-214°C).

Infra-red 2125s 1593m 1572w 1569w 1480s 1434s 1315m 1286w 1218w 1193w 1185w 1161w 1119w 1101s 1095s 1069w 1031m 1004m 1000m 972vw 922w 906w 849w 755s 745s 708s 693vs 619w 571w 549w 541w 525s 514s 508s,sh 501s 493m,sh 444vw 428m 320m. (i.r. reported to aid comparison with other platinum complexes.)

ii Phenylbromoacetylene in benzene

Repetition of the above method, using 0.3g (0.33mmol) of $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ and 0.12g (0.66mmol) of phenylbromoacetylene gave the known compound trans- $(\text{PtBr}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$. Yield = 0.17g, 58% M. Pt. 225°C (decomp.)

Infra-red 2130w 2125w 1591w 1572vw 1566vw 1471m 1434s 1314w,br 1272w 1265vw 1212vw 1171w 1159w 1099m 1072w 1028w 999w 920vw 757m 746s 732m 709m 692s 667vw 524s 512m 500m 461w 437w 427w.

iii Phenyliodoacetylene in benzene

Repetition of the method using 0.3g (0.33mmol) of $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ and 0.089g (0.35mmol) of phenyliodoacetylene, gave pale yellow trans- $(\text{PtI}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, which was recrystallised from dichloromethane/methanol. Yield = 0.13g, 42%

M. Pt. 214-220°C (decomp.)

Analysis Calculated: C, 55.8; H, 3.7%

Found: C, 55.8; H, 4.0%

Infra-red 2125w 1587w 1573w 1566w 1469s 1433s 1209vw 1161w 1155w
1095m 1070w 1063vw 1028w 996w 972w,br 842vw 769vw 755m 743s
722w 705m 688s 665w 616w 522s 510s 499s 457m 425m.

iv Phenylchloroacetylene in diethyl ether

0.3g (0.33mmol) of $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ and 0.05g (0.36mmol) of phenylchloroacetylene were stirred together as a suspension in diethyl ether at room temperature for 30 hours under an atmosphere of dry nitrogen. The resulting white precipitate was collected by filtration, washed with ether, and dried in vacuo. The compound was identified as cis- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ by infra-red spectroscopy and analytical data. Yield = 0.24g, 84%

Analysis Calculated: C, 61.8; H, 4.1%

Found: C, 61.8; H, 4.2%

Infra-red 2125m 1596w 1587w 1437w 1432m 1311w 1218w 1186w 1158w
1098s 1091m,sh 1071w 1026m 1000m 850w 802vw 763m 755s 741s 725w
706m,sh 689s 666vw 617w 564w 544s 526s 513m,sh 510s 496s 467m
439w 426m 306m.

Attempted recrystallisation from dichloromethane/methanol gave a yellow solid, which could also be obtained by stirring the compound around in methanol. Purification of the yellow solid by preparative T.L.C. (eluent = chloroform: petroleum ether (B. Pt. 40-60°C), 3:2; adsorbent = activated alumina) gave trans- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, identified by comparison with an authentic sample, and by its i.r. spectrum, and a yellow solid, tentatively formulated as either cis- $(\text{PtCl}(\text{HC}=\text{C}(\text{OCH}_3)\text{Ph})(\text{PPh}_3)_2)$, or cis- $(\text{PtCl}(\text{CH}_3\text{OC}=\text{CHPh})(\text{PPh}_3)_2)$.

M. Pt. 263-266°C (decomp.)

Analysis Calculated: C, 60.8; H, 4.4%

Found: C, 61.6, H, 4.3%

Infra-red 1587w 1573w 1481m 1435s 1202w 1186w 1159w 1097m 1020w
998w 763m,sh 747m 740m 724w 706m,sh 696s,sh 692s 670w 618w 573w
543m 523s 516s 500m 425w 295w.

v Phenylbromoacetylene in diethyl ether

Repetition of the above method, using 0.3g (0.33mmol)

(Pt(PPh₃)₂(trans-stilbene)) and 0.08g (0.44mmol) of phenylbromoacetylene gave, after 4 hours, a white precipitate of cis-(PtBr(C≡CPh)(PPh₃)₂), identified by i.r. spectroscopy and analytical data. Yield = 0.21g, 71%.

M. Pt. 223-224°C

Analysis Calculated: C, 58.7; H, 3.9%

Found: C, 57.9; H, 4.2%

Infra-red 2125m 1595w 1586w 1570w,br 1485s 1480s 1432s 1312w
1217w 1186w 1158w 1098s 1091s 1069w 1026m 997m 970vw 920vw
904vw 848vw 843w 801vw 761m,sh 753s 740s 704s 690vs 617w 561w
541s 523vs 511s 496s 465w 456w 439w 425m.

An attempt to recrystallise this compound from dichloromethane/methanol resulted only in isomerisation to trans-(PtBr(C≡CPh)(PPh₃)₂), which was also obtained when the cis isomer was stirred in benzene solution for 48 hours.

vi Phenyliodoacetylene in diethyl ether

Repetition of the method using 0.3g (0.33mmol) of

(Pt(PPh₃)₂(trans-stilbene)) and 0.08g (0.35mmol) of phenyliodoacetylene, gave, after 24 hours, a pale yellow precipitate of cis-(PtI(C≡CPh)(PPh₃)₂). Yield = 0.21g, 67%

M. Pt. 224-229°C (decomp.)

Analysis Calculated: C, 55.7; H, 3.7%

Found: C, 55.7; H, 3.8%

Infra-red 2125m 1594w 1586w 1571w 1469s 1432s 1210vw 1185vw
1176vw 1161vw 1155w 1120vw 1099m 1095m,sh 1070vw 1028vw 997w
844vw 756m 743s 705m 690s 617vw 540m 524s 513s 498m 460w 426w.

An attempt to recrystallise this compound from dichloromethane/
methanol resulted only in the isolation of trans-(PtI(C≡CPh)(PPh₃)₂),
which was also obtained when the cis-isomer was stirred in benzene
solution for 48 hours.

B Reactions of phenylhaloacetylenes with cis-(PtCl₂(PPh₃)₂) and hydrazine hydrate

i Phenylchloroacetylene

0.25g (0.28mmol) of cis-(PtCl₂(PPh₃)₂) was suspended in ethanol
(5cm³) and treated with hydrazine hydrate (0.25cm³). After stirring
for 5 minutes the yellow solution was filtered, and 0.06g (0.56mmol)
of phenylchloroacetylene was added to the solution. After warming to
60°C for 5 minutes, crystallisation began to occur, and the mixture was
then cooled to 0°C. The pale yellow crystals were filtered, washed with
water, ethanol and ether, and dried in vacuo. The compound was identified
as (Pt(PPh₃)₂(PhC≡CCl)) by its infra-red spectrum and analytical data.
Yield = 0.16g, 65%.

M. Pt. 225--27°C (decomp.)

Analysis Calculated: C, 61.8; H, 4.1; Cl, 4.1%

Found: C, 61.5; H, 3.8; Cl, 4.3%

Infra-red 1698m 1592m 1572w 1479s 1437s 1310w 1207w 1173vw 1168vw
1158w 1100s 1073w 1030m 1002m 974w 852vw 754m,sh 746s 725w 694s
676w 621vw 555vw 543s 526s 512s 503s 461w 441w 426w.

On heating a suspension of (Pt(PPh₃)₂(PhC≡CCl)) in methanol at 35°C

for 24 hours, a white solid was obtained. This was filtered, washed with ether, and identified as trans-(PtCl(C≡CPh)(PPh₃)₂) from its infra-red spectrum and melting point. This isomerisation also occurred on stirring the acetylene complex in benzene solution for several days.

ii Phenylbromoacetylene

Repetition of the above method, using 0.2g (0.25mmol) of cis-(PtCl₂(PPh₃)₂), 0.2cm³ of hydrazine hydrate and 0.08g (0.50mmol) of phenylbromoacetylene, yielded, after warming to 60°C for 15 minutes followed by cooling to 0°C, pale yellow crystals of trans-(PtBr(C≡CPh)(PPh₃)₂), identified by its infra-red spectrum and melting point. Yield = 0.13g, 64%.

iii Phenyliodoacetylene

Repetition of the method, using 0.25g (0.28mmol) of cis-(PtCl₂(PPh₃)₂), 0.25cm³ of hydrazine hydrate and 0.12g (0.56mmol) of phenyliodoacetylene gave, after warming to 60°C for 5 minutes, followed by cooling in ice, pale yellow crystals of trans-(PtI(C≡CPh)(PPh₃)₂), identified by its infra-red spectrum and melting point. Yield = 0.19g, 71%.

C Reactions of phenylchloroacetylene with (PtCl₂(diphos)) and sodium borohydride in ethanol (diphos = Ph₂PCH₂CH₂PPh₂).

0.33g (0.5mmol) of (PtCl₂(diphos)) was suspended in degassed ethanol with 0.14g (1.0mmol) of phenylchloroacetylene. 0.13g (3.4mmol) of sodium borohydride dissolved in degassed ethanol was added with stirring, and the mixture was then stirred at room temperature, for 20 hours, under an atmosphere of dry nitrogen. The resulting cream coloured solid was filtered, washed with water and ethanol, and then recrystallised from dichloromethane/methanol, to give grey-white (Pt(diphos)(PhC≡CCl)), which was dried in vacuo. Yield = 0.24g, 66%.

M. Pt. 148-153°C (decomp).

Analysis Calculated: C, 55.9; H, 4.0%

Found: C, 55.8; H, 4.2%

Infra-red 1667m 1596w 1588w 1572w 1434s 1308vw 1299vw 1187vw
1159w 1105s 1070w 1029w 1000w 976w,br 921vw 909vw 848vw 823m
813m 751m 718m 707s 694s 679m,sh 636w 616w 532s 525s,sh
491m 446w.

Heating a suspension of (Pt(diphs)(PhC≡CCl)) in methanol at 35°C for 16 hours resulted only in the recovery of the unreacted complex. The solution contained a small amount of a yellow-brown powder, having no absorptions in its infra-red spectrum above 1600cm⁻¹, but bands due to phosphine ligands at 720m, 706m, 694s and 533s.

D Reactions of phenylhaloacetylenes with (Pd(PPh₃)₄)

i Phenylchloroacetylene

0.38g (0.33mmol) of (Pd(PPh₃)₄) and an excess of phenylchloroacetylene were stirred together as a suspension in diethyl ether, at room temperature, under an atmosphere of dry nitrogen. After 24 hours, the pale yellow solid was filtered, washed with ether, and dried under vacuum.

Yield = 0.20g, 80%. Infra-red spectroscopy and analytical data identified the complex as trans-(PdCl(C≡CPh)(PPh₃)₂).

M. Pt. 149-157°C (decomp.)

Analysis Calculated: C, 68.8; H, 4.6%

Found: C, 68.5; H, 4.7%

Infra-red 2125m 1595m 1589m 1569m 1478s 1434s 1310w 1280w 1211w
1185w,br 1160w 1092s 1066w 1027m 1000m 970w 922w 906w 849m 756s
743s 695vs,br 622w 526s 513s 501s 495s,sh 456m 440vw 426m 331m.

ii Phenylbromoacetylene

Repetition of the above reaction, using 0.4g (0.35mmol) of

$(\text{Pd}(\text{PPh}_3)_4)$ and an excess of phenylbromoacetylene, gave a yellow solid, identified as trans- $(\text{PdBr}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ by its infra-red spectrum and analytical data. Yield = 0.26g, 85%.

M. Pt. 157-162°C (decomp.)

Analysis Calculated: C, 65.1; H, 4.3%

Found: C, 64.7; H, 4.4%

Infra-red 2120w 1594w 1586w 1571w 1478s 1433s 1312vw,br 1269vw
1211w 1191w 1183vw 1175vw 1159w 1099s 1091s 1068w 1027m 1000m
969vw 919w 904w 844w 797vw 752s 741s 703s 691vs 618w 561vw
522s 508s 496s 489s,sh 454m 435w 425m.

Stirring this compound in benzene solution, at room temperature, under an atmosphere of dry nitrogen, resulted in a colour change from yellow to brown. Removal of the solvent, followed by addition of diethyl ether, gave a brown solid, which was filtered and dried in vacuo. The i.r. spectrum of this solid is identical with that of the starting material, suggesting that some decomposition, but no isomerisation, has occurred.

iii: Phenyliodoacetylene

Repetition of the reaction using 0.38g (0.33mmol) of $(\text{Pd}(\text{PPh}_3)_4)$ and excess phenyliodoacetylene gave the known compound trans- $(\text{PdI}_2(\text{PPh}_3)_2)$, identified by its infra-red spectrum. Yield = 0.27g, 90%.

E Reactions of phenylhaloacetylenes with $(\text{RhCl}(\text{PPh}_3)_3)$

i Phenylchloroacetylene

0.46g (0.50mmol) of $(\text{RhCl}(\text{PPh}_3)_3)$ and an excess of phenylchloroacetylene were stirred together as a suspension in diethyl ether, in the dark, at room temperature, under an atmosphere of dry nitrogen, for 24 hours. The resulting bright orange product was filtered, washed with ether, and dried in vacuo. Infra-red spectroscopy and analytical data identified the compound as $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$. Yield = 0.37g, 93%. The compound

is fairly light-sensitive, but even in the dark decomposition starts to occur after 7 days.

M. Pt. 149-154°C (decomp.)

Analysis Calculated: C, 66.0; H, 4.4%

Found: C, 66.1; H, 4.6%

Infra-red 1883m 1588m 1572w 1565w,sh 1479s 1438s,sh 1433s 1310w
1185m 1163w 1158w 1097s 1072m 1029m 1025w,sh 999m 974w,br 928vw
919vw 839m 816vw 762s 753m,sh 744s 707s 693vs 671m,sh 625w
583m 547w 519vs 513s,sh 498s 457w 437w 430w 414m 346vw 321m
289m.

On heating a suspension of $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ in methanol at 40°C for 12 hours in the dark, the solution darkened considerably, and the solid changed from bright orange to dark orange. It was filtered, washed with ether, and dried in vacuo. The infra-red spectrum suggests that this is an acetylide complex.

M. Pt. 99-102°C (decomp.)

Analysis for $(\text{RhCl}_2(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$

Calculated: C, 66.1; H, 4.4%

Found: C, 60.1; H, 4.8%

Infra-red 2125vw 1588w 1573w 1437m 1312w 1181m,br 1173m,br
1159m 1120m 1093s 1073w 1030w 1000w 850w 747m 742m 725s 694vs
619w 544vs 529s 517s 496m 459w 443w 429w 309w.

ii Phenylbromoacetylene .

0.46g (0.50mmol) of $(\text{RhCl}(\text{PPh}_3)_3)$ was stirred with 0.12g (0.75mmol) of phenylbromoacetylene as a suspension in diethyl ether in the dark, at room temperature, under an atmosphere of dry nitrogen, for 24 hours. The dark orange solid was filtered, washed with diethyl ether, and dried in vacuo. The infra-red spectrum suggests that this is an acetylide complex. Yield = 0.24g.

M. Pt. 152-155°C (decomp.)

Analysis for $(\text{RhBrCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$

Calculated: C, 62.6; H, 4.2%

Found: C, 58.9; H, 4.2%

Infra-red 2125m 1588w 1572w 1479s 1433s 1186w 1155w 1092s 1069vw
1028w 996m 847w,br 746s 739s 721w 704s 692s 665vw 540w,sh 518s
511s,br 455m 431w 320w,br.

iii Phenyliodoacetylene

0.46g (0.5mmol) of $(\text{RhCl}(\text{PPh}_3)_3)$ suspended in diethyl ether was stirred with 0.17g (0.175mmol) of phenyliodoacetylene, at room temperature in the dark, under an atmosphere of dry nitrogen. After 24 hours, the chocolate-brown precipitate was filtered, washed with ether, and dried in vacuo. Yield = 0.32g. The i.r. spectrum revealed an acetylide absorption at 2120cm^{-1} , but analytical data consistent with the most probable formulation $(\text{RhClI}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ could not be obtained.

F Reactions of phenylhaloacetylenes with $\text{trans}-(\text{IrCl}(\text{CO})(\text{PPh}_3)_2)$

i Phenylchloroacetylene

0.26g (0.33mmol) of trans- $(\text{IrCl}(\text{CO})(\text{PPh}_3)_2)$ and 0.05g (0.36mmol) of phenylchloroacetylene were mixed together in benzene, at room temperature, under an atmosphere of dry nitrogen. The solution was stirred for several hours, whereupon a white precipitate began to be formed. After 4 days, precipitation was judged to be complete. The solid was collected, washed with a small amount of benzene, and recrystallised from dichloromethane/benzene to yield grey-white microcrystals of a compound, which was identified as $(\text{IrCl}_2(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)_2)$ from infra-red and analytical data. Yield = 0.18g, 59%.

M. Pt. 252-255°C (decomp.)

Analysis Calculated: C, 58.9; H, 3.8%

Found: C, 59.3; H, 3.9%

Infra-red 2142m 2070s 1594w 1587vw 1574w 1482s 1440s 1434s
1215vw 1191m 1169vw 1160vw 1104m 1099m,sh 1095s 1091s 1073w
1035w 1028w 1000m 762m 753m 743m 711m 702m 696s 688m,sh 671vs
618vw 565m 536w,sh 525s 517s 505s 461m 453vw 440w 426vw 312w
285w,br.

When the above reaction was stopped after 12 hours, removal of the benzene solvent gave a yellow solid, the infra-red spectrum of which has bands at 2142m, 2070s, 1964s and 1700s, suggesting that it is probably a mixture of $(\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ and $(\text{IrCl}_2(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)_2)$. Attempts to purify this mixture by recrystallisation or column chromatography, resulted only in isolation of the acetylide complex.

ii Phenylbromoacetylene

Repetition of the above reaction, using 0.26g (0.33mmol) of trans- $(\text{IrCl}(\text{CO})(\text{PPh}_3)_2)$ and 0.08g (0.44mmol) of phenylbromoacetylene yielded, after recrystallisation from dichloromethane/benzene, white crystals of $(\text{IrBrCl}(\text{C}\equiv\text{CPh})(\text{CO})(\text{PPh}_3)_2)$, identified by infra-red and analytical data. Yield = 0.16g, 51%.

M. Pt. 243-246°C (decomp.)

Analysis Calculated: C, 56.2; H, 3.7%

Found: C, 56.3; H 3.9%

Infra-red 2140m 2070s 1594w 1587w 1574w 1472s 1436s 1191w 1163vw
1096m,sh 1091m 1072vw 1028w 998w 761m 753m 746vw 741m 705m 692s
671s 617vw 563m 556w 522s 514s 503m 459w 300w.

iii Phenyliodoacetylene

Repetition of the reaction using 0.26g (0.33mmol) of

trans-(IrCl(CO)(PPh₃)₂) and 0.08g (0.35mmol) of phenyliodoacetylene gave, after recrystallisation from dichloromethane/benzene, grey-white crystals of (IrClI(C≡CPh)(CO)(PPh₃)₂), identified by infra-red and analytical data. Yield = 0.23g, 69%.

M. Pt. 158-160°C (decomp.)

Analysis Calculated: C, 53.5; H, 3.6%

Found: C, 52.2; H, 3.4%

Infra-red 2140m 2070s 1586w 1572w 1478s 1434s 1315w 1190w 1159vw
1098m,sh 1089m 1071w 1027w 1001m 764m 754m 746m 711s 706vw 699s
684s 568m 556m 526s 521s 507m 463m 438w 423w 309w.

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CHAPTER 4

A KINETIC STUDY OF THE ISOMERISATION REACTIONS OF

$(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ TO $\text{trans}-(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, AND OF

$(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ TO $(\text{RhCl}_2(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$.

(Note: the isomerisation product of the platinum complex has been characterised as trans-($\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2$), but that of the rhodium compound has not been obtained analytically pure, although the evidence suggests $(\text{RhCl}_2(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$.)

4.1 Introduction

Several kinetic studies have been undertaken in recent years on the isomerisation of platinum(0)-olefin complexes to platinum(II)-vinyl complexes. This type of isomerisation has been discussed in chapter 3, and it is the purpose of this introduction simply to note those reactions on which kinetic work has been done. The first such system to be the subject of a kinetic study^{1,2} was $(\text{Pt}(\text{PPh}_3)_2(\text{Cl}_2\text{C}=\text{CCl}_2))$, which is readily isomerised in refluxing ethanol to the cis vinyl complex³. Preliminary results, obtained using ethanol as solvent, show that in 98% ethanol (2% dichloromethane) the initial rates of reaction are proportional to the initial concentration of olefin complex over the range 5.0 to $20.0 \times 10^{-5} \text{ M}$, and in addition, plots of logarithms of olefin concentration against time are straight lines for at least 70% of complete reaction. These observations both indicate first-order kinetics, and allow activation parameters to be obtained by measuring the first-order rate constant in 98% ethanol at various temperatures. The values thus obtained are:

$$\Delta H^\ddagger = 21.4 \pm 1.0 \text{ kcal. mole}^{-1} \text{ and } \Delta S^\ddagger = -9 \pm 4 \text{ e.u.}$$

The small negative value of ΔS^\ddagger may suggest that the volume of

activation ΔV^\ddagger is similarly small and negative⁴. This is a very useful correlation, since ΔV^\ddagger is a very valuable criterion for distinguishing between possible reaction mechanisms, but is difficult to measure independently since its determination involves the use of elaborate high-pressure equipment. A small, negative value of ΔV^\ddagger in this case suggests slightly greater ordering of the solvent molecules in the transition state, caused by increased charge-separation in the reacting molecule, although ΔV^\ddagger can also be used as a measure of associative or dissociative character in a reaction.

Four possible mechanisms are consistent with the first-order kinetics:

- 1) intramolecular;
- 2) loss of a Ph_3P ligand, followed by rearrangement of the intermediate and recombination with Ph_3P ;
- 3) loss of the C_2Cl_4 ligand, followed by recombination and fission of the ligand, with formation of Pt-Cl and Pt-C bonds;
- 4) cleavage of a C-Cl bond, giving chloride ion, followed by rearrangement of the carbonium ion thus formed and nucleophilic attack of the chloride on platinum.

Addition of triphenylphosphine to the reaction mixture should cause retardation of rate if mechanism 2 is correct (if the rate-determining step is the rearrangement, then any retardation may be slight), but this is not observed. Further, if loss of triphenylphosphine is rate-determining then ΔV^\ddagger would be expected to be positive, which is not consistent with the kinetic results.

If mechanism 3 is correct, then isomerisation of the olefin complex in the presence of tetracyanoethylene should result in some incorporation of $\text{C}_2(\text{CN})_4$ into the product. This does not

occur, and since C_2Cl_4 does not displace $C_2(CN)_4$ from $(Pt(PPh_3)_2(C_2(CN)_4))^{3-}$, mechanism 3 also seems unlikely.

Distinction between mechanisms 1 and 4 is made by studying the reaction in a variety of solvents, and thus obtaining a relationship between reaction-rate and ionising power of solvent. The Grunwald-Winstein equation^{5,6} provides a means of quantifying this relationship, by relating the rate constant (k) for reaction in a particular solvent to the rate constant (k_o) in a standard solvent using the formula:

$$\log_{10} \frac{k}{k_o} = mY,$$

in which m is a characteristic of the compound, and Y is a solvent characteristic, often termed the "ionising power". The reference values used are for the solvolysis of *t*-butyl chloride in 80% ethanol solution, which is considered to go via a mechanism approaching limiting S_N1 : the values assigned are $Y = 0$ and $m = 1$.

A plot of $\log k$ against Y for $(Pt(PPh_3)_2(C_2Cl_4))$ isomerisation gives a straight line of slope $m = 0.88$. This is similar to m values obtained for S_N1 solvolysis of organic halides⁶, and indicates that the rate-determining step in this arrangement is cleavage of a C-Cl bond (mechanism 4, Figure 4.1). (It is worth noting that S_N2 solvolysis of organic halides commonly gives plots of $\log k$ vs Y which are curved, and have m values of 0.2 to 0.4.⁷)

Kinetic and stereochemical studies on the isomerisation of analogous complexes of platinum(0) with a mixture of cis- and trans- $CFCl=CFCl$ also indicate a dissociative mechanism⁸, and suggest that the leaving chloride ion forms a tight ion-pair with the platinum-carbonium ion species, since the stereochemistry

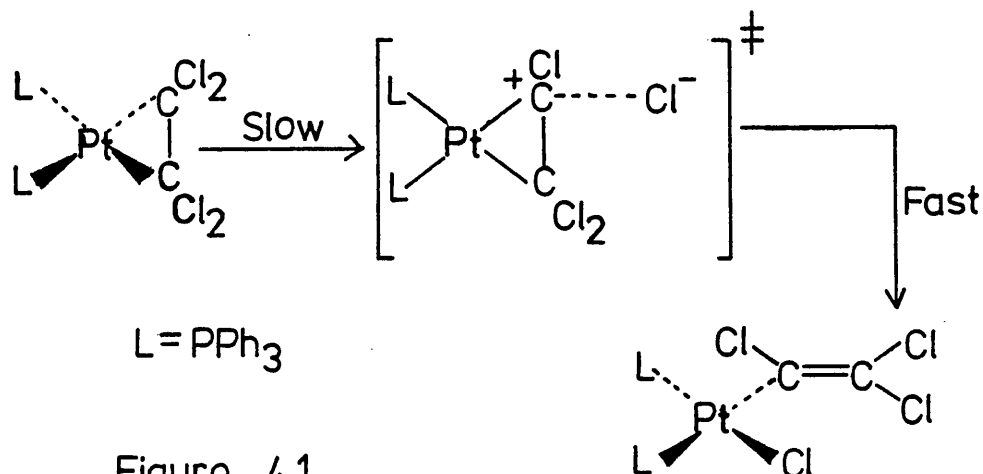


Figure 4.1

about the olefinic double-bond is retained during the reaction.

A further equation relating reaction rate to solvent parameters is that due to Brownstein⁹:

$$\log_{10} \frac{x}{x_0} = RS$$

This equation allows extension of the analysis to weakly ionising solvents such as chloroform and benzene, for which Y values can not be obtained, since *t*-butyl chloride does not react in such solvents. In this expression, x and x_0 are obtained using such techniques as n.m.r., u.v. and i.r., or from kinetic and equilibrium data, and relate a pair of values (e.g. i.r. frequency, reaction rate) for two solvents to the parameters R and S , which are equivalent to m and Y respectively in the Grunwald-Winstein equation. The reference values used are $S = 0$ for ethanol, and $R = 36$ for *t*-butyl chloride solvolysis, and for the isomerisation of $(Pt(PPh_3)_2(C_2Cl_4))$ discussed above, an R value of 18 is obtained, which is approaching the values obtained for S_N1 solvolysis of organic halides and again suggests the mechanism shown in Figure 4.1. Results obtained from extension of the analysis to weakly ionising solvents, however, suggest that a different mechanism - possibly dissociation of a triphenylphosphine ligand -

is operating in benzene.

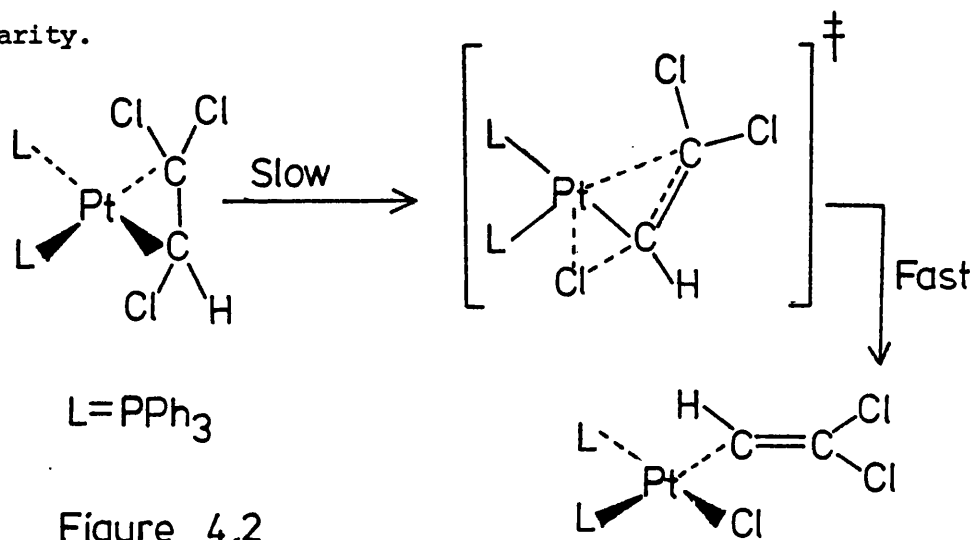
These methods for investigating the mechanism of isomerisation of platinum(0)-olefin complexes have been extended to the compounds $(\text{Pt}(\text{PPh}_3)_2(\text{Cl}_2\text{C}=\text{CHCl}))^{10}$ and $(\text{Pt}(\text{AsPh}_3)_2(\text{F}_2\text{C}=\text{CFBr}))^{11}$. m and R values for these isomerisations are listed below (Table 4.1), along with those for $(\text{Pt}(\text{PPh}_3)_2(\text{Cl}_2\text{C}=\text{CCl}_2))$ and t -butyl chloride solvolysis.

Table 4.1 m and R values for the isomerisation of various platinum(0)-olefin complexes

<u>Compound</u>	<u>R</u>	<u>m</u>
$(\text{Pt}(\text{PPh}_3)_2(\text{Cl}_2\text{C}=\text{CCl}_2))$	18.0 ± 1.0	0.86 ± 0.07
$(\text{Pt}(\text{PPh}_3)_2(\text{Cl}_2\text{C}=\text{CHCl}))$	10.2 ± 0.5	0.54 ± 0.07
$(\text{Pt}(\text{AsPh}_3)_2(\text{F}_2\text{C}=\text{CFBr}))$	4.9 ± 1.2	0.32 ± 0.12
$(\text{H}_3\text{C})_3\text{CCl}$	36	1.00

The mechanism for isomerisation of $(\text{Pt}(\text{PPh}_3)_2(\text{Cl}_2\text{C}=\text{CHCl}))$ is thus seen to have more intramolecular character than that for the tetrachloroethylene analogue. In addition, the rate of isomerisation of the trichloroethylene complex is considerably faster, primarily due to a lowering in the activation enthalpy. This may be due to a weaker platinum-olefin bond, caused by decreased electronegativity of the olefin substituents, and also the fact that chloride should more easily leave the group $\text{H}-\text{C}-\text{Cl}$ than $\text{Cl}-\text{C}-\text{Cl}$. In accordance with this latter statement, the product of this reaction is thought to be cis- $(\text{PtCl}(\text{HC}=\text{CCl}_2)(\text{PPh}_3)_2)$. The intramolecular pathway is illustrated in Figure 4.2, although it should be stressed that this reaction proceeds either by a mixture of the intramolecular and dissociative routes, or by a path intermediate between the two. The geometry of the

transition-state in the intramolecular process is unlikely to be planar. This distortion results from the chloride group attacking from a position out of the square-plane, since the olefin is slightly tilted even in the initial complex, and also, the partial five-coordination involved in the transition-state will produce steric-crowding, and a consequent relief of strain by loss of planarity.



The isomerisation of $[Pt(AsPh_3)_2(F_2C=CFBr)]$ goes via an intramolecular mechanism as shown by the very small variation of reaction rate with the nature of the solvent. This path is in accordance with the known preference of platinum(II) to coordinate to bromide more than chloride¹². Since, however, other variables have been introduced into this system by using the triphenylarsine ligands and the fluorine-substituted olefin, it is hard to be specific about the factors which result in this intramolecular mechanism.

An interesting comparison is given by $(Pt(PPh_2CH_3)_2(F_2C=CFCl))$ and $(Pt(PPh_2CH_3)_2(F_2C=CFBr))$, which are presumed from activation parameters to isomerise via a dissociative mechanism, although unfortunately the solvent dependences of the reaction rates have not been investigated⁸. These authors suggest that steric

factors play a part in the driving force leading to carbon-halogen bond breaking, and also that electronic effects, such as some population of the carbon-halogen bond σ^* -antibonding orbitals due to back-bonding effects, could enhance this cleavage.

Clearly, a considerable amount of investigation still needs to be carried out on this type of isomerisation, and one possibility is to extend the work to metal-acetylene complexes. No kinetic data are as yet available on the isomerisation of metal-acetylene systems to metal-acetylides, and consequently kinetic studies have been carried out on two such processes.

4.2 The isomerisation of $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ to trans- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$

The acetylene complex $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ isomerises readily in methanol at 40°C , giving the trans platinum-acetylide complex. The vinyl isomerisation reactions of $(\text{Pt}(\text{PPh}_3)_2(\text{Cl}_2\text{C}=\text{CCl}_2))$ and $(\text{Pt}(\text{PPh}_3)_2(\text{Cl}_2\text{C}=\text{CHCl}))$ which have been the subjects of kinetic studies^{1,2,10} both lead to the cis platinum-vinyl isomers, but in the case of $(\text{Pt}(\text{AsPh}_3)_2(\text{F}_2\text{C}=\text{CFBr}))$, the stereochemistry of the product is uncertain¹³. Isomerisations of square-planar metal-olefin systems to trans metal-vinyl complexes are well known however - for example, the compounds $(\text{Pt}(\text{PR}_3)_2(\text{F}_2\text{C}=\text{CFX}))$ ($\text{R}_3=\text{Ph}_3$ or Ph_2CH_3 , $\text{X}=\text{Br}$ or Cl) are isomerised in refluxing alcohols to the trans platinum-vinyl products¹⁴ - but as mentioned earlier, only activation parameters, and not solvent dependences, have been studied for these reactions⁸.

Isomerisation of a square-planar system leading to a trans metal-vinyl or trans metal-acetylide product might be expected to make any kinetic investigation of the system more intricate, since it is possible that two reactions are occurring

in solution-rearrangement of a metal-acetylene complex to a cis metal-acetylide, followed by isomerisation to the trans isomer (Figure 4.3).

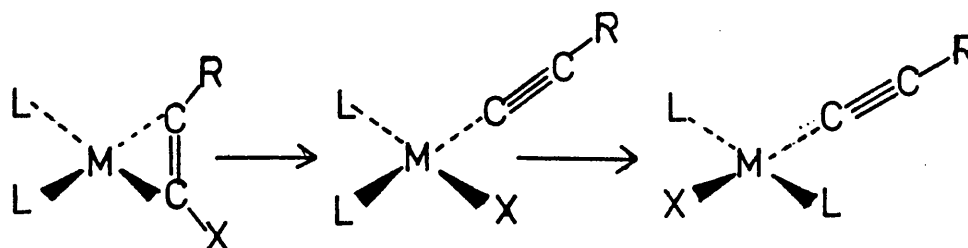


Figure 4.3

It is also feasible that the isomerisation does not go through the cis complex as an intermediate, but instead goes straight to the trans isomer. This probably depends on the degree of freedom enjoyed by the departing halide ion in the first step: if this is largely intramolecular, then the cis intermediate seems more likely to result since this involves formation of a metal-halide bond simultaneously with cleavage of the carbon-halogen bond, and therefore demands that the metal atom, olefinic double-bond and halide ion should remain relatively close to each other (Figure 4.4a). Alternatively, this reaction may be largely dissociative, giving a halide ion, which although held in an ion-pair, has greater freedom to attack so as to give the thermodynamically more favoured (in this case) trans isomer (Figure 4.4b), without first going through the cis intermediate.

As mentioned in Section 4.1, the two other possible mechanisms for this type of reaction, other than the dissociative or intramolecular, involve either dissociation of the acetylene, or dissociation of a triphenylphosphine ligand. N.m.r. studies¹⁵ on the complex $(\text{Pt}(\text{P}(\text{C}_6\text{D}_5)_3)_2(\text{D}_5\text{C}_6\text{C}\equiv\text{CH}))$ show no indication of

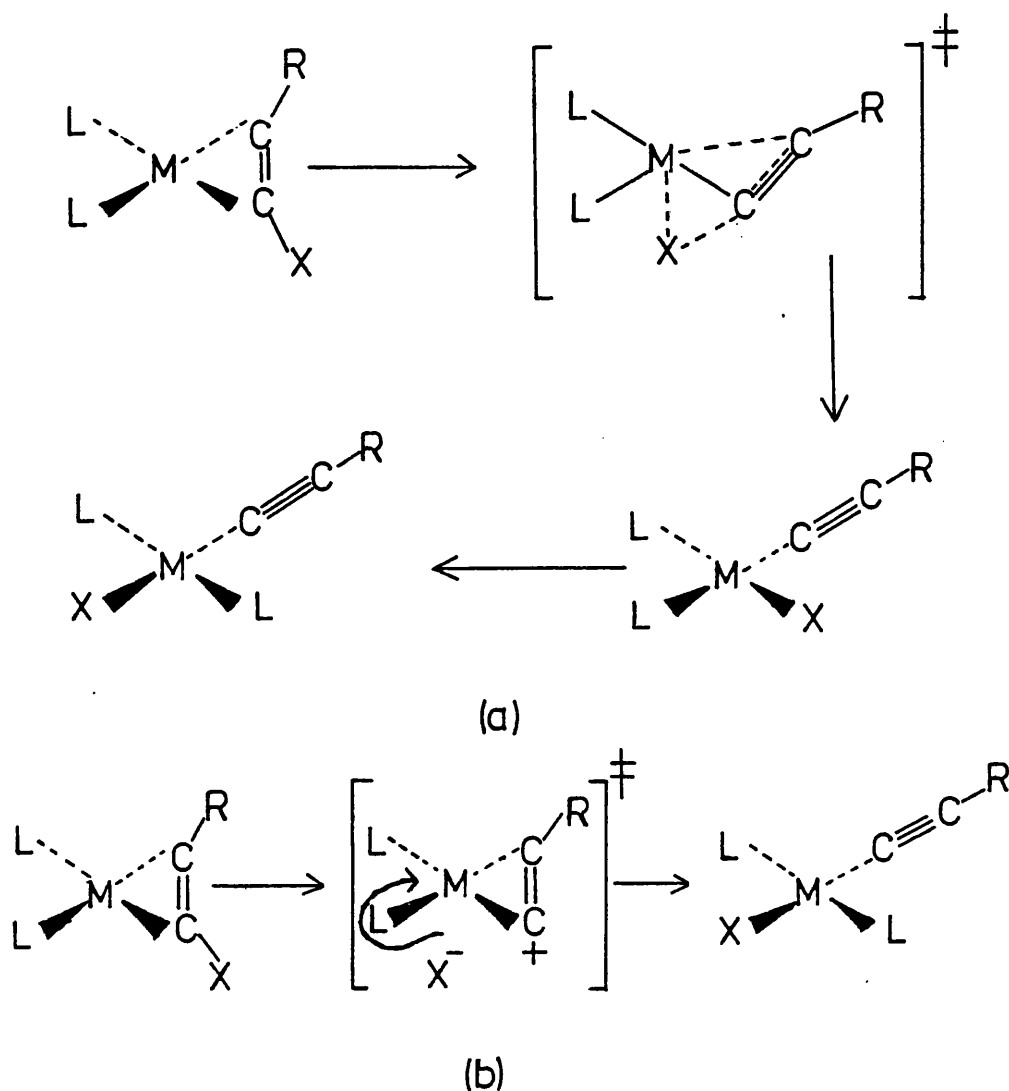


Figure 4.4

acetylene dissociation in solution, and more work using mono-substituted phenylacetylene ligands is in agreement with this, so that the acetylene-dissociation mechanism seems unlikely. The phosphine-dissociation route has been tested for the isomerisation of $(\text{Pt}(\text{PPh}_3)_2 (\text{Cl}_2\text{C}=\text{CCl}_2))$ by adding phosphine to the solution - a process which would be expected to decrease the rate if a pre-equilibrium involving loss of a phosphine occurs previous to the rate determining step - but no effect is observed¹. One of the problems involved in introducing phosphine to the solution is

the effect it might have on the cis-trans equilibrium which appears to be taking place, since this isomerisation is known to be catalysed by added phosphine ligand¹⁶. Alternatively, it is possible that the phosphine could become coordinated to the metal during the reaction, and as this π -acid ligand would be expected to stabilise platinum(0) more than platinum(II), a decrease in isomerisation-rate would result. Consequently, experiments involving adding phosphine to the solution are not expected to produce definitive results, and it seems more advisable to take the measured volume of activation ΔV^\ddagger as an indicator as to the probability of this phosphine-dissociation mechanism taking place.

In the case of the reaction under investigation - isomerisation of $(\text{Pt}(\text{PPh}_3)_2 (\text{PhC}\equiv\text{CCl}))$ - activation parameters were not obtained, for reasons which are explained shortly. The reaction follows first-order kinetics as shown by plots of logarithms of acetylene complex concentration against time, which are straight lines for over 80% of the reaction. It was therefore possible to measure the first-order rate constants in a range of solvents at 35°C; the mean rate constants, as well as the solvent parameters, Y and S, are listed in Table 4.2. This table also lists the ratio

$$\frac{\text{final optical density reading}}{\text{initial optical density reading}}$$

estimated for each solvent by extrapolation of optical density vs. time curves.

The ratios a:b are particularly significant, since the figures obtained for this ratio should be approximately constant for an irreversible first-order reaction. Closer examination of the figures reveals that, with the exception of iso-propanol, the order of decrease of the ratios a:b is the same as the order of

Table 4.2 Average first-order rate constants for the isomerisation of (Pt(PPh₃)₂(PhC≡CCl)) in a range of solvents, at 35°C

<u>Solvent</u>	<u>Average rate constant (K_{obs}) x 10⁴</u>	<u>y</u>	<u>s</u>	<u>$\frac{a}{b}$</u>
Methanol	2.00	-1.09	0.05	0.82
Ethanol	1.88	-2.03	0.0	0.74
n-Propanol	1.58	-2.3*	-0.016	0.63
iso-Propanol	1.83	-2.73	-0.041	0.48
n-Butanol	1.41	-	-0.024	0.60
t-Butyl alcohol	0.79	-3.26	-0.105	0.57

No isomerisation was observed in chloroform, dichloromethane, or dichloroethane.

$\frac{a}{b}$ = final optical density reading
initial optical density reading

* estimated from Z and E_T values¹⁷.

decrease of the rate constants. These figures suggest an equilibrium process, in which the rate at which the equilibrium is being established is in the order methanol > ethanol > n-propanol > n-butanol > t-butyl alcohol, but that the position of the equilibrium lies increasingly to the right in the order t-butyl alcohol > n-butanol > n-propanol > ethanol > methanol. The reaction in iso-propanol is anomalous, showing an unexpectedly fast rate of reaction, and an equilibrium position lying the furthest to the right of any of the solvents studied

Examination of the u.v. spectra of solutions of $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$, cis- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ and trans- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, followed by comparison with the u.v. spectra of the products obtained from the isomerisation reaction in various solvents is of some assistance in attempting to clarify the situation (Table 4.3).

Table 4.3 Comparison of ultra-violet spectra of $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ and the products of its isomerisation, with those of cis- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ and trans- $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$

<u>Compound</u>	<u>λ_{max} (mμ)</u>
$(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$	292 (shoulder) (in ethanol)
<u>cis</u> - $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$	296 (shoulder) (in methanol)
<u>trans</u> - $(\text{PtCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$	312 (in methanol)
Isomerisation product after 3 hrs. at 35°C in methanol, ethanol, n- propanol, n-butanol or t-butyl alcohol	293-296 (shoulders) (dependent on solvent)
Isomerisation product after 3 hrs. at 35°C in iso-propanol	314 (in i-propanol)

The main conclusion to be drawn from this evidence is that the reactions over 3 hours at 35°C in five of the six hydroxylic

solvents used, appear to give a product containing more of the cis isomer, whereas in iso-propanol, under the same conditions, the product appears to contain far more of the trans isomer. It is interesting, however, that in ethanol at a temperature of 43.2°C, over a period of three hours, the product shows a developing peak in the u.v. at 315 mμ, and reactions in methanol, n-propanol, n-butanol and t-butyl alcohol over time periods of six to twelve hours at 35°C, also give products with u.v. peaks at 314-316 mμ. It therefore seems that at 35°C the cis- trans isomerisation is considerably greater in iso-propanol, but over longer time periods, or at increased temperatures, the isomerisation also occurs to a substantial extent in the other hydroxylic solvents.

The cause of the increased production of the trans isomer in iso-propanol is not entirely clear, but a consideration of the current theories for the mechanism of this reaction is helpful. A mechanism which is in agreement with the available data for both platinum and palladium is shown in Figure 4.5¹⁶.

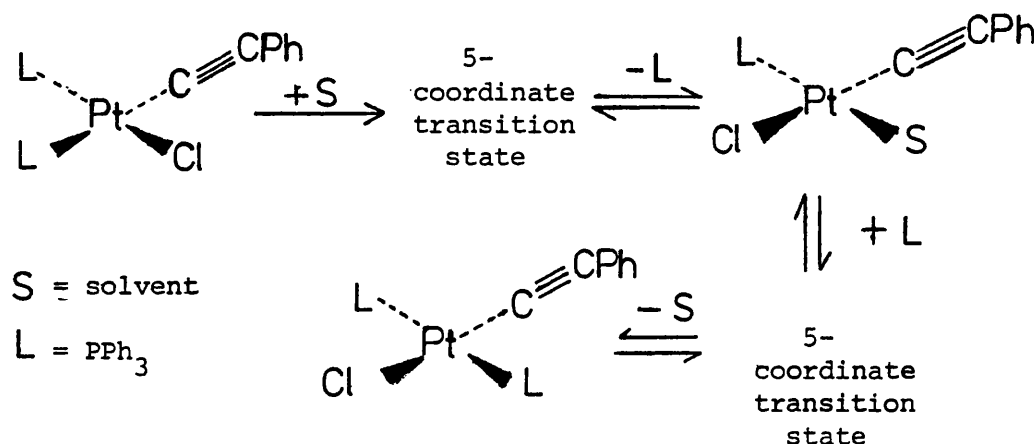


Figure 4.5

The geometry of the 5-coordinate transition states is not known, but is thought to be irregular. From this mechanism, one would predict that a more basic solvent molecule would result in a lower activation energy for the reaction and therefore in this

case, where the trans isomer appears to be thermodynamically favoured, increase the rate at which this trans isomer is produced.

In the system being studied, the two most basic solvents used are iso-propanol and t-butyl alcohol, and accordingly, under constant reaction conditions, reaction in these two solvents produces more of the trans isomer. The reaction appears to be more complete in iso-propanol, and this may be due to two factors:

1. the size of t-butyl alcohol may inhibit its coordination to platinum;
2. the rate of the initial acetylene-acetylide isomerisation is expected to be faster in iso-propanol, this being a more polar solvent, and therefore the cis complex is made available more rapidly for conversion to the trans isomer.

To summarise, the reaction in iso-propanol seems to be giving mostly trans isomer at 35°C, whereas the reactions in other hydroxylic solvents are giving largely cis isomer. It therefore seems prudent to consider the iso-propanol reaction separately, and therefore when obtaining m and R values from plots of log k against Y and S respectively, the points due to iso-propanol are omitted from the calculations.

Figures 4.6 and 4.7 show these two plots for this isomerisation of $(\text{Pt}(\text{PPh}_3)_2 (\text{PhC}\equiv\text{CCl}))$: from the gradients of the graphs, values of $m = 0.15 \pm 0.04$ and $R = 2.13 \pm 0.33$ are obtained. Comparison of these figures with the values obtained for olefin-vinyl isomerisations investigated previously (Table 4.1) show that $(\text{Pt}(\text{PPh}_3)_2 (\text{PhC}\equiv\text{CCl}))$ isomerisation has more intramolecular character than any of these reactions, and may be considered to react by an almost completely intramolecular route. That the reaction should be largely intramolecular, rather than dissociative (e.g. for $(\text{Pt}(\text{PPh}_3)_2 (\text{Cl}_2\text{C}=\text{CCl}_2))$ isomerisation) is consistent with

Figure 4.6

Variation of $\log_{10} k$ with Y for isomerisation of

$(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ in a range of solvents

Solvent

- 1 Methanol
- 2 Ethanol
- 3 n-Propanol
- 4 t-Butyl alcohol

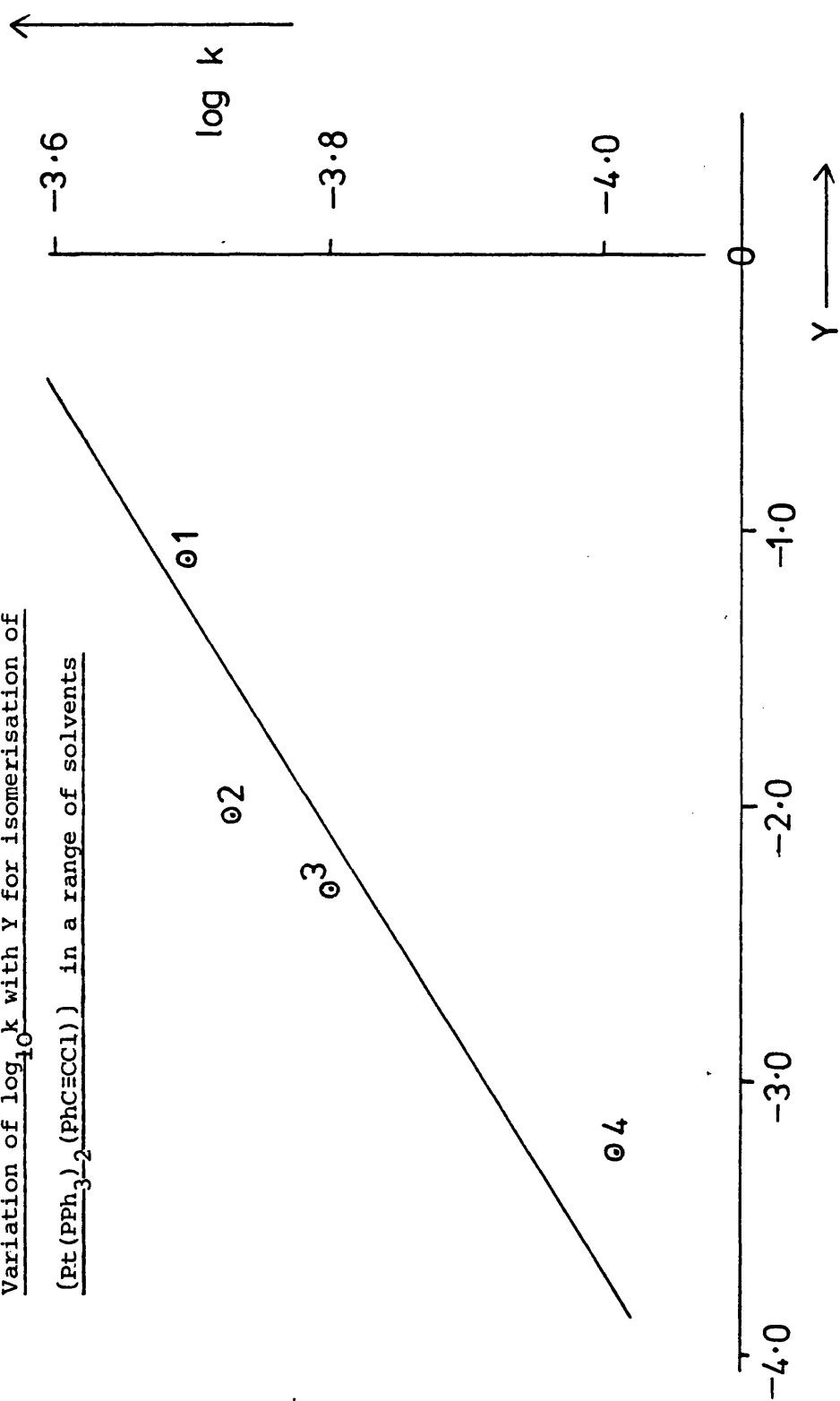
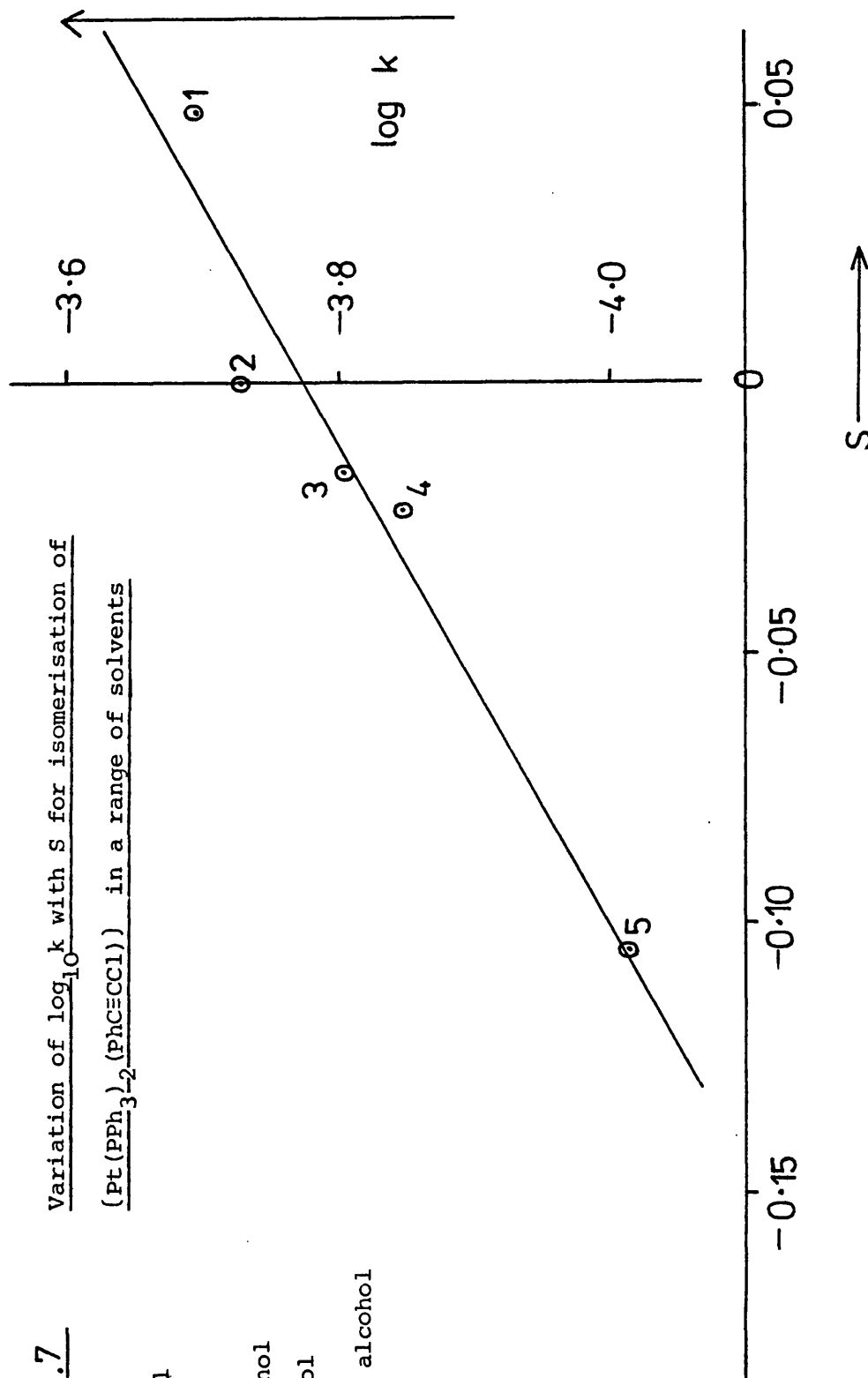


Figure 4.7

Solvent

- 1 Methanol
- 2 Ethanol
- 3 n-Propanol
- 4 n-Butanol
- 5 t-Butyl alcohol



the nature of the carbon-chlorine bond which is being broken. It would be expected that a chlorine atom attached to a carbon atom which is between sp and sp^2 hybridisation (e.g. a π -bonded acetylene) would be held more tightly than a chlorine atom joined to a carbon intermediate between sp^2 and sp^3 (e.g. a π -bonded olefin) and therefore the development of any dissociated chloride ion is likely to be small, and a mechanism involving simultaneous cleavage of the C-Cl bond and formation of a Pt-Cl bond is expected to predominate.

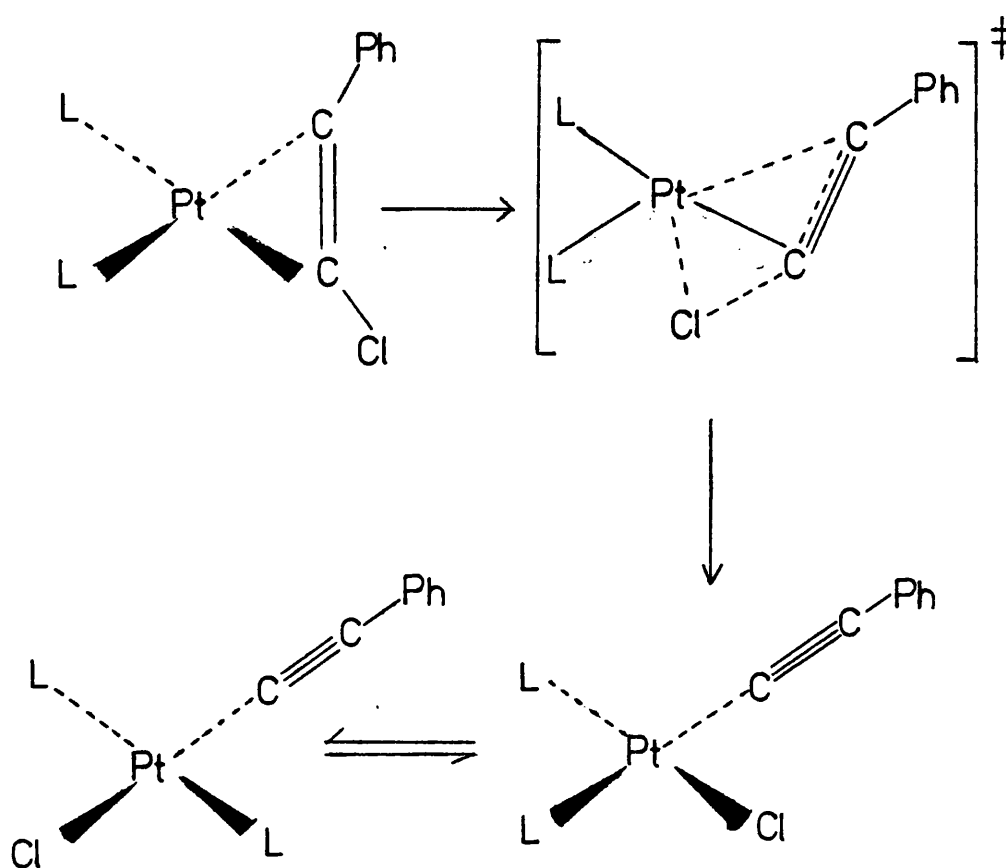
Since the u.v. spectra suggest that, under the conditions of the kinetic study, the product is largely the cis platinum-acetylide compound (except in the case of iso-propanol), it seems reasonable to interpret the observed lack of solvent dependence as being characteristic of the acetylene-acetylide isomerisation. The fact that the reaction under investigation involves two stages, one of which is reversible, however, precludes any determination of activation parameters for this process, since not only the rate constants, but also the equilibrium positions, vary with temperature and therefore no regular variation in rate is observed.

Isomerisation of $(Pt(PPh_3)_2(PhC\equiv CCl))$ is therefore thought to proceed via a largely intramolecular step to cis-($PtCl(C\equiv CPh)(PPh_3)_2$) which in turn undergoes a reversible isomerisation to the trans isomer (Figure 4.8).

Although the compound cis-($PtCl(C\equiv CPh)(PPh_3)_2$) can be made, it is easily isomerised to the trans isomer simply by stirring in benzene solution, and it does seem that the trans isomer is the more stable. In this context, it is interesting to note that an attempt to isomerise $(Pt(diphos)(PhC\equiv CCl))$ in methanol at $35^\circ C$ which would have lead to the cis isomer, resulted, after six hours only in recovery of the unchanged acetylene complex, so it appears

Suggested mechanism for isomerisation

of $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$



$\text{L} = \text{PPh}_3$

Figure 4.8

that the ability to go through to the trans isomer is important to this reaction (although it should be noted that bis-diphenylphosphinoethane is a slightly more basic ligand than triphenylphosphine, and may therefore slightly increase the stability of the phenylchloroacetylene complex).

It is apparent from the slopes of the plots of $\log k$ against Y and S values that the reaction mechanism does have some dissociative character - for a purely intramolecular mechanism, there would be very little, or no variation of reaction rate in different solvents - and therefore it might be expected that there would be some reaction, although very slow, in the less polar solvents such as chloroform, dichloromethane and dichloroethane (which have S values of -0.2 , -0.19 and -0.15 respectively¹⁷). No isomerisation is observed in these solvents, however, at 35°C over time-periods of up to twelve hours; it seems probable that the separation of charge in the transition-state (i.e. the degree of dissociation giving a carbonium ion and chloride ion) is insufficient to give any interaction with these solvents, which on the other hand are quite able to stabilise the relatively non-polar starting complex $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$. This differing ability of solvents such as chloroform and ethanol to stabilise relatively polar and non-polar species is reflected by a qualitative examination of the solubility of the acetylene complex in the two solvents - it is only very sparingly soluble in ethanol (and other alcohols) but very soluble in chloroform, and other chlorinated-hydrocarbon solvents.

4.3 The isomerisation of $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ to $(\text{RhCl}_2(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$

Isomerisations of rhodium-olefin complexes analogous to the well known olefin-vinyl rearrangements of platinum(0) compounds have not been studied to date, and therefore an investigation of the kinetics of $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ isomerisation should not only aid in the understanding of acetylene-acetylide rearrangement, and its relation to the olefin-vinyl process, but also allow comparison between platinum(0) and rhodium(I) species in this type of reaction. $(\text{RhCl}(\text{PPh}_3)_2(\text{F}_2\text{C}=\text{CFCl}))$ has been prepared¹⁸, but no isomerisation process has been noted for it, whereas $(\text{Pt}(\text{PPh}_3)_2(\text{F}_2\text{C}=\text{CFCl}))$ and $(\text{Pt}(\text{PPh}_2\text{CH}_3)(\text{F}_2\text{C}=\text{CFCl}))$ both isomerise in refluxing n-butanol, with migration of the chloride onto platinum, giving trans platinum-vinyl compounds^{14,19}. The bromotrifluoroethylene analogues of these platinum-olefin complexes have also been made, and found to isomerise more readily than the chlorotrifluoroethylene derivatives^{14,20} but for rhodium, although $(\text{Rh}(\text{acac})(\text{PPh}_2\text{CH}_3)_2(\text{F}_2\text{C}=\text{CFBr}))$ and $(\text{RhCl}(\text{PPh}_3)_2(\text{F}_2\text{C}=\text{CFBr}))$ are known^{21,25}, no reports have been made of any possible isomerisation reactions.

The rearrangement of $(\text{RhCl}(\text{PPh}_2)_3(\text{PhC}\equiv\text{CCl}))$ would be expected to lead to a five-coordinate rhodium(III) compound, $(\text{RhCl}_2(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$. Five-coordination in rhodium(III) is not well known, however, although the crystal-structure²³ of the compound formed from $(\text{RhCl}(\text{PPh}_3)_3)$ and excess methyl iodide²², shows it to have a square-pyramidal structure.

Five-coordination is also possible for $(\text{RhClH}_2(\text{PPh}_3)_2)$ in the solid state, but in solution six-coordination, with a solvent molecule filling the vacant site, is likely²⁴: similar considerations probably apply to the σ -allyl compound $(\text{RhCl}_2(\text{CH}_2\text{CH}=\text{CH}_2)(\text{PPh}_3)_2)$ ²². The instability of five-coordinate rhodium(III) relative to

octahedral rhodium(III) and square-planar rhodium(I) may be an important factor in the lack of success in obtaining isomerisation products from rhodium(I)-olefin compounds, since five-coordinate rhodium(III)-vinyl species would be expected to result, so it is interesting that warming a suspension of $(\text{RhCl}(\text{PPh}_3)_2)(\text{PhC}\equiv\text{CCl})$ in methanol at 35°C for several hours gives a complex, which on the basis of infra-red evidence, appears to be a rhodium-acetylide. It should be noted, however, that microanalytical data do not exactly fit the formula $(\text{RhCl}_2(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$, and that the compound may be partially solvated.

For this reaction, plots of logarithms of rhodium-acetylene complex concentration against time are straight lines for over 80% of reaction, and therefore this isomerisation also follows first-order kinetics. The reaction was initially studied in ethanol, at various temperatures, in order to obtain activation parameters and then in various solvents at 35°C to examine any solvent dependence of the reaction rate. Average first-order rate constants for the isomerisation in ethanol at various temperatures are shown in Table 4.4.

Table 4.4 Variation of average rate constant (k) with temperature, for the isomerisation of $(\text{RhCl}(\text{PPh}_3)_2)(\text{PhC}\equiv\text{CCl})$ in ethanol

<u>Temperature ($^\circ\text{C}$)</u>	<u>$k \times 10^3 \text{ (s}^{-1}\text{)}$</u>
20.3	0.25
30.3	0.89
33.0	1.45
40.6	2.74
43.5	4.83

The activation energy, E_a , of the reaction was calculated using the Arrhenius equation:

$$k = A \exp. \left(\frac{-E_a}{RT} \right)$$

A plot of $\log k$ against $\frac{1}{T}$ gave a straight line graph, from the gradient of which was obtained a value for E_a of $22.8 \pm 1.0 \text{ kcal.mole}^{-1}$.

By using equations (i), (ii), and (iii), the entropy of activation, ΔS^\ddagger , can then be calculated.

$$(i) \quad \Delta H^\ddagger = E_a - RT$$

$$\Delta H^\ddagger = \text{the enthalpy of activation. Calculated}$$

$$\Delta H^\ddagger = 22.2 \pm 1.0 \text{ kcal.mole}^{-1}.$$

$$(ii) \quad k' = \frac{kT}{h} \exp \left(\frac{-\Delta G^\ddagger}{RT} \right)$$

$$k' = \text{experimental first-order rate constant}$$

$$k = \text{Boltzmann constant}$$

$$h = \text{Planck's constant}$$

$$\Delta G^\ddagger = \text{Gibbs free energy of activation. Calculated}$$

$$\Delta G^\ddagger = 22.0 \text{ kcal.mole}^{-1}.$$

$$(iii) \quad \Delta G^\ddagger = \Delta H - T\Delta S.$$

$$\Delta S^\ddagger = \text{entropy of activation. Calculated } \Delta S^\ddagger = 0.7 \pm 3 \text{ e.u.}$$

The value of ΔS^\ddagger obtained from these calculations is very close to zero, and may indicate that ΔV^\ddagger , the volume of activation, is also almost zero⁴, implying an almost complete lack of dissociation in the transition state. These preliminary results are therefore consistent with a largely intramolecular mechanism, as was observed for isomerisation of $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$.

Measurement of the average first-order constants at 35°C in a range of solvents yields further information as to the nature of this acetylene-acetylide isomerisation. The values obtained are

listed in Table 4.5.

Table 4.5 Average first-order rate constants (k) for

$(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ isomerisation in various solvents at 35°C

<u>Solvent</u>	<u>$k \times 10^3 (\text{s}^{-1})$</u>	<u>S</u>
Methanol	1.61	0.05
Ethanol	1.31	0.0
n-Propanol	2.44	-0.016
i-Propanol	0.96	-0.041
n-Butanol	1.90	-0.024
t-Butyl alcohol	0.40	-0.105
Chloroform	1.31	-0.20

S = solvent parameter, from Brownstein equation.

The plot of $\log k$ against S is shown in Figure 4.9, and, from the gradient, R is obtained; a similar plot of $\log k$ against Y, which is not shown, gives a value for m. From these graphs, it is apparent that the correlation between reaction rate and the ionising power of the solvent is not very strong for this reaction, and in particular, reactions in the solvents n-propanol and n-butanol appear to be considerably faster than would be predicted by either the Brownstein or the Grunwald-Winstein theories. Table 4.6 lists the values obtained for m and R, a) including the points for n-propanol and n-butanol in the calculation, and b) not including them.

Two main conclusions can be drawn from this treatment of the rate constant data:

1. comparison with the figures obtained for $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ isomerisation and with the values listed in Table 4.1 for various olefin-vinyl rearrangements, indicates that this reaction is also

Figure 4.9

- Solvents
- 1 Methanol
 - 2 Ethanol
 - 3 n-Propanol
 - 4 n-Butanol
 - 5 i-Propanol
 - 6 t-Butyl alcohol

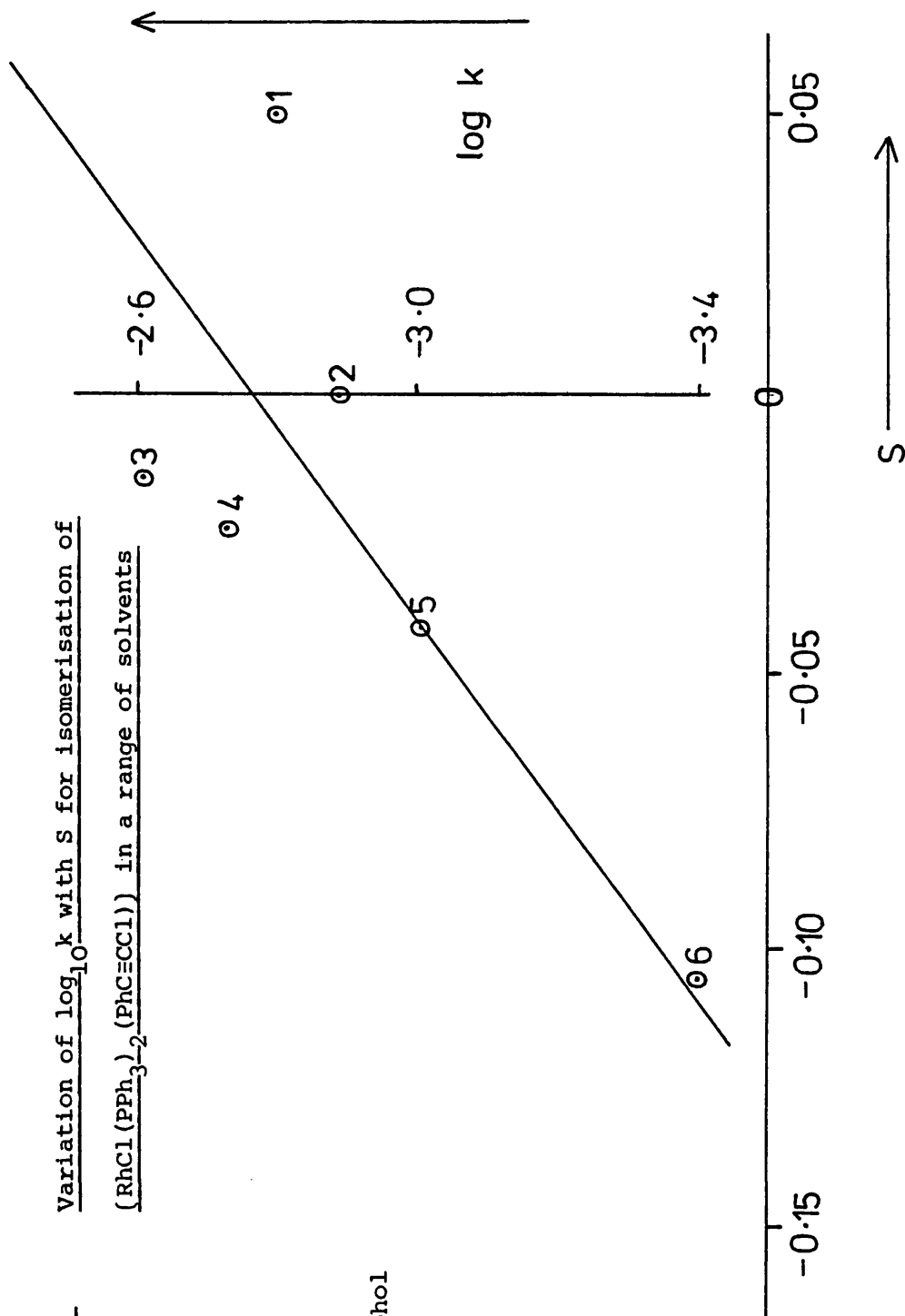


Table 4.6 Values of m and R for $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ isomerisation

	<u>a</u>	<u>b</u>
m	0.25 ± 0.15	0.26 ± 0.09
R	4.08 ± 1.82	3.92 ± 0.74

(Compare with $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ isomerisation: $\overset{m}{M} = 0.15 \pm 0.04$,
 $R = 2.13 \pm 0.33$.)

going via a largely intramolecular mechanism, consistent with the strength of the carbon-chlorine bond in $\text{RC}\equiv\text{CCl}$ molecules being greater than in $\text{R}_2\text{C}=\text{C}(\text{R})\text{Cl}$ species;

2. there is not a regular decrease of reaction rate with decreasing solvent polarity, and therefore some other property of the solvent must be affecting the reaction rate.

One obvious factor which could cause this apparent inconsistency is impurity in the solvent. In an attempt to exclude this possibility the solvents were purified by standard methods²⁶, and their purity checked by g.l.c. It was found, however, that the previously obtained results were reproducible with solvents purified in this way and that, therefore, some other postulate should be invoked in an attempt to explain the results.

The proposed intramolecular mechanism for this rearrangement is shown in Figure 4.10. The starting material may be regarded as four coordinate rhodium(I), with the acetylene perpendicular to the plane defined by the rhodium atom and the three other ligands, with the phosphines probably trans to each other (c.f.

$(\text{RhCl}(\text{PPh}_3)_2(\text{F}_2\text{C}=\text{CF}_2))$ ¹⁸). The product, however, is five coordinate rhodium(III), and, as mentioned earlier, in solution the vacant sixth position is probably occupied by a solvent molecule. The stereochemistry of the transition-state may more closely resemble

Suggested mechanism for isomerisation

of $(\text{RhCl}(\text{PPh}_3)_2)(\text{PhC}\equiv\text{CCl})$

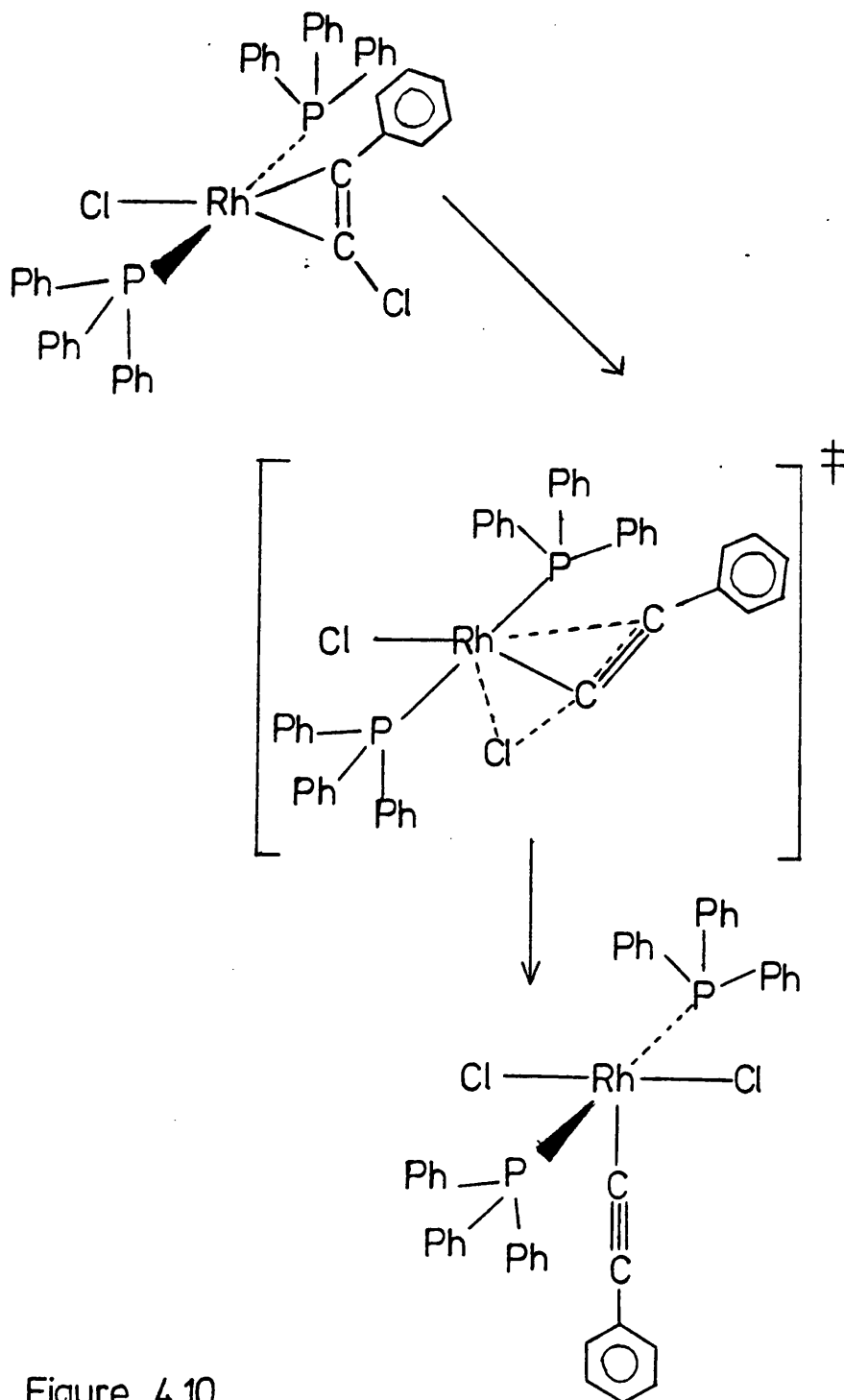


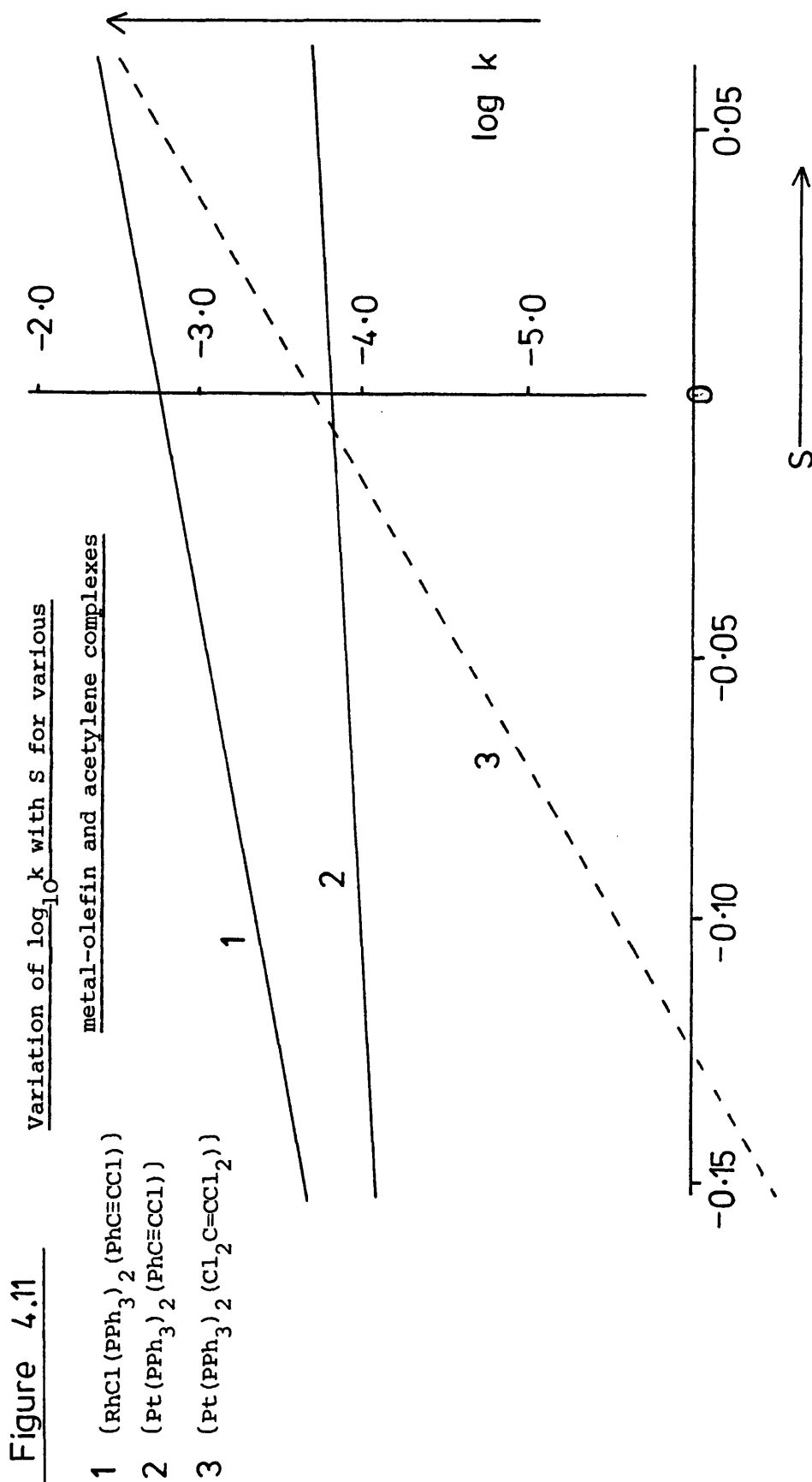
Figure 4.10

that of the product or the starting material, depending on the degree of rhodium-carbon bond-breaking and rhodium-chlorine bond-formation. If it more closely resembles that of the product, then solvent coordination to the rhodium would be expected to stabilise the transition-state, resulting in a decrease in its free energy, a decrease in the activation energy, and an increase in reaction rate. If, however, the stereochemistry is closer to that of the starting material, with little rhodium-carbon bond-breaking, and with the acetylene still largely perpendicular to the square-plane, then solvent coordination above the plane may well result in steric crowding, due to the presence of the phenyl group of the acetylene, whereas coordination below the plane will interfere with movement of the rhodium-carbon bond into the apical position. The two triphenylphosphine ligands will add to this overcrowding, the nett effect being an increase in transition-state free energy, and an increase in reaction rate. With a transition-state involving more rhodium-carbon bond-cleavage, the phenyl group is moving away from this position, towards the apical position, and therefore less steric interaction will be produced by a coordinated solvent molecule.

These effects may explain the deviation of the solvent dependence of the reaction rate from that expected, since this behaviour may be regarded either as a faster rate than expected in n-butanol and n-propanol, or a slower rate than expected in methanol and ethanol. Of these solvents, methanol and ethanol are the more basic, and would therefore be expected to coordinate more strongly to the rhodium atom: if the transition-state more closely resembles the starting material than the product, this will produce steric interaction, and therefore a decrease in the reaction rate from that expected purely from polarity considerations. The less basic solvents, n-propanol and n-butanol, would be expected to coordinate

either very weakly, or not at all, to the metal and consequently no overcrowding will result - a factor which would explain the faster rate in these two solvents than in methanol and ethanol. Of the solvents studied, the most basic is t-butyl alcohol, coordination of which would produce very large steric interference in the transition-state, and this would account for the rate in this solvent being considerably slower than envisaged from extrapolation of the line through points due to methanol, ethanol and iso-propanol in Figure 4.9. It therefore seems plausible that factors other than solvent polarity are important to this system, and that an awareness of solvent basicity, as well as transition-state stereochemistry, are essential to the understanding of this reaction and probably many others.

The point for chloroform on the graph of $\log k$ against S does not fall anywhere near the best line which can be drawn for the hydroxylic solvents. This, however, does not appear to be a particularly significant observation, since an examination of the variation in charge-transfer spectra of $(W(CO)_4(bipy))$ ($bipy$ = bipyridine) with solvent parameters shows no correlation between hydroxylic and aprotic solvents²⁷, and the isomerisation of $(Pt(AsPh_3)_2(F_2C=CFBr))$ shows a similar lack of correlation¹¹. One possible factor affecting the rate in a solvent such as chloroform is the possibility of a small amount of dichlorocarbene, or HCl , in solution.



4.4 Summary

Although these first two investigations of the kinetics of acetylene-acetylide isomerisation have presented problems which have not been encountered in studies of the olefin-vinyl process - namely the two-step nature of the platinum example, and the solvent involvement in the rhodium case - the results provide a clear comparison between the two types of rearrangement. For both the platinum and rhodium complexes, acetylene-acetylide rearrangement is seen to have considerably more intramolecular character than olefin-vinyl isomerisation, and this is consistent with the strength of the carbon-chlorine bond which is being broken. These observations are clearly illustrated in Figure 4.11, where the slopes of the $\log k$ vs S plot for the olefin system is seen to be considerably closer to the limiting value of 36 (pure S_N1) than those of the acetylene complexes. These comparisons help to put the extreme insensitivity of acetylene-acetylide isomerisation to solvent polarity into perspective, since for the solvents studied the rate varies only by an overall factor of 3 for $(Pt(PPh_3)_2(PhC\equiv CCl))$ and 6 for $(RhCl(PPh_3)_2(PhC\equiv CCl))$ whereas for $(Pt(PPh_3)_2(Cl_2C=CCl_2))$ the factor is 350.

4.5 Experimental

The compounds $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ and $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ were prepared as outlined in Chapter 3, dried under vacuum, and their purity checked by infra-red spectra and melting points.

$(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ was stored in the dark, and used within 24 hours of preparation.

All solvents used were purified by standard methods²⁶, and stored over molecular sieves. Their purity was checked by g.l.c.

$(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$ has $\lambda_{\text{max}} = 292\text{m}\mu$ (shoulder): the cis-acetylide complex has $\lambda_{\text{max}} = 296\text{m}\mu$ (shoulder), whilst the trans-acetylide has $\lambda_{\text{max}} = 312\text{m}\mu$. Absorbance readings during the kinetic runs were made at $295\text{m}\mu$, since at this wavelength the greatest decrease in absorption during the isomerisation reaction was observed. For $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$, $\lambda_{\text{max}} = 283\text{m}\mu$ (broad shoulder), whilst the acetylide product has $\lambda_{\text{max}} = 268\text{m}\mu$. For this isomerisation, absorbance readings were made at $285\text{m}\mu$ during the kinetic experiments, in order to observe the greatest decrease in absorption during reaction.

Kinetic runs were conducted in 1 cm. cells in the thermostatted cell compartment of a Unicam SP800A spectrophotometer. In the case of $(\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$, a saturated solution ($\approx 10^{-4}\text{M}$) was prepared in the solvent at 35°C , and this was filtered carefully before use. Solutions prepared in this way were found to give the required initial absorbance reading. A similar technique was employed for $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$, although for methanol, ethanol and chloroform it was found necessary to dilute the saturated solutions in order to obtain satisfactory absorbance readings.

Results were computed on a Digital pdp11 computer, rate constants being calculated from values of $\log(A_t - A)$ (where

A_t = absorbance reading at time t , A = absorbance reading after complete reaction) and t , using an unweighted least squares programme. Values for m and R for the two reaction studied were also calculated using an unweighted least squares programme. For $(\text{RhCl}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CCl}))$, the value for chloroform was ignored in the calculation of m and R .

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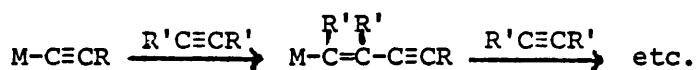
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CHAPTER 5

INVESTIGATION OF THE INSERTION REACTIONS OF ELECTROPHILIC ACETYLENES
INTO PALLADIUM-CARBON BONDS

Insertion reactions of acetylenes into metal-carbon bonds are well known¹⁻⁵. More specifically, insertions of acetylenes into metal-acetylide bonds have recently been reported⁶. This latter type of insertion is believed to be an important step in the transition-metal catalysed oligomerisation of acetylenes⁷⁻⁹. (Scheme 5.1)



Scheme 5.1

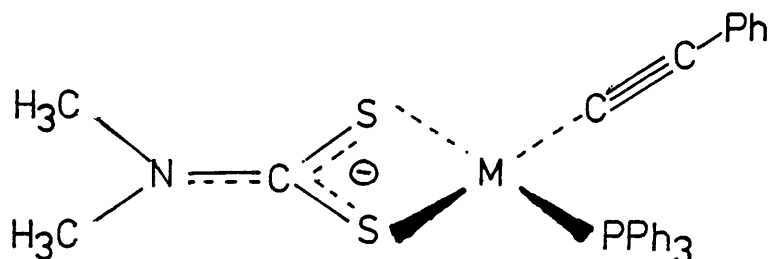
In order to investigate this type of reaction further, the dimethyldithiocarbamate complexes $(M(\text{dmdtc})(C\equiv CPh)(PPh_3))$ ($M=Pt, Pd$) have been prepared, and their reactivity towards acetylene insertion compared with that of the complexes $(MX(C\equiv CPh)(PPh_3)_2)$ ($M=Pd$; $X=Cl, Br$). Two compounds, $(M(HC\equiv CH_2)(\text{dmdtc})(PPh_3))$ ($M=Pt, Pd$) have also been prepared, and a preliminary investigation of their reactivity towards insertion has been made.

5.1 Preparation of the dimethyldithiocarbamate complexes

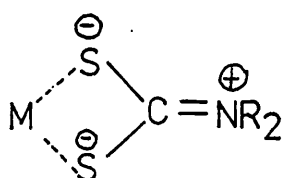
Reaction of either of the complexes trans-($PdX(C\equiv CPh)(PPh_3)_2$) ($X=Br, Cl$) with sodium dimethyldithiocarbamate in acetone gave a good yield of the palladium complex (5.1). The platinum derivative (5.2) was prepared similarly from any of the compounds cis- or trans-($PtX(C\equiv CPh)(PPh_3)_2$) ($X=Cl, Br, I$). Both derivatives are yellow, air-stable solids, fairly soluble in acetone, and very soluble in chloroform or dichloromethane.

The i.r. spectra of the products include $C\equiv C$ stretching-frequencies at 2120cm^{-1} , and a strong band due to the dimethyldithiocarbamate ligand between 1540 and 1550cm^{-1} . The spectra also show medium-intensity

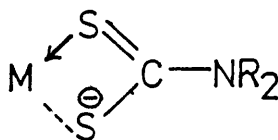
bands at 377cm^{-1} ($\text{M}=\text{Pt}$) and 372cm^{-1} ($\text{M}=\text{Pd}$).

(5.1) $\text{M}=\text{Pd}$ (5.2) $\text{M}=\text{Pt}$

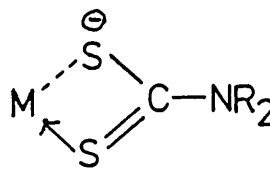
Three canonical forms are possible for metal-dialkyldithiocarbamate complexes (5.3). Chatt et al.¹⁰ have suggested that the three forms contribute equally to the structure of N-alkyl and N,N-dialkyldithiocarbamate complexes, but some later work suggests that form (5.3a) makes a greater contribution than the others¹¹.



(a)



(b)



(c)

(5.3)

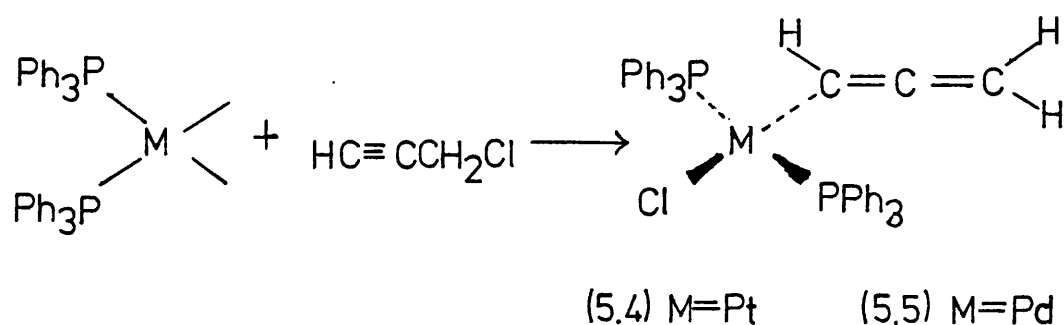
Both sets of workers assign an i.r. absorption between 1560 and 1480cm^{-1} to the $\text{C}=\text{N}$ bond, showing that resonance form (5.3a) makes an important contribution to the structures of these complexes. The absorptions between 1540 and 1550cm^{-1} observed in compounds (5.1) and (5.2) can therefore be assigned to $\text{C}=\text{N}$ stretching, while the bands at 377 and 372cm^{-1} , by analogy with other systems¹¹, are due to $\text{M}-\text{S}$ stretching.

These dialkyldithiocarbamate complexes are in some ways analogous to the nickel-acetylacetonate compounds, $(\text{Ni}(\text{acac})\text{R}(\text{PR}'_3))$

(R = alkyl or phenyl) which have been reported¹²⁻¹⁴. Attempts to prepare acetylacetonate derivatives from $(MX(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ ($M=\text{Pt}, \text{Pd}$) were, however, unsuccessful. This is a reflection of the "soft-acid" character of Pt(II) and Pd(II) , involving a greater affinity for sulphur than for oxygen.

Two further dimethyldithiocarbamate complexes, $(M(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$ were prepared. This involved the initial synthesis of the σ -bonded metaloallenes $(M\text{Cl}(\text{HC}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2)$ from propargyl chloride and either $(\text{Pd}(\text{PPh}_3)_4)$ or $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$. Previous work on propargyl halides by Collman et al. has involved the preparation of a platinum complex having bromine as the halogen¹⁵: no work has been published on palladium analogues.

The reaction shown in Scheme 5.2 is an example of the well known "propargylic rearrangement", in which the acetylene has rearranged to an allene, e.g.¹⁶.



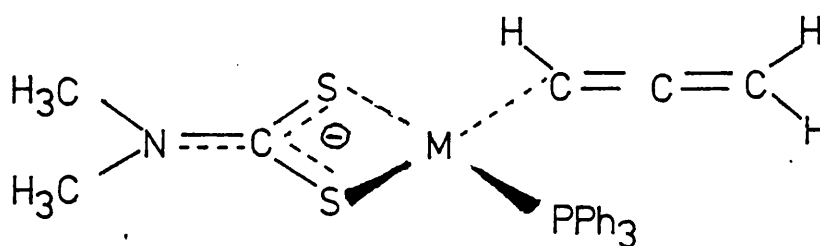
Scheme 5.2

The i.r. spectrum of the platinum complex (5.4), prepared from $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$ in benzene solution, indicates trans geometry (see Section 3.1); the palladium compound (5.5) is also probably trans. Both complexes have i.r. absorptions near 1920cm^{-1} due to the stretching vibration of the allene moiety.

The ^1H n.m.r. spectra of these complexes, whilst showing a resonance due to the methylene protons at $\tau \approx 6$, and a peak due to the remaining

allenic proton at $\tau \approx 5$, are not very well resolved. Better spectra are obtained, however, on preparing the dimethyldithiocarbamate complexes.

Dimethyldithiocarbamate derivatives of compounds (5.4) and (5.5) were prepared in a similar manner to those of $(MX(C\equiv CPh)(PPh_3)_2)$ and are of the form (5.6). They too, are yellow, air-stable solids, having the expected spectroscopic properties. Relevant i.r. and n.m.r. data for all the new dimethyldithiocarbamate complexes are given in Tables 5.1 and 5.2.



(5.6) $M = Pt \text{ or } Pd$

The n.m.r. spectra of compounds (5.6) clearly show the presence of the σ -allenyl ligand. The two methyl groups of the dithio ligand appear as separate resonances for all the complexes studied, except for $(Pd(dmdtc)(C\equiv CPh)(PPh_3))$ in which only one line is observed. The presence of two methyl resonances is good evidence for considerable amounts of C=N character, resulting in a lack of rotation about this bond. The occurrence of only one methyl resonance in one of the compounds may simply be due to accidental equivalence, or may possibly indicate less C=N character, although the i.r. spectrum is not in agreement with this latter theory.

Table 5.1 N.m.r.* data for some dimethyldithiocarbamate complexes of platinum and palladium

Complex	$\text{N}(\text{CH}_3)_2$	$\text{HC}\equiv\text{C}$	$\text{C}=\text{CH}_2$	Phenyl
$(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$	6.73 (s, 6H)			2.1 - 2.8 (br, 15H)
				2.97 (br, 5H)
$(\text{Pt}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$	6.73 (s, 3H)			2.0 - 2.8 (br, 15H)
	6.83 (s, 3H)			2.97 (br, 5H)
$(\text{Pd}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$	6.64 (s, 3H)	4.94 (d x t $J_{\text{PH}}=16\text{Hz}, J_{\text{HH}}=6\text{Hz}$)	6.07 (d, $J_{\text{HH}}=6\text{Hz}$)	2.58 (br, 15H)
	6.75 (s, 3H)			
$(\text{Pt}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$	6.70 (s, 3H)	4.64 (m)	6.10 (d, $J_{\text{HH}}=6\text{Hz}$; Pt satellites, $J_{\text{PtH}}=50\text{Hz}$)	2.56 (br, 15H)
	6.80 (s, 3H)			

* Measured in CDCl_3 solution. Values are in τ .

Table 5.2 I.r* data for some dimethyldithiocarbamate complexes of palladium and platinum

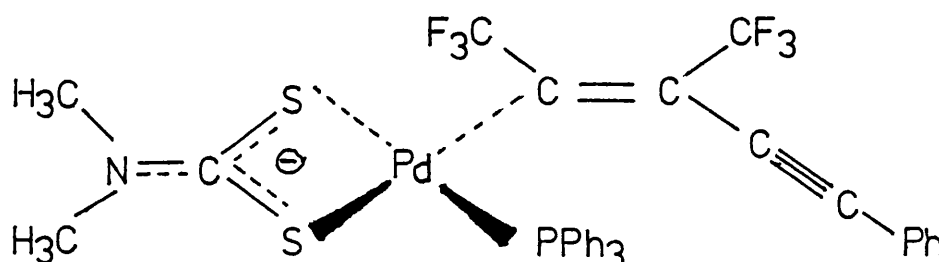
<u>Complex</u>	<u>$\nu(\text{C}\equiv\text{C})$</u>	<u>$\nu(\text{C}=\text{C}=\text{C})$</u>	<u>$\nu(\text{C}=\text{N})$</u>	<u>$\nu(\text{M}-\text{S})$</u>
$(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$	2122, 2110		1543	372
$(\text{Pt}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$	2120		1548	377
$(\text{Pd}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$		1900	1545	368
$(\text{Pt}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$		1907	1555	376

* Values are in cm^{-1} . Spectra measured as Nujol mulls.

5.2 Insertion of electrophilic acetylenes into the palladium-carbon bond of the complex $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$

The preparation of the new dimethyldithiocarbamate complexes of platinum and palladium prompted an investigation of the possibility of inserting acetylenes into the metal-acetylide bond.

Hexafluorobut-2-yne readily reacted with $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$ at room temperature to give a pale-yellow, crystalline solid identified as $(\text{Pd}(\text{dmdtc})((\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)\text{C}\equiv\text{CPh})(\text{PPh}_3))$ (5.7).



(5.7)

The ^{19}F n.m.r. spectrum of (5.7) shows two resonances at -2.25 (d x q, 3F, $J_{\text{FF}} = 13.3\text{Hz}$, $J_{\text{PF}} = 1.7\text{Hz}$) and + 5.43 (d x q, 3F, $J_{\text{FF}} =$

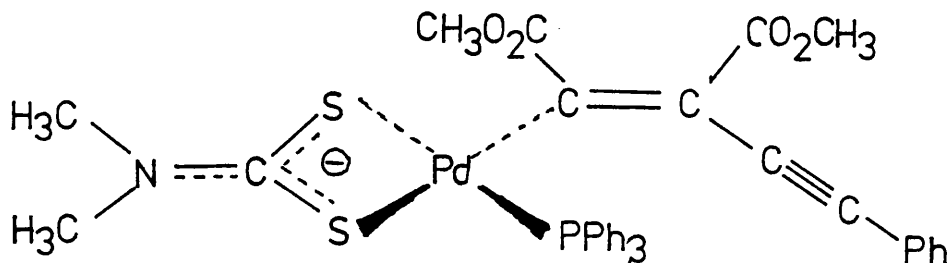
13.3Hz, $J_{\text{PF}} = 2.3\text{Hz}$) relative to α,α,α -trifluorotoluene. By analogy with some $\text{Pt-C}(\text{CF}_3)=\text{C}(\text{CF}_3)-$ systems^{1,17}, the high-field signal may be assigned to the $\beta\text{-CF}_3$ group, and the low-field signal to the $\alpha\text{-CF}_3$. The large quartet splitting due to fluorine-fluorine coupling, having a J value of 13.3Hz, indicates that cis insertion has occurred¹⁷, since trans insertion would be expected to give J values of 1 - 3Hz¹⁸. The smaller doublet splittings must be due to fluorine-phosphorus coupling. Clark¹⁷ has observed a similar long-range splitting in the system P-Pt-C=CF- .

The i.r. spectrum of (5.7) has a weak absorption at 2205cm^{-1} , attributable to the acetylide group. The dimethyldithiocarbamate group gives rise to a C=N stretching-vibration at 1538cm^{-1} ; there is a palladium-sulphur stretch at 371cm^{-1} , whilst a medium intensity band at 1570cm^{-1} may be due to the vinylic double-bond. The ^1H n.m.r. spectrum is as anticipated, the two methyl groups appearing as separate resonances at 6.70 and 6.80 τ .

The isolation of this insertion-product from room temperature reaction suggests that the dmdtc ligand is increasing the reactivity of the palladium-carbon bond towards insertion, since the insertion of dimethylacetylenedicarboxylate into a palladium-acetylide bond, recently carried out by Sonogashira and co-workers⁶, required the use of more forcing conditions (2 hours in dioxan at 85°C). These workers also employed rather more basic phosphines bonded to the palladium.

An interesting side-product in the hexafluorobut-2-yne insertion reaction is a very small amount of a yellow, insoluble solid. The i.r. spectrum of this shows strong C-F absorptions between 1100 and 1250cm^{-1} , and also a C=N band at 1550cm^{-1} . The low yield, and insolubility of this solid makes characterisation difficult, but it is possible that it is a polymeric product, formed by multiple insertion of C_4F_6 into a palladium-carbon bond.

Reaction of $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$ with dimethylacetylenedicarboxylate at room temperature also gave an insertion product, (5.8).



(5.8)

The insertion is probably cis, by analogy with the hexafluorobut-2-yne product. The ^1H n.m.r. of this compound has two signals due to the $\text{N}(\text{CH}_3)_2$ group at 6.72 and 6.86 τ whilst the two methyl ester groups give rise to just one line, at 6.42 τ . The i.r. spectrum has a very weak $\text{C}\equiv\text{C}$ absorption at 2200cm^{-1} , and a shoulder on the $\text{C}=\text{N}$ band at 1541cm^{-1} may be due to the vinylic double bond.

This reaction also gave rise to a very low yield of a yellow insoluble solid, the i.r. spectrum of which indicates the presence of $\text{C}=\text{O}$ groups, and a dimethyldithiocarbamate ligand.

Attempts to obtain insertion products from $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$ with tetrafluoroethylene and carbon monoxide were unsuccessful, giving only unreacted starting material. Reaction of the platinum derivative, $(\text{Pt}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$, with dimethylacetylenedicarboxylate, failed to produce a product analogous to (5.8), this being a reflection of the relative strengths of the $\text{M}-\text{C}$ bonds. A similar failure to obtain a product by insertion into a platinum-carbon bond has been observed by Hagihara et al.¹⁹.

In order to test further the deduction that the dimethyldithiocarbamate ligand is labilising the palladium-carbon bond towards insertion, reactions were carried out between trans- $(\text{PdX}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ ($\text{X} = \text{Cl}, \text{Br}$) and the

electrophilic acetylenes. The isolation of insertion products from these reactions would tend to refute this suggestion.

5.3 Reaction of electrophilic acetylenes with $\text{trans}-(\text{PdX}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$

Room temperature reaction of $\text{trans}-(\text{PdCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ with hexafluorobut-2-yne gave a yellow solution (in benzene) and large amounts of a white, insoluble solid. The white material had very broad, strong absorptions in the C-F region of the infra-red, but few other bands were visible. This, therefore, appears to be a high polymer of C_4F_6 ²⁰.

The yellow solid obtained from solution appears, on the basis of ¹⁹F n.m.r. to be a mixture. The major component is $(\text{Pd}(\text{PPh}_3)_2(\text{C}_4\text{F}_6))$ formed in <30% yield which gives rise to a doublet at -11.62 ($J_{\text{PF}}=11.3\text{Hz}$) relative to α,α,α -trifluorotoluene, in good agreement with the reported spectrum²¹. A minor component is revealed by two very weak quartets at -12.55 and -3.55 ($J_{\text{FF}}\approx 13.8\text{Hz}$). This may be an insertion product, but the very low yield did not permit its isolation. The i.r. spectrum also suggests the presence of $(\text{Pd}(\text{PPh}_3)_2(\text{C}_4\text{F}_6))$, there being bands at $\sim 1800\text{cm}^{-1}$ attributable to the coordinated triple-bond. The formation of this π -bonded acetylene complex involves the reductive elimination of $\text{PhC}\equiv\text{CCl}$ from the starting material.

An attempt to purify this mixture by recrystallisation from dichloromethane/ethanol showed that it also contains $\text{trans}-(\text{PdCl}_2(\text{PPh}_3)_2)$ ($\sim 6\%$ yield). The remaining components underwent slow decomposition in solution, and no pure compounds could be isolated. It therefore seems that any insertion reaction taking place in this system is less favourable than formation of $(\text{C}_4\text{F}_6)_n$, $(\text{Pd}(\text{PPh}_3)_2(\text{C}_4\text{F}_6))$, and $\text{trans}-(\text{PdCl}_2(\text{PPh}_3)_2)$.

Reaction of $(\text{PdCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ with dimethylacetylenedicarboxylate also failed to produce an insertion-product. A dark green, insoluble

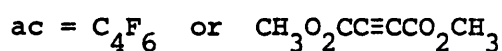
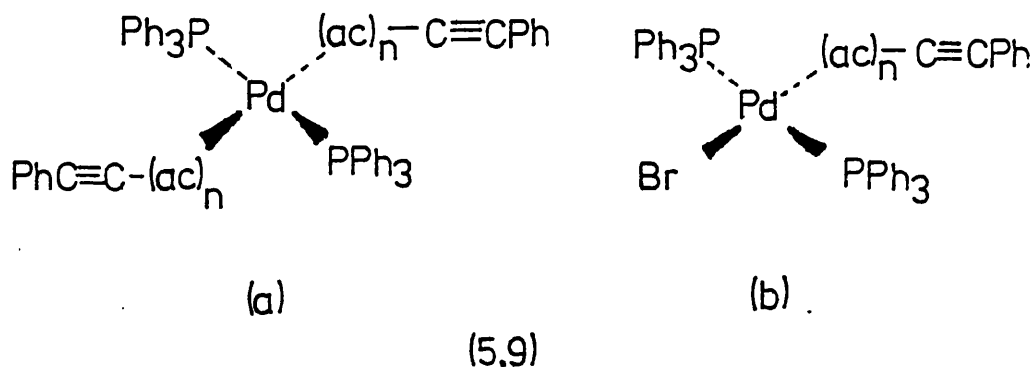
solid was obtained from this reaction (i.r.:only very broad bands, with possible C=O at 1608cm^{-1}), and although an orange solid obtained from the residual solution had C=O absorptions in the i.r., attempted purification gave only trans-(PdCl₂(PPh₃)₂).

When the bromo-analogue, (PdBr(C≡CPh)(PPh₃)₂), was reacted with hexafluorobut-2-yne, no formation of the π -bonded acetylene complex occurred. Instead, the only products obtained from the reaction were trans-(PdBr₂(PPh₃)₂), in high yield, and a dark-green insoluble solid. The latter product has C-F i.r. bands and phosphine absorptions in the regions $1570\text{--}1600\text{cm}^{-1}$, $690\text{--}770\text{cm}^{-1}$ and $490\text{--}530\text{cm}^{-1}$. There is also a medium intensity band at 1606cm^{-1} .

Dimethylacetylenedicarboxylate also reacted with (PdBr(C≡CPh)(PPh₃)₂) to give good yields of trans-(PdBr₂(PPh₃)₂) and a green, insoluble solid, having strong carbonyl and phosphine absorptions in the i.r. A third product, obtained in low yield, was an orange-brown solid. The i.r. of this shows C=O bands, and the n.m.r. contains a very broad resonance at 6-7 τ , but no satisfactory analytical data were obtained.

The isolation of trans-(PdBr₂(PPh₃)₂) in these last two reactions suggests that a second product may be of the form (PdYZ(PPh₃)₂) (Y,Z \neq Br). Although trans-(Pd(C≡CPh)₂(PPh₃)₂) might have been expected to be a product, it was not observed. A possible explanation for the formation of the dark green, insoluble materials is that they derive from insertion of one or more molecules of the acetylenes into the palladium carbon bonds (5.9a or b).

It is not possible, on the basis of this evidence, to judge whether or not insertion into the Pd-C bonds is occurring in trans-(PdX(C≡CPh)(PPh₃)₂) compounds. It is, however, apparent that mono-insertion products analogous to (5.7) and (5.8) are either not formed, or are not stable relative to further reaction, in these systems.



It may therefore be either that the dimethyldithiocarbamate group labilises the Pd-C bond towards acetylene insertion, or that the mono-insertion product formed in this case is more stable. If the latter is true, it may be because breakdown to $(\text{Pd}(\text{dmdtc})_2)$, equivalent to breakdown to $(\text{PdBr}_2(\text{C}\equiv\text{CPh})_2)$, is not favoured. The basicity of the dmdtc ligand may also influence the reaction, as may the relief of steric interaction caused by substitution of a halogen and triphenylphosphine by dmdtc.

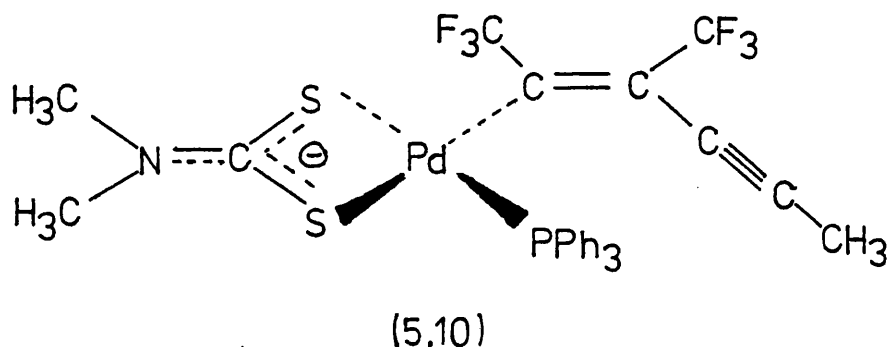
5.4 Reaction of hexafluorobut-2-yne with $(\text{Pd}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$

Reaction of $(\text{Pd}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$ with C_4F_6 in benzene solution, over 2 days, gave large amounts of a yellow solid, insoluble in common organic solvents. The i.r. spectrum of this solid clearly indicates the presence of a dmdtc ligand ($\text{C}=\text{N}$ at 1555cm^{-1}), triphenylphosphine groups, and C-F bonds. A possible explanation for the formation of this material is that it results from multiple insertion of C_4F_6 into the Pd-C bond, as was postulated for the reaction of C_4F_6 with $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$ described in section 5.2. Once again, however, the insolubility of the material makes characterisation difficult.

The remaining product from reaction of C_4F_6 with

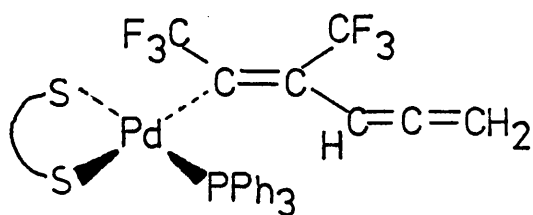
(Pd(HC=C=CH₂)(dmdtc)(PPh₃)) consists of an oily, red solid. An attempt to purify this was made using preparative T.L.C., and a yellow solid was obtained in low yield. The i.r. spectrum of this has a weak absorption at 2200cm⁻¹ (possibly C≡C, as in complex 5.7), and other bands include those due to the dmdtc ligand, C-F bonds, and triphenylphosphine groups. The ¹⁹F n.m.r. spectrum shows, however, that it has not been possible to obtain a single compound by this method, since although two nicely resolved quartets are visible at -11.45 and -3.02 ppm (J=14Hz) relative to α,α,α-trifluorotoluene, a large number of other signals, several of them very broad, are present between -13.0 and +6.0 ppm. Neither was it possible to achieve purification by recrystallisation of the solid.

The spectroscopic data suggest that one product of this reaction is (5.10), formed by insertion of C₄F₆ into the metal-allene bond, followed by rearrangement of the allene group to an acetylene. Other

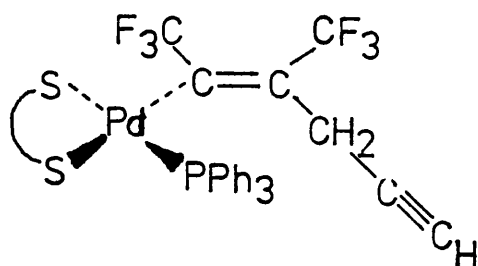


possible products formed by insertion of C₄F₆ into the metal-allene bond are (5.11) and 5.12), and these two compounds may both be present in the mixture.

The ¹H n.m.r. spectrum also strongly suggests the presence of (5.10), since it contains a sharp singlet at 8.73τ, attributable to the methyl group joined to the acetylenic triple-bond. Apart from signals due to the triphenylphosphine and the dimethyldithiocarbamate



(5.11)



(5.12)

groups, there are also two weak signals at 4.0 and 6.29 , which may be due to the allenic proton and the methylene protons respectively of a complex (5.11).

Consequently, although it has not proved possible to fully explain the complexity of the ^{19}F n.m.r. spectrum, a principal product of the reaction appears to be an insertion product (5.10), formed via rearrangement of (5.11), which, on the basis of spectroscopic evidence, may also be present in the mixture.

5.5 Summary

Stable products, resulting from mono-insertion of the acetylene into the palladium-carbon bond, have been isolated from the reactions of C_4F_6 and $\text{CH}_3\text{O}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3$ with $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$. No reaction was observed with the analogous platinum complex.

Comparison of these reactions with those of $(\text{MX}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ ($\text{M} = \text{Pd}$, $\text{X} = \text{halogen}$) shows that no mono-insertion products are obtained from the latter complexes, although multiple insertion may be occurring. The influence of the dimethyldithiocarbamate ligand may therefore involve either labilisation of the metal-carbon bond towards insertion, or a stabilisation of the mono-insertion product towards further reaction.

A preliminary examination of the reactivity of the palladium-allene σ -bond towards acetylene insertion suggests that a mono-insertion product is formed, and that the allene group is isomerised to an acetylenic linkage. A full characterisation of all the products of this reaction has not yet proved possible.

5.6 Experimental

Melting points, analytical data, and infra-red, ^1H n.m.r. and ^{19}F n.m.r. spectra are presented in this section for all new compounds.

Melting points were recorded on a Reichart hot-stage apparatus, and are uncorrected. Microanalytical data were obtained by D. Butterworth, The Butterworth Microanalytical Consultancy Ltd., 41, High Street, Teddington, Middlesex, or by C.H.N. Analysis Ltd., Alpha House, South Wigston, Leicester.

Infra-red spectra were recorded on a Perkin Elmer 580 spectrophotometer, using Nujol mulls, between CsI plates, and were calibrated using a polystyrene film. Values quoted are in cm^{-1} .

^1H n.m.r. spectra were recorded on a Jeol JNM-PS-100 spectrometer, operating at 100MHz, chemical shifts (τ) being reported relative to internal T.M.S. ^{19}F n.m.r. spectra were recorded on a Jeol JNM-PS-100 spectrometer, operating at 94.1MHz, chemical shifts (ppm) being reported relative to external α,α,α -trifluorotoluene.

Solvents

Analar benzene and diethyl ether were dried by standing over sodium wire, and were filtered and 'pump-freeze' degassed under high vacuum before use.

All other solvents used were normal reagent grade, and were used without further purification, unless otherwise stated.

Ligands and reagents

The following materials were purchased:

sodium dimethyldithiocarbamate dihydrate	- Aldrich Chemical Co.
propargyl chloride	- Aldrich Chemical Co.
dimethylacetylenedicarboxylate	- Eastman Kodak Ltd.

Other materials were purchased as outlined in Chapters 2 and 3.

Palladium dichloride and potassium tetrachloroplatinite were obtained on loan from Johnson Matthey Ltd.

The preparations (or references thereto) of $(\text{Pd}(\text{PPh}_3)_4)$, $(\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene}))$, $(\text{PdX}(\text{C}\equiv\text{CPh})(\text{PPh}_3))$ ($\text{X} = \text{Cl}, \text{Br}$) and $(\text{PtX}(\text{C}\equiv\text{CPh})(\text{PPh}_3))$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are given in Chapter 3.

A Preparation of some dithiocarbamate complexes of the type
(M(dmdtc) (C≡CPh) (PPh₃)₂) and (M(dmdtc) (CH=C=CH₂) (PPh₃)₂) (M = Pt or Pd)

i Dimethyldithiocarbamato(phenylacetylido)(triphenylphosphine)platinum(II)

This complex could be prepared starting from any of the compounds cis- or trans-(Pt(C≡CPh)X(PPh₃)₂) (X=Cl,Br,I). Thus, for example, a suspension of cis-(PtI(C≡CPh) (PPh₃)₂) (0.27g, 0.28mmol) in acetone was stirred with 0.07g (0.39mmol) of sodium dimethyldithiocarbamate, at room temperature, under an atmosphere of dry nitrogen. An immediate reaction occurred, giving a lemon coloured suspension. After 2 hours, the yellow solid was filtered, washed with water, ethanol, and diethyl ether, dried, and identified as (Pt(dmdtc) (C≡CPh) (PPh₃)₂). Evaporation of the solvent from the filtrate, followed by addition of ethanol, gave a further quantity of the product. Yield = 0.16g, 85%.

M. Pt. 224 - 226°C (decomp.)

Analysis Calculated: C, 51.3; H, 3.9%

Found: C. 51.5; H, 3.9%

Infra-red 2120m 1595m 1548s,br 1482s 1434s 1400s 1314w 1272w 1250m
 1217w 1185m 1176w 1160m 1154m 1099s 1070w 1054w 1031m 1000m 974m
 932w 912w 861vw 846vw 758s 749m,sh 745m,sh 712s 696s 618w 567w
 539s 519s 500s 460m 438m 377m 332w 263w.

¹H n.m.r. (in CDCl₃): 2.0 - 2.8(br, 15H); 2.97(br, 5H); 6.73(s,3H)
 6.83(s,3H).

ii Dimethyldithiocarbamato(phenylacetylido)(triphenylphosphine)palladium(II)

This complex could be prepared from either of the compounds trans-(Pd(C≡CPh)X(PPh₃)₂) (X = Br,Cl). Thus, for example, a suspension of 0.60g (0.74mmol) of trans-(PdBr(C≡CPh) (PPh₃)₂) was stirred with sodium dimethyldithiocarbamate (0.21g, 1.17mmol), at room temperature, under an atmosphere of dry nitrogen. Reaction occurred immediately, giving a lemon coloured suspension. After 1 hour, the yellow solid

was filtered, washed with water, ethanol and diethyl ether, dried and identified as $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$. Evaporation of the solvent from the filtrate, followed by addition of ethanol, gave a further quantity of the product. Yield = 0.36g, 83%.

M. Pt. 151 - 152°C (decomp.)

Analysis Calculated: C, 59.0; H, 4.4%

Found: C, 59.4; H, 4.7%

Infra-red 2122m 2110m 1595m 1543s,br 1481s 1437s 1399s 1311vw
1255m,br 1209w 1184m 1158m 1153m 1102m 1096s 1070w 1053vw 1026w
999w 973m 907w 853vw 795vw 759s 750s 708m 695s 617vw 575vw
530s 511s 498s 465w 441w 372m.

^1H n.m.r. (in CDCl_3): 2.1 - 2.8(br, 15H); 2.97(br, 5H); 6.73(s, 6H).

iii σ -allenyl(dimethyldithiocarbamato)(triphenylphosphine)platinum(II)

This compound was prepared from the previously unknown trans- $(\text{PtCl}(\text{HC}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2)$, the preparation of which is given first. A solution of $(\text{Pt}(\text{PPh}_3)_2)$ (trans-stilbene) (0.45g, 0.5mmol) in benzene was stirred with 0.05g (0.67mmol) of propargyl chloride at room temperature, under an atmosphere of dry nitrogen, for 3 hours. Slow concentration of the solution, with addition of ethanol, gave white microcrystals of trans- $(\text{PtCl}(\text{HC}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2)$. Yield = 0.24g, 90%.

M. Pt. 197-203°C (decomp.)

Analysis Calculated: C, 59.0; H, 4.2%

Found: C, 58.9; H, 4.5%.

Infra-red 1922m 1586w 1571w 1480s 1436s 1433s 1281m 1267w 1098s
1064w,br 1028w 998m 971vw 922vw 852w 845w 817m 754m 745s
707s 692s 617w 543vw 525s 510s 502s 458w 439w 422w 299m.

$(\text{Pt}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$ was prepared by stirring a suspension of trans- $(\text{PtCl}(\text{HC}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2)$ (0.08g, 0.10mmol) in acetone with sodium dimethyldithiocarbamate (0.02g, 0.12mmol). An immediate reaction

occurred, giving a yellow solution. After $\frac{1}{2}$ hour, the yellow precipitate was filtered, washed with water, ethanol and diethyl ether, dried and identified as $(\text{Pt}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$. Removal of the solvent from the filtrate, followed by addition of ethanol, gave a further quantity of the product. Yield = 0.04g, 65%.

M. Pt. 189-191°C

Analysis Calculated: C, 46.7; H, 3.9%

Found: C, 46.4; H, 3.9%

Infra-red 1907m 1555s 1469m 1431s 1400s 1249w 1178w 1166w
1158m 1099s 1068w 1027w 999w 971w 859w 794m 751m 744m 738m
708s 692s 619vw 539s 516s 500s 452w 437w 376m 337w.

^1H n.m.r. (in CDCl_3): 2.56(br, 15H); 4.64(m, 1H); 6.10(d, 2H, $J_{\text{HH}} = 6\text{Hz}$; platinum sidebands, $J_{\text{PtH}} = 50\text{Hz}$); 6.70(s, 3H); 6.80(s, 3H).

iv σ -allenyl(dimethyldithiocarbamate)(triphenylphosphine)palladium(II)

This compound was prepared from the previously unknown complex $(\text{PdCl}(\text{HC}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2)$, the preparation of which is given first. A suspension of $(\text{Pd}(\text{PPh}_3)_4)$ (0.57g, 0.49mmol) in diethyl ether was stirred with 0.05g (0.67mmol) of propargyl chloride, at room temperature, under an atmosphere of dry nitrogen. After 4 hours, the white precipitate was filtered, washed with diethyl ether, dried in vacuo and identified as $(\text{PdCl}(\text{HC}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2)$. Yield = 0.32g, 92%.

M. Pt. 168-172°C (decomp.)

Analysis Calculated: C, 66.4; H, 4.7%

Found: C, 66.5; H, 4.7%

Infra-red 1917m 1585w 1570w 1470m 1432s 1180w 1155w 1148w
1096s 1070w 1038w 1026w 998m 920vw 831w 812m 752m,sh 743s
705m 690s 618w 531s 508s 497s 455w 437w 420vw 393w 293m.

$(\text{Pd}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$ was prepared by stirring an acetone suspension of $(\text{PdCl}(\text{HC}=\text{C}=\text{CH}_2)(\text{PPh}_3)_2)$ (0.32g, 0.45mmol) with sodium dimethyldithiocarbamate (0.18g, 0.10mmol). An immediate reaction occurred, giving a yellow suspension. After $\frac{1}{2}$ hour, the yellow solid was filtered, washed with water, ethanol and diethyl ether, dried and identified as $(\text{Pd}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$. Removal of the solvent from the filtrate, followed by addition of ethanol gave a further quantity of the product. Yield = 0.20g, 84%.

M. Pt. 128 - 131°C (decomp.)

Analysis Calculated: C, 54.5; H, 4.6%

Found: C, 55.0; H, 4.7%

Infra-red 1900s 1570w 1545s,br 1479s 1432s 1400s 1250m 1178w
1165w 1158m 1150m,sh 1096s 1070w 1051w 1030w 998w 972w 854w
838w 783m 752m 745m 739m 725w,br 707s 694s 620w 552vw 528s
512s 495s 460w 448w 436w 397w 368m 343w.

^1H n.m.r. (in CDCl_3): 2.58 (br, 15H); 4.94 (6 lines, 1H, $J_{\text{PH}} = 16\text{Hz}$, $J_{\text{HH}} = 6\text{Hz}$); 6.07 (d, 2H, $J_{\text{HH}} = 6\text{Hz}$); 6.64 (s, 3H); 6.75 (s, 3H).

B Insertion into the M-C bond of the compounds $(\text{M}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$
(M = Pd or Pt)

i $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3)) + \text{hexafluorobut-2-yne}$

An excess of hexafluorobut-2-yne (1.0cm^3) was condensed (-196°C) onto a benzene solution of $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$ (0.3g, 0.5mmol) contained in a Carius tube. The tube was sealed, and shaken at room temperature for 48 hours, after which it was opened, and volatile material removed. A small amount (0.03g) of a yellow solid (insoluble in benzene, CHCl_3 , CH_2Cl_2 , acetone; i.r. spectrum shows C-F absorptions between 1100 and 1250cm^{-1}) was filtered. The solvent was removed from the orange filtrate, giving an oily solid, which crystallised on cooling in ice and scratching with methanol. The pale yellow microcrystals

were washed with diethyl ether, dried, and identified as

$(\text{Pd}(\text{dmdtc})((\text{CF}_3)\text{C}=\text{C}(\text{CF}_3)\text{C}\equiv\text{CPh})(\text{PPh}_3))$. Yield = 0.2g, 53%.

M. Pt. 170 - 172°C (decomp.)

Analysis Calculated: C, 52.6; H, 3.6%

Found: C, 53.0; H, 3.8%

Infra-red 2205vw 1598w 1589w 1570m 1538m,br 1325m 1292w 1220s
1187vw 1178vw 1166m 1160m 1154m 1143s 1124s 1099s 1070w 1060w,br
1030m 1000m 974m 920w 902m 847w 812m 771w,sh 760s 753s 745s
725w 715w,sh 712m 693s,br 620w 576m 560vw 531s 511s 496s
479w 453m 439m 371m.

^1H n.m.r. (in CDCl_3): 2.60(br, 2OH); 6.70(s, 3H); 6.80(s, 3H).

^{19}F n.m.r. (in CDCl_3): -2.25(d x q, 3F, $J_{\text{FF}} = 13.3\text{Hz}$, $J_{\text{PF}} = 1.7\text{Hz}$);
+ 5.43(d x q, 3F, $J_{\text{FF}} = 13.3\text{Hz}$, $J_{\text{PF}} = 2.3\text{Hz}$).

ii $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3)) + \text{dimethylacetylenedicarboxylate}$

An excess (0.14g, 1.0mmol) of dimethylacetylenedicarboxylate was added to a benzene solution of $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$ (0.3g, 0.5mmol), and the solution stirred at room temperature, under an atmosphere of dry nitrogen. After 15 hours, a small amount (0.03g) of a yellow solid, insoluble in CHCl_3 , CH_2Cl_2 , $(\text{CH}_3)_2\text{CO}$ was filtered (i.r. spectrum - very broad C=O at 1680cm^{-1} ; dmdtc at 1550cm^{-1}). Evaporation of the solvent from the filtrate left a red oil, which gave a yellow solid on addition of ethanol. The solid was recrystallised from dichloromethane/ethanol, and identified as

$(\text{Pd}(\text{dmdtc})((\text{CO}_2\text{CH}_3)\text{C}=\text{C}(\text{CO}_2\text{CH}_3)\text{C}\equiv\text{CPh})(\text{PPh}_3))$. Yield = 0.30g, 81%.

M. Pt. 207 - 210°C (decomp.)

Analysis Calculated: C, 57.4; H, 4.4%

Found: C, 56.7; H, 4.7%

Infra-red 2200vw 1711s 1696s 1597w 1587vw 1560m,sh 1541m 1435s
1395s 1315m 1232s 1208s 1184w 1157w 1098s 1072vw 1029vw 1017w

999w 973m 912vw 902vw 786w 758s 750m 725vw 709m 700m 691m
668vw 639vw 620vw 529s 511m 498m 454w 442w 426vw 369w.

^1H n.m.r. (in CDCl_3): 2.65 (br, 2OH); 6.42 (s, 6H); 6.72 (s, 3H);
6.86 (s, 3H).

iii $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3)) + \text{carbon monoxide}$

Slow passage of carbon monoxide through a benzene solution of $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$, resulted, after 2 hours, only in the recovery of the starting material.

iv $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3)) + \text{tetrafluoroethylene}$

An excess of tetrafluoroethylene was condensed (-196°C) onto a benzene solution of $(\text{Pd}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$ contained in a Carius tube. The tube was sealed, and shaken for 48 hours, but work-up of the reaction mixture gave only unchanged starting material.

v $(\text{Pt}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3)) + \text{dimethylacetylenedicarboxylate}$

Stirring a suspension of $(\text{Pt}(\text{dmdtc})(\text{C}\equiv\text{CPh})(\text{PPh}_3))$ in diethyl ether with excess dimethylacetylenedicarboxylate for 3 days resulted only in the recovery of unreacted starting material. Similarly, no reaction occurred on refluxing a benzene solution of the complex with the acetylene for 24 hours.

C Reactions of the compounds $(\text{Pd}(\text{C}\equiv\text{CPh})\text{X}(\text{PPh}_3)_2)$ ($\text{X} = \text{Cl}, \text{Br}$) with hexafluorobut-2-yne and dimethylacetylenedicarboxylate

i Chloro(phenylacetylido)(bis-triphenylphosphine)palladium(II)
+ hexafluorobut-2-yne

An excess of hexafluorobut-2-yne (1.0cm^3) was condensed (-196°C) onto a benzene suspension of $(\text{PdCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2)$ (0.48g, 0.62mmol) contained in a Carius tube. The tube was sealed, shaken at room

temperature for 72 hours, and then opened. Volatile material was removed, and a grey-white solid (0.7g) was filtered (insoluble in all common solvents: i.r. has broad C-F bands at 1240, 1200 and 1170cm^{-1}). Removal of the solvent from the filtrate gave an orange oil, which gave a yellow solid on addition of ethanol. (i.r. includes 1835m, 1815m, 1800m, 1256s, 1221s, 1135s, 1115s, 1096s, 360w, 310w. ^{19}F n.m.r.: $-11.62(\text{d}, J_{\text{PF}} = 11.3\text{Hz})$; $-12.55(\text{q}, J_{\text{FF}} \approx 13.8\text{Hz})$; $-3.55(J_{\text{FF}} = 13.8\text{Hz})$. The first signal is very large, the others are very weak.

Attempted recrystallisation of the yellow solid from dichloromethane/ethanol resulted in the separation of trans-($\text{PdCl}_2(\text{PPh}_3)_2$), (fairly insoluble in dichloromethane, and identified by its i.r. spectrum and M.Pt.), and the decomposition of the remaining solid in solution.

ii Chloro(phenylacetylido)(bis-triphenylphosphine)palladium(II) + dimethylacetylenedicarboxylate

Excess dimethylacetylenedicarboxylate (0.14g, 1.0mmol), was added to a suspension of 0.4g (0.52mmol) of ($\text{PdCl}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2$) in benzene. The mixture was stirred for 48 hours, at room temperature, under an atmosphere of dry nitrogen. A small amount (0.01g) of a green solid, insoluble in common organic solvents, was filtered (i.r.: possible $\text{C}=\text{O}$ at 1608cm^{-1}), and the solvent was then evaporated from the filtrate. Addition of ethanol to the resulting oily solid gave an orange solid (0.15g) having an i.r. spectrum including $\text{C}=\text{O}$ bands at 1710, 1696 and 1688cm^{-1} , but a poor ^1H n.m.r. spectrum. Attempted recrystallisation from dichloromethane/ethanol gave pale yellow crystals of trans-($\text{PdCl}_2(\text{PPh}_3)_2$). (i.r.: $\nu(\text{Pd}-\text{Cl}) = 360\text{cm}^{-1}$; M. Pt. = 270°C (decomp.).

iii Bromo(phenylacetylido)(bis-triphenylphosphine)palladium(II) + hexafluorobut-2-yne

An excess (1.0cm^3) of hexafluorobut-2-yne was condensed (-196°C) onto a benzene suspension of $[\text{PdBr}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2]$ (0.5g, 0.62mmol) in a Carius tube. The tube was sealed, and shaken at room temperature for 40 hours, after which it was opened, and volatile material removed. A dark green solid (0.1g) was filtered (i.r.: C-F bands at 1240 and 1175cm^{-1}) but was found to be insoluble in common organic solvents. The solvent was evaporated from the red filtrate to leave an oily solid. Addition of dichloromethane to this gave trans- $(\text{PdBr}_2(\text{PPh}_3)_2)$ (i.r.: $\nu(\text{Pd-Br}) = 285\text{cm}^{-1}$), and concentration of the dichloromethane solution to 5cm^3 gave only more trans- $(\text{PdBr}_2(\text{PPh}_3)_2)$ (0.3g). The remaining red solution contained no discernible resonances in its ^{19}F n.m.r. spectrum.

iv Bromo(phenylacetylido)(bis-triphenylphosphine)palladium(II) + dimethylacetylenedicarboxylate

An excess (0.14g, 1.0mmol) of dimethylacetylenedicarboxylate was added to a suspension of $[\text{PdBr}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2]$ (0.5g, 0.62mmol) in benzene. After 48 hours, a green solid (0.1g) was filtered (i.r. shows C=O bands at 1686 and 1710cm^{-1}) but it was found to be insoluble in common organic solvents. Concentration of the filtrate gave a red oil. Addition of dichloromethane to this gave trans- $(\text{PdBr}_2(\text{PPh}_3)_2)$ (0.15g), and addition of ethanol, followed by slow concentration of the dichloromethane extract, gave an orange-brown solid (0.04g). This has a broad carbonyl absorption in the i.r. ($\sim 1710\text{cm}^{-1}$), but the ^1H n.m.r. shows, in addition to triphenylphosphine ligands, only a very broad, unresolved, peak at $6\rightarrow 7\tau$. Analytical data were obtained (C, 54.4; H, 4.1%), but these do not fit the more probable formulations for this product.

D Reaction of dimethyldithiocarbamate(σ -allenyl) (triphenylphosphine) palladium(II) with hexafluorobut-2-yne

An excess (1.5cm^3) of hexafluorobut-2-yne was condensed (-196°C) onto a solution of 0.63g (1.2mmol) of $(\text{Pd}(\text{HC}=\text{C}=\text{CH}_2)(\text{dmdtc})(\text{PPh}_3))$ in benzene, contained in a Carius tube. The tube was sealed, and shaken at room temperature for 48 hours, after which a yellow solid had formed, and the solution had become red. The tube was then opened, volatile material was removed, and the yellow solid was filtered, washed with benzene and dried. Yield = 0.32g . It was found to be insoluble in common organic solvents, whilst its i.r. spectrum includes bands at 1555 , 1240 , 1175 , 720 , 620 and 500cm^{-1} . Evaporation of the solvent from the filtrate gave a red amorphous solid (0.3g). Attempted purification of this by preparative T.L.C., using benzene eluant and activated alumina adsorbent, gave a yellow solid (0.09g). The i.r. spectrum of this includes bands at 2200w , 1542m , 1245s , 1226s , 1160s , 695m , 530m , 511m , 497w , 370w , but the ^{19}F n.m.r. (in CDCl_3) includes a large number of unresolved resonances between -13.0 and $+6.0$ ppm, as well as two quartets at -11.45 and -3.02 ($J \approx 14\text{Hz}$).

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