

REACTIONS OF SOME d^8 METAL COMPLEXES.

A thesis presented for the
Degree of Doctor of Philosophy
in the

Faculty of Science

by

DAVID MICHAEL BARLEX

University of Leicester

September 1970

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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 1967 and September 1970, under the supervision of Dr. R.D.W. Kemmitt. The work has not been, and is not concurrently being, presented for any other degree.

D.M. Barley:

September 1970

REACTIONS OF SOME d^8 METAL COMPLEXES

A thesis presented for the Degree of Doctor of Philosophy in the Faculty of Science by DAVID MICHAEL BARLEX. University of Leicester. September 1970.

SUMMARY

A brief review of the oxidative addition reactions of square planar d^8 complexes is presented.

The reaction of some carboxylate complexes of platinum, $Pt(OCOR)_2L_2$ in both alcoholic and aprotic media, with acids, unsaturated molecules and organo-halo compounds are reported. New platinum complexes have been isolated and characterised. Some related reactions of cis - dichloro bis(triphenylphosphine)platinum(II) have been investigated.

The oxidative addition of o - quinones to complexes of the platinum metals in low oxidation state have been investigated. New complexes containing the metal - 1,2 - dioxylene system have been isolated and characterised.

The reaction of some acetylacetonato rhodium complexes of the type $Rh(acac)L_2$, unsaturated molecules and organohalo compounds have been investigated. New rhodium complexes have been isolated and characterised including a novel complex in which the rhodium acetylacetonate system has undergone a 1,4 - addition reaction with hexafluorobut -2- yne.

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I acknowledge the help of my fellow research students whose healthy brand of cynicism did so much to maintain rational thought in the face of chemical intuition.

My greatest debt is to my parents without whose help over many years this work would not have been possible.

As to my wife who typed this thesis I am reminded of Proverbs Ch.31 vv.10-12.

The award of a maintenance grant from the Science Research Council is acknowledged.

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For Christine
and
'Thumper'

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INTRODUCTION

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OXIDATIVE - ADDITION REACTIONS OF SQUARE PLANAR d^8
COMPLEXES

Square planar d^8 metal complexes are coordinately unsaturated and readily undergo oxidative addition reactions with both polar and non polar molecules¹.

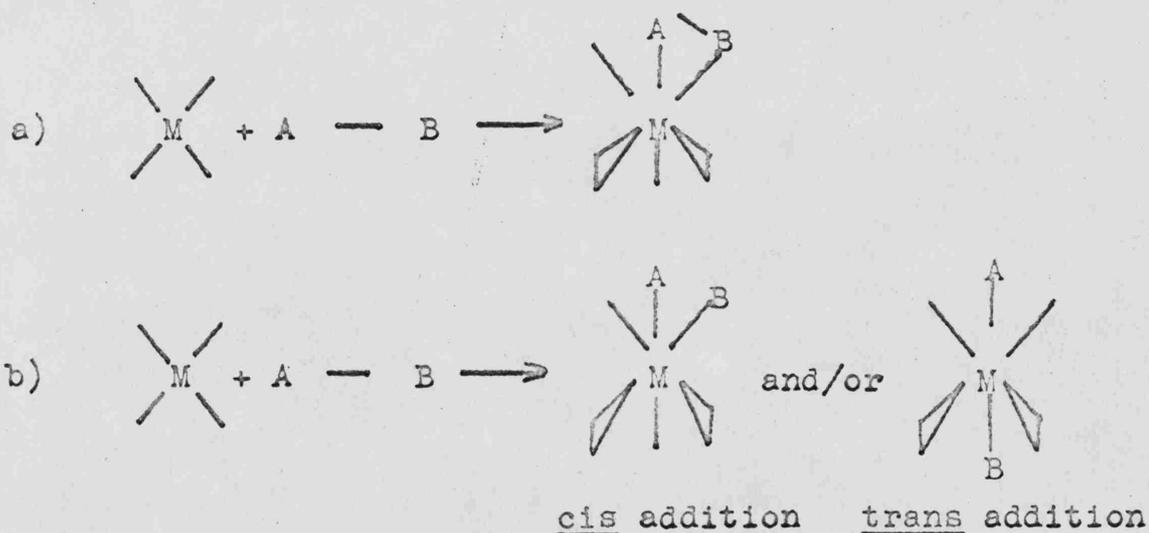
Such reactions may be subdivided into several groups:

1) Those reactions in which the addendum (A - B) does not break into two fragments upon reaction with the metal complex (Fig. 1a).

2) Those reactions in which the A - B bond is broken upon addition. As shown in Fig. 1b there are two modes of addition possible: cis or trans.

3) Those reactions in which oxidative addition as in 2) occurs but is followed by a reductive elimination.

The oxidative addition reactions of some d^8 complexes reported in the literature will now be discussed under these headings.



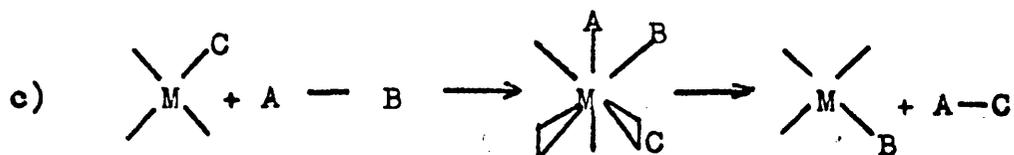


Fig. 1

REACTIONS WITH RETENTION OF A - B BOND

The molecular oxygen complexes $\text{IrX}(\text{CO})(\text{PPh}_3)_2\text{O}_2$ ($\text{X}=\text{Cl}, \text{I}$), $[\text{M}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{O}_2]^+ [\text{PF}_6]^-$ ($\text{M}=\text{Ir}, \text{Rh}$) have been the subject of X-ray structural determinations; relevant molecular dimensions are summarised in Table 1.

TABLE 1.

Structural data concerning molecular complexes of Iridium and Rhodium.

<u>Complex</u>	<u>M-O distance(Å)</u>	<u>O-O distance(Å)</u>
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2\text{O}_2$	2.07	1.30
$\text{IrI}(\text{CO})(\text{PPh}_3)_2\text{O}_2$	2.06	1.51
$[\text{Ir}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{O}_2]^+$	1.976	1.625
$[\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{O}_2]^+$	2.025	1.418
R-O-O-R	-	1.49
O_2	-	1.21

-3-

The reaction of O_2 with trans $IrX(CO)(PPh_3)_2$ is reversible but the iodide complex retains O_2 more strongly than the chloride², and the reaction of $[Rh(Ph_2PCH_2CH_2PPh_2)_2]^+[PF_6]^-$ with O_2 is reversible³ whereas the reaction of the iridium analogue is not. Several factors emerge from this data.

1. There is extensive back donation from the central metal atom into antibonding orbitals of the O_2 molecule leading in some cases to O - O bond lengths greater than a single σ O - O bond.

2. The strength of the metal - O_2 bond is dependent upon the electron density at the metal and this is dependent upon the ligands in the complex. The more electron density at the central metal atom the stronger the metal - O_2 interaction. Hence the iodo complex $IrI(CO)(PPh_3)_2O_2$ is more stable with respect to loss of O_2 , than its chloro analogue because iodide is a "soft" ligand which transfers charge, onto the metal, whereas chloride does not. This is further exemplified by the recent synthesis of the complexes $IrXCO(PPhMe_2)_2O_2$ (X=Cl, Br) where the bromo complex⁶ is found to be more stable than its chloro analogue.

3. The nature of the central metal atom must obviously have a considerable effect as is seen from the differing stabilities of the nearly isostructural complexes

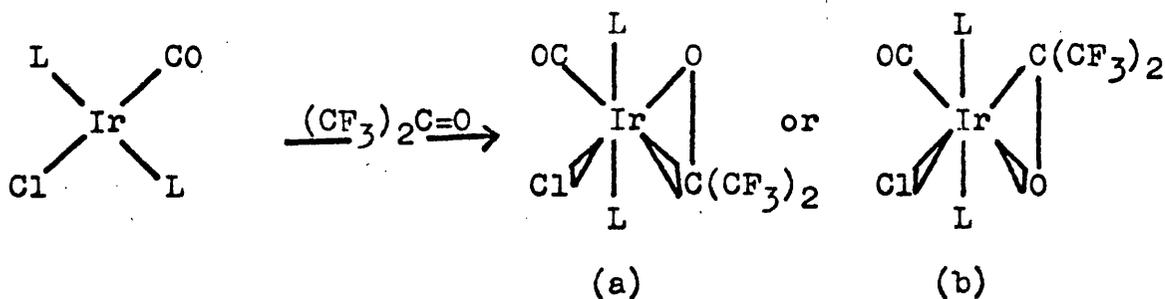
$[M(Ph_2PCH_2CH_2PPh_2)_2O_2]^+[PF_6]^-$ (M=Ir, Rh). As both the

the iridium and rhodium atoms are in identical environments this differing stability must be due to variation of d orbital energy, the lower energy iridium atom d orbitals having a greater interaction with the antibonding orbitals of the oxygen molecule.

trans $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ forms 1:1 adducts with a number of olefins. These complexes dissociate reversibly their stability being enhanced by electronegative substituents on the olefin. Baddley has prepared a series of cyano substituted ethylene adducts and put forward a bonding model which rationalises their observed relative stabilities. As cyano groups are introduced into ethylene both the π and π^* orbitals of the olefin are stabilised. An estimation of the iridium d orbital energy shows the overlap between the π^b orbital of the olefin and the iridium d orbitals decreases as cyano groups are introduced, whereas the reverse occurs for the π^* orbital. The stability of the complexes is seen to increase as the olefin is changed from ethylene, to acrylonitrile, to fumaronitrile, to tetracyanoethylene. Thus the formation of strong metal \rightarrow olefin π interaction even when accompanied by loss in olefin \rightarrow metal σ interaction is seen to have a strong stabilising effect. The crystal structure of $\text{IrBr}(\text{CO})(\text{PPh}_3)_2[\text{C}_2(\text{CN})_4]$ has been determined by X ray diffraction. The C-C bond length of tetracyanoethylene in the complex is longer than that in free

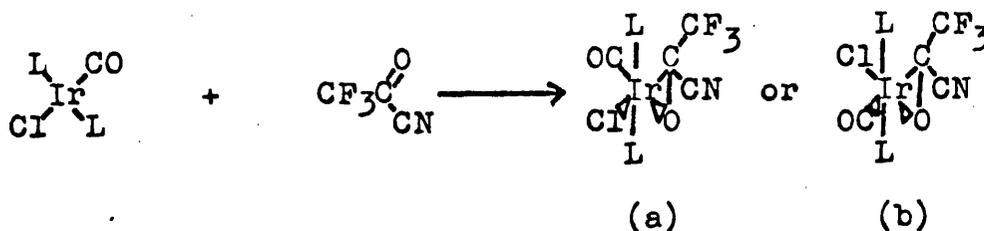
tetracyanoethylene indicating back bonding from the metal to the olefin. Like the O_2 complexes the stability of such complexes is enhanced by "soft" ligands⁴. Unlike the O_2 complexes the phosphines in $IrBrCO(PPh_3)_2[C_2(CN)_4]$ are cis⁵. This has also been observed for the complex $IrCl(CO)(PPhMe_2)_2[C_2(CN)_4]$ ⁶ from 1H n.m.r. studies. There has in both these cases been a change from trans phosphines in the starting material to cis phosphines in the product. Similarly trans - $RhCl(CO)_2(PPh_3)$ reacts with tetracyanoethylene to give $RhCl(CO)_2(PPh_3)[C_2(CN)_4]$ ⁷ in which the carbonyl groups are thought to be cis. However cis - $RhCl(CO)_2(L)$ (L = pyridine or *p* - toluidine) forms adducts with tetracyanoethylene and fumaronitrile in which a trans⁷ dicarbonyl configuration is adopted. These results indicate the delicate balance of factors which govern the direction of addition to square planar d^8 complexes.

Recently oxidative addition of the $>C=O$ bond to d^8 complexes has been reported for the addenda⁸ hexafluoroacetone⁸ and trifluoroacetylnitrile⁹.



$L = PPh_3, PPh_2Me.$

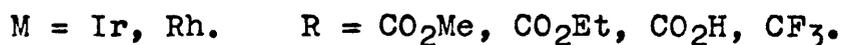
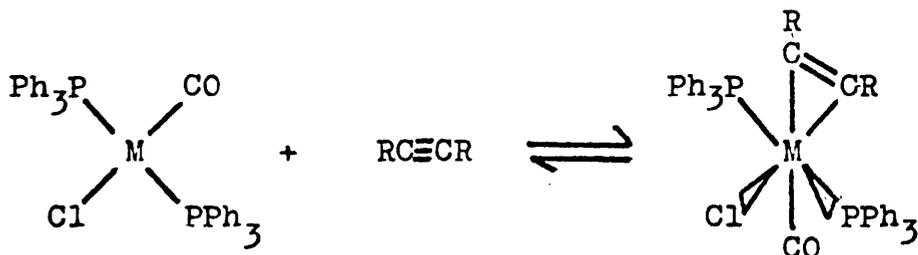
At 40°C the above addition is stereospecific, only one complex is obtained and the phosphines are determined as being trans from ¹H n.m.r. spectral studies. The structures shown are consistent with i.r. studies but the positions of carbonyl and chloride ligands relative to the C - O addendum was not established. At 25°C the reaction is not stereospecific, giving a mixture, presumably of a) and b). The reaction of trifluoroacetylnitrile is similar:



L = PPh₃ and PPh₂Me

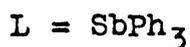
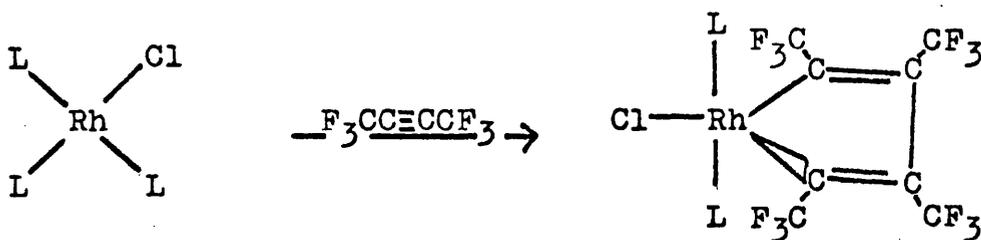
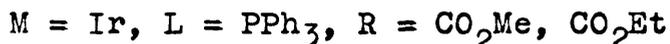
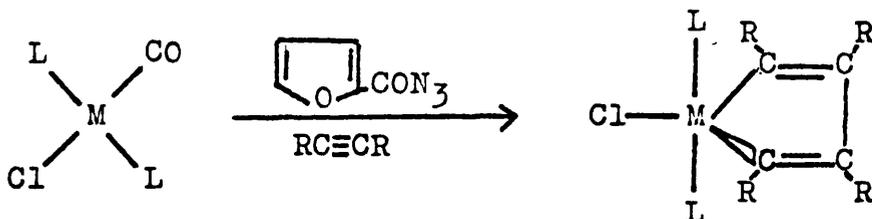
The reaction at room temperature is stereospecific either a) or b) being formed; the trans - phosphine arrangement being confirmed by ¹H and ¹⁹F n.m.r. studies. It is interesting to note that the rhodium complex trans - RhCl(CO)(PPh₂Me)₂ reacts with trifluoroacetylnitrile to give an adduct containing cis phosphine.

Acetylenes with electronegative substituents combine reversibly with Ir(I) and Rh(I) complexes to form 1:1 adducts .



The carbon - carbon bond order of the complexed acetylene may, from the position of $\nu(\text{C}\equiv\text{C})$, in some cases be considered to approach that of an olefin.^{10,11}

Two recent reports cite the oxidative addition of two moles of an acetylene to Ir(I) and Rh(I) to give a metallocyclopentadiene complex.



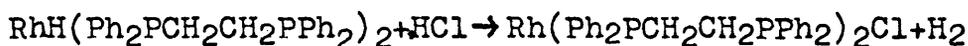
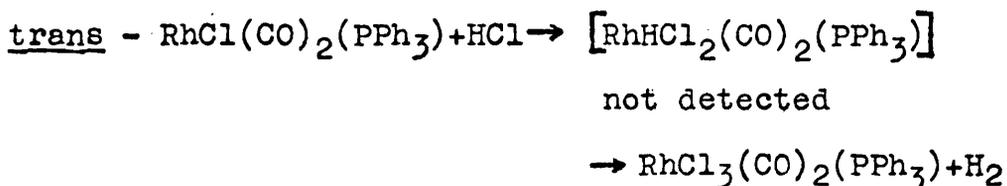
The complex $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{SbPh}_3)_2$ has been the subject of a single crystal X-ray study, and the metallocyclopentadiene structure predicted from i.r. and n.m.r. studies was confirmed. Such complexes are coordinately unsaturated and have been shown to catalyse the cyclotrimerisation of disubstituted acetylenes.

Reactions with fission of A - B bond

Only the most reactive d^8 complexes form stable adducts with hydrogen. The complex trans - $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ reacts readily with hydrogen whereas the isostructural rhodium complex does not form a stable dihydride. The rhodium complex $\text{RhCl}(\text{PPh}_3)_3$ however reacts readily with hydrogen at atmospheric pressure and is a well known hydrogenation catalyst. The analogous iridium complex forms an even more stable dihydride which is not a hydrogenating agent. This lack of catalytic activity is ascribed to 1) the greater strength of the Ir - H bond and 2) the lack of dissociation of $\text{IrCl}(\text{PPh}_3)_3$ in solution. The rate of hydrogen addition is increased if iodide replaces chloride in trans - $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ and bromide replaces chloride in trans - $\text{IrX}(\text{CO})(\text{PPhMe}_2)_2$. Thus it is seen, as in the formation of O_2 adducts,

soft σ donor ligands favour the addition of hydrogen, whereas π acids reduce the tendency for metal complexes to undergo addition. The course of hydrogen addition has been found to be cis in all cases where the stereo-¹⁶chemistry has been examined .

In the oxidative addition reaction the metal is acting as a base; oxidative addition being envisaged as the conceptual removal of electrons from the basic metal centre. Thus once a proton is coordinated to a metal it is considered a hydride and this hydridic character is exemplified by the protonated complex reacting with a further proton to yield H_2 gas and the metal with an increase of two charge units. Two examples^{17,18} are given below.



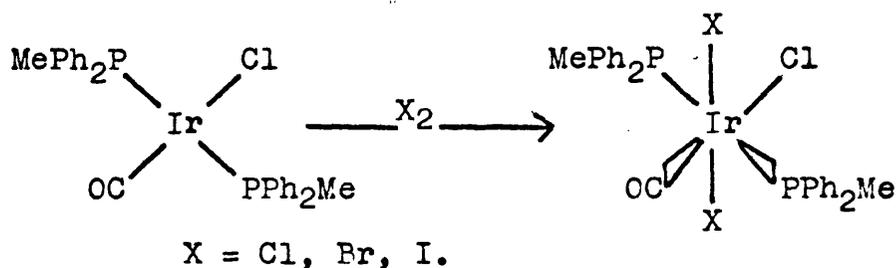
Square planar d^8 complexes usually react with both the proton and its conjugate union to give stable six coordinate d^6 species. Thus the weak acids RSH , ($R=H, p-C_6H_4CH_3, C_6H_3(SH)CH_3$) and HCN add to the complex trans - $IrCl(CO)(PPh_3)_2$ ¹⁹. The stereo-chemistry of these adducts was established by i.r. and 1H n.m.r. spectroscopy. The rhodium complex

addition takes place 3) a combination of 1) and 2).

The partial protonation by carboxylic acids of complexes of the type trans IrX(CO)L₂ has been investigated²¹ and although no n.m.r. or i.r. evidence for the formation of a metal hydride species was found a good correlation between the pK_a of the acid and the extent of conversion of Ir(I) to Ir(III) (detected spectrophotometrically) was obtained. The basicity of the complex trans - IrX(CO)(PMe₂Ph)₂ (X=Cl, Br, I) increased as the electronegativity of the halide ligand decreased. This is in accord with the previously discussed stabilities of iridium hydride complexes and O₂ adducts. The extent of conversion of the complex trans - IrCl(CO)L₂ decreases in the order PMe₃ > PMe₂Ph > PMePh₂ > PPh₃. This is the order of decreasing ligand basicity and also the probable order of increasing steric hindrance. The tertiary arsine complexes are converted to a greater extent than the corresponding tertiary phosphine complexes and this order is opposite to that expected from the basicity of the ligands towards protons. The reason for this is not clear but it is not an isolated example; IrCl(CO)(AsPh₃)₂O₂ is more stable than the corresponding²² PPh₃ complex and the hydrogen adduct of RhCl(AsPh₃)₃ is more stable than that of RhCl(PPh₃)₃²¹. The addition of anhydrous halogenoacids to complexes

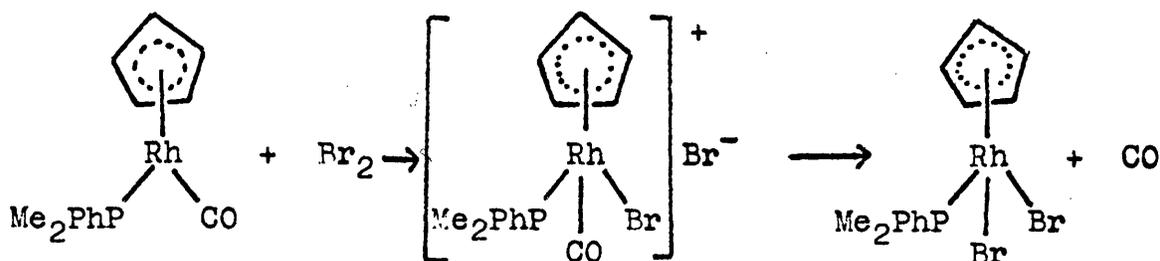
of the type trans - IrCl(CO)L₂ (L = tertiary phosphine)²³ in polar and non polar solvents has been investigated. In benzene and chloroform cis addition takes place but in the presence of methanol, acetonitrile, water or dimethylformamide mixtures of cis and trans isomers are obtained. Whether the isomers resulted from a rapid exchange of halide ions before addition, exchange in the product or a bonafide trans addition was not determined.

With the exception of Ni(II) and Pd(II) complexes all d⁸ complexes of the Group VIII metals form stable adducts with halogens¹ trans - IrCl(CO)(PPh₂Me)₂²⁰ undergoes oxidative addition with halogens and in the case of bromine and iodine this addition has been shown to be trans and not solvent dependent.



The reaction of the complex Rh(C₅H₅)(CO)(PPhMe₂)²⁴ with halogens is particularly interesting. At low temperatures ionic derivatives [Rh(C₅H₅)(X)(CO)(PPhMe₂)]⁺X⁻ are formed and the bromide may be isolated as a solid. The tetraphenyl boron salts of both the chloro and bromo cations are stable. On warming to room temperature both the bromide and chloride ionic derivatives lose

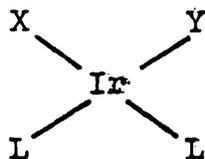
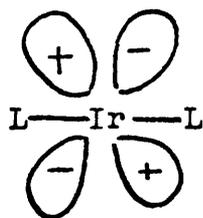
carbon monoxide to give high yields of the non-ionic dihalides $\text{Rh}(\text{C}_5\text{H}_5)\text{X}_2(\text{CO})(\text{PPhMe}_2)$. Iodine reacts to give the non-ionic dihalide but the ionic derivative is not observed.



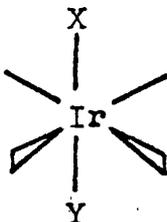
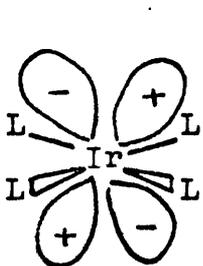
The addition of alkyl halides to square planar d^8 complexes is well known¹ and for trans - $\text{IrCl}(\text{CO})(\text{PPh}_2\text{Me})_2$ and trans - $\text{IrBr}(\text{CO})(\text{PPh}_2\text{Me})$ with methyl bromide and methyl chloride respectively the addition has been shown to be specifically trans²⁰. The reaction of trans - $\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$ with a series of substituted methyl chlorides has been described⁶ and while it is possible to determine the configuration of the product it is not possible to elucidate the stereochemistry of the addition. Methyl iodide and methyl bromide however add specifically trans to trans - $\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$. In the presence of methanol a mixture of cis and trans isomers is obtained plus a diiodo species in the methyl iodide case.⁶

The reaction of methyl iodide with trans - $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ has been the subject of a kinetic study^{25a} and this was taken to indicate a bimolecular

displacement at carbon with Ir(I) acting as a nucleophile. However a later communication^{25b} reported that in the presence of $^{131}\text{I}^-$ ions no incorporation of radioactive iodine into the Ir(III) compound occurred. It is apparent that a classical $\text{S}_{\text{N}}2$ reaction at carbon by Ir(I) followed by attack of iodide ion to give an Ir(III) complex is not consistent with this data. A recent report²⁹ cites retention of configuration at carbon during the oxidative addition of the optically active ester $\text{CH}_3\text{CHBrCO}_2\text{C}_2\text{H}_5$ to the complex trans - $\text{IrCl}(\text{CO})(\text{PMePh}_2)_2$. The stereochemistry of the addition was not elucidated but the authors postulated, from orbital symmetry considerations, mechanisms by which cis or trans addition could take place with retention of configuration:



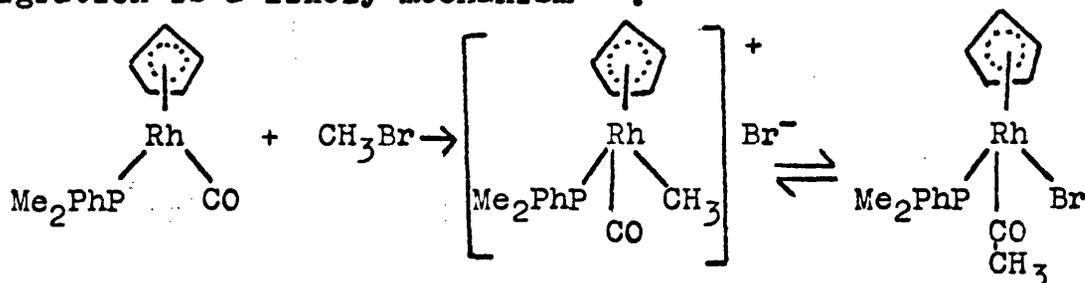
Cis addition.



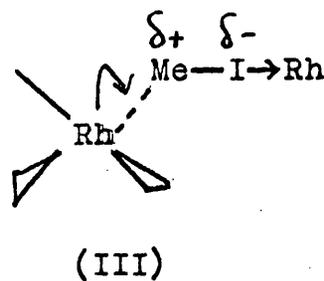
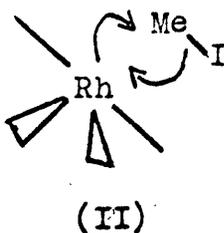
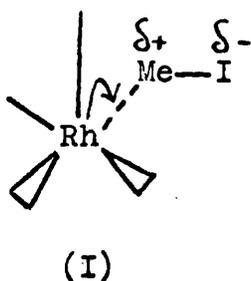
Trans addition.

It is noteworthy that for trans addition to take place as indicated above a rehybridisation of the dxz and dxy orbitals is necessary. Oxidative addition of trans - 1 - bromo - 2 - fluoro - cyclohexane to the complex trans - $IrCl(CO)(PMe_3)_2$ has been reported ²⁶ to be accompanied by inversion of configuration at carbon. It has been noted ²⁹ that nucleophilic attack at carbon by $Ir(I)$ via the d_z^2 orbital is consistent with orbital symmetry requirements and would lead to inversion of configuration at carbon. Thus it is apparent that the factors controlling the mechanism of simple oxidative addition reactions are subtle and at present not well defined.

The reaction of methyl bromide with $Rh(C_5H_5)(CO)(PPhMe_2)$ yields an acyl complex and while detailed kinetic data have not yet been published the formation of an ionic intermediate followed by halide ion assisted methyl group migration is a likely mechanism ²⁴.



The oxidative addition of methyl iodide to trans -
 $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ has been studied kinetically ²⁷. The
 reaction gives an alkyl and an acyl complex identified
 by their i.r. spectra by comparison with the spectra
 of the known compounds $\text{RhCl}_2(\text{Me})(\text{CO})(\text{PR}_3)_2$ and
 $\text{RhCl}_2(\text{COMe})(\text{PR}_3)_2$ ¹⁴. The complexes could not be sep-
 arated and the complexity of the ^1H n.m.r. spectra
 indicated that various isomers of both the alkyl and
 acyl complexes were formed. The data shows that the
 acyl complex is obtained only by isomerisation of an
 intermediate in which the methyl group is bonded to
 rhodium and is consistent with the formation of the
 intermediate via three - centre intermediates such as
 (I) or (II). The presence of an induction period,
 longest when the phosphine ligand is $\text{P}(\text{p-FC}_6\text{H}_4)_3$,
 which disappears on the addition of acyl complex, is
 rationalised in terms of the participation of the five
 coordinate acyl complex in the formation of the inter-
 mediate methyl complex as shown in (III).

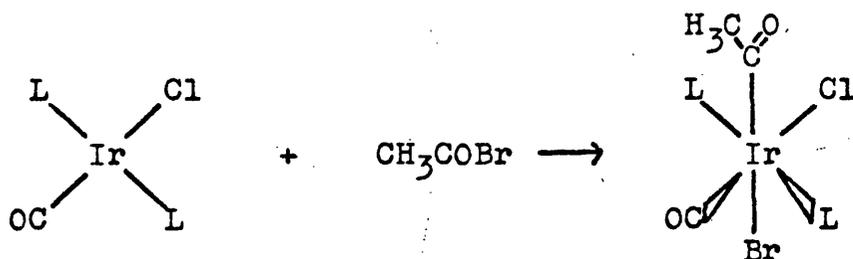


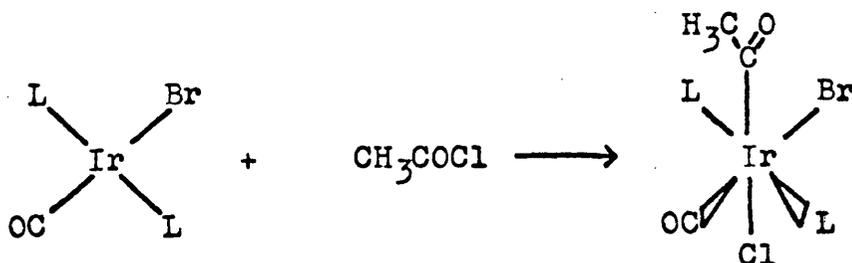
The length of the induction period reflects the increasing acid character of the metal from the $P(p\text{-MeOC}_6\text{H}_4)_3$ to the $P(p\text{-FC}_6\text{H}_4)_3$ complex in the reactant i.e. the more acid (electrophilic) that the central metal atom becomes the less likely it is to react with $\delta^+\text{CH}_3\text{-}\delta^-\text{I}$ at the δ^+ centre. The reverse reaction i.e. the formation of the d^8 complex from the alkyl intermediate is increasingly important in changing the phosphine ligand from $P(p\text{-MeOC}_6\text{H}_4)_3$ to $P(p\text{-FC}_6\text{H}_4)_3$. The reactivity of the complexes is best reflected by the trend in the equilibrium constant $K_{\text{forward}}/K_{\text{reverse}}$ and is in the order $P(p\text{-MeOC}_6\text{H}_4)_3 \gg PPh_3 > P(p\text{-FC}_6\text{H}_4)_3$. The increase in acid character of the metal may in the extreme case ($P(p\text{-FC}_6\text{H}_4)_3$ complex) result in coordination of methyl iodide to rhodium through the iodine thereby blocking a potential reaction site. The equilibrium constants for alkyl formation decrease with increasing temperature. Both K_f and K_r increase but the latter much more so; as expected from the activation enthalpies. Hence on increasing the temperature the equilibrium is shifted away from the product and oxidative addition is favoured at lower temperatures. The alkyl to acyl isomerisation reaction is slower than the initial oxidative addition reaction and the rate of isomerisation increases with the electron withdrawing power of the phosphine ligand. This trend is

consistent with the weakening of the Me - Rh bond as the electron withdrawing power of the ligand is increased and also with the increased tendency of methyl iodide to coordinate to rhodium via iodine. Hence the data is consistent with a solvent (methyl iodide) assisted migration of the methyl group to form an acyl group.

The similar reaction of methyl iodide with trans - $\text{RhCl}(\text{CO})_2(\text{PPh}_3)$ has been studied kinetically²⁸. As with the reaction of trans - $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ a two step mechanism was proposed but in this case the intermediate was not identified but postulated to be the methyl complex $\text{RhClI}(\text{Me})(\text{CO})_2(\text{PPh}_3)$. The second step, formation of the acyl complex was found to be slower than the intermediate formation, as with trans - $\text{RhCl}(\text{CO})(\text{PR}_3)_2$ and to consist of two parallel routes; solvent and methyl iodide assisted; again similar to the reaction of trans - $\text{RhCl}(\text{CO})(\text{PR}_3)_2$.

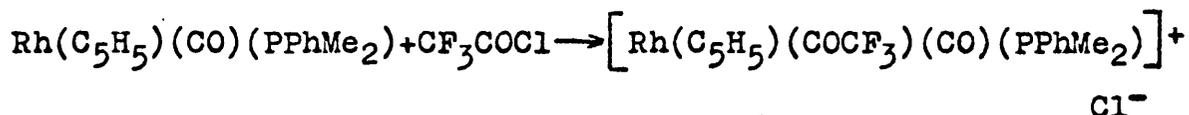
The addition of acyl halides to square planar d^8 complexes has been reported¹ and where investigated the stereochemical course of the addition has been shown to be trans^{6,20}.





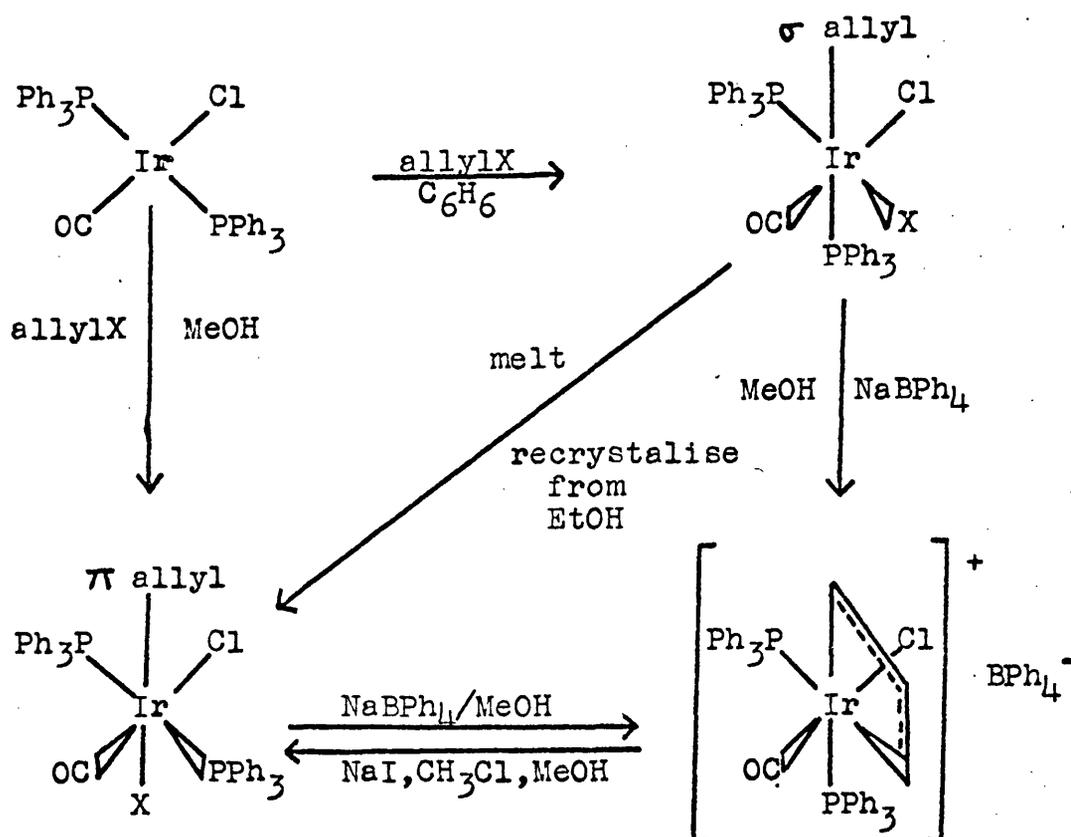
L = PMe₂Ph, PMePh₂.

The reaction of Rh(C₅H₅)(CO)(PPhMe₂) with acetyl bromide and trifluoroacetyl chloride has been investigated²⁴ and as in the reactions of halogens with the complex, unstable ionic products are obtained at low temperatures. The decomposition products at room temperature were not reported.



The addition of allyl halides to the complexes trans-IrCl(CO)L₂ (L=PMe₂Ph, AsMe₂Ph) has been thoroughly investigated³⁰. In benzene cis addition takes place. On melting or recrystallisation from ethanol the trans isomer is formed, and the reaction of the initial d⁸ complexes in methanol yields the trans isomer. It seems likely that the cis - trans isomerisation proceeds via a π - allyl intermediate which may be isolated as a tetraphenylboron salt. From the stereochemistry of the π allyl complex it is apparent that the halide

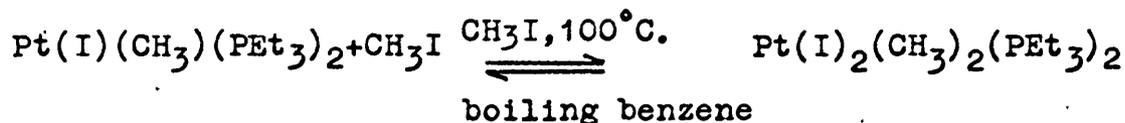
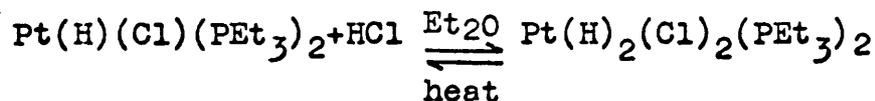
ligand trans to the strong trans - bond weakening ligand, σ - allyl or PPh_3 , is solvolysed off in the formation of the π - allyl complex. This series of reactions is summarised below and highlights that overall trans addition can take place via initial cis addition and subsequent isomerisation involving solvolysis of a halide ligand. This indicates that such possibilities should be investigated before trans addition is postulated from the final stereochemistry of an adduct.



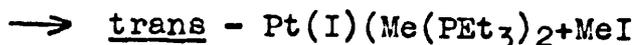
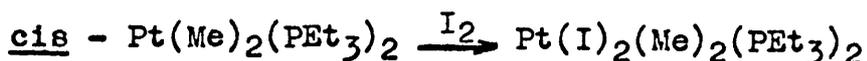
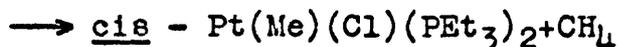
X = Cl, Br.
allyl = allyl, 2-methylallyl.

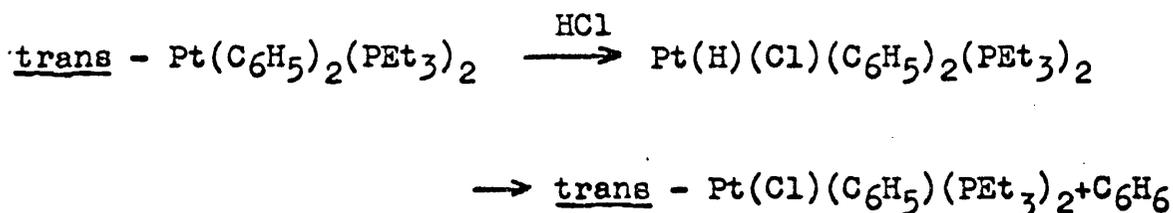
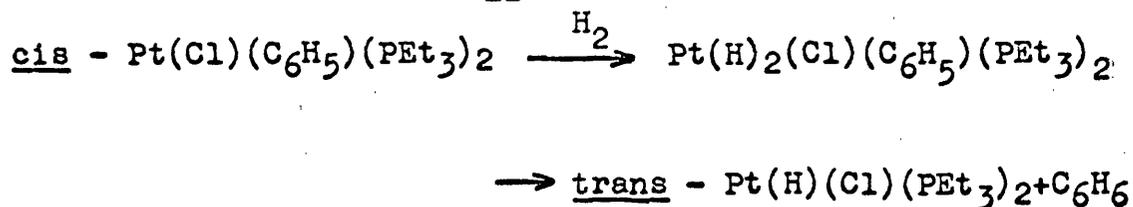
Addition - elimination reactions

The tendency for d^8 complexes to form oxidised adducts of d^6 configuration increases upon descending a triad or passing from left to right within Group VIII¹. Hence the examples quoted so far have been mainly concerned with rhodium and iridium. Oxidative addition to Pt^{II} complexes have been reported but the Pt^{IV} complexes produced are usually unstable and easily lose the addenda^{31,32}. Examples of this are cited below:

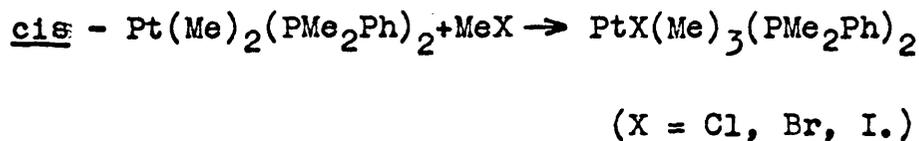
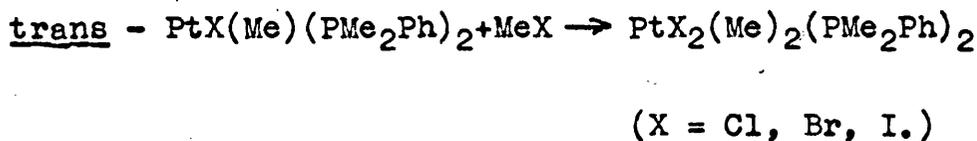
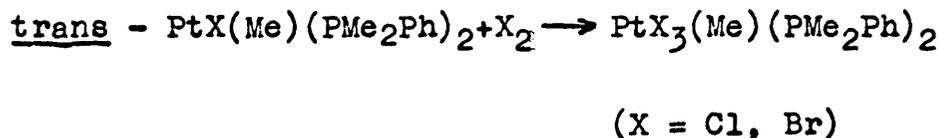


Oxidative addition to $Pt(II)$ complex is in some cases thought to take place initially, but this is then followed by a reductive elimination to give a $Pt(II)$ complex^{31,32}. Examples of this are given below:



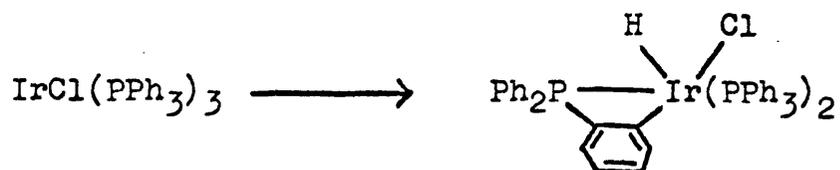


However some relatively stable Pt(IV) complexes may be produced by oxidative addition reactions:

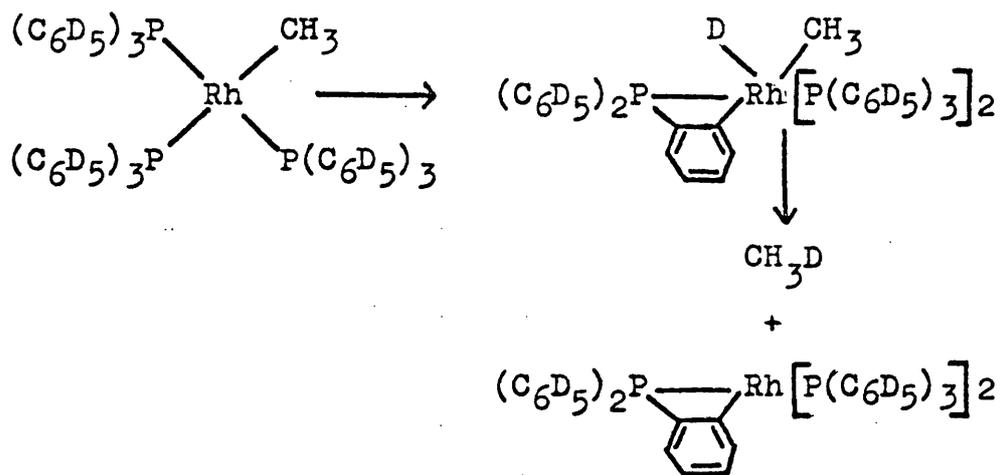


However studies on such Pt(IV) methyl complexes show that pyrolysis occurs at fairly low temperatures about 200°C. and in most cases a gaseous and solid Pt(II) complex could be identified from such decompositions. The mechanisms of these pyrolyses were not investigated.

Perhaps some of the most interesting examples of oxidative addition are those which occur intramolecularly. An example of this is supplied by the thermolysis of $\text{IrCl}(\text{PPh}_3)_3$ ¹⁵. A phenyl ring of one of the phosphine ligands undergoes ortho substitution to give a six-coordinate Ir(III) complex as shown.



Bennett and Milner¹⁵ have shown that ortho substitution is promoted by electron donating substituents on the aromatic ring. For the para substituted phosphine complexes $\text{IrCl}(\text{P}(\text{XC}_6\text{H}_4)_3)_3$ the rate of reaction decreases in the series $\text{CH}_3 > \text{OCH}_3 > \text{H} \gg \text{F}$ ¹⁵. The acceleration of the reaction may be due to either or both of two effects: 1) an enhancement of electron density in the ring should promote electrophilic substitution; 2) enhanced electron density on the metal atom should promote oxidative addition to the metal. The more common type of ortho substitution is exemplified by the thermolysis of $\text{Rh}(\text{CH}_3)(\text{PPh}_3)_3$ ³⁶. The ortho substitution is envisaged as giving initially a Rh(III) complex which then undergoes reductive elimination to form a Rh(I) complex plus methane. Consistent with this postulation is the pyrolysis of $\text{Rh}(\text{CH}_3)[(\text{C}_6\text{D}_5)_3\text{P}]_3$ which gives CH_3D ³⁷.



CHAPTER 1

"Behold, the fear of the Lord that is wisdom;
and to depart from evil is understanding."

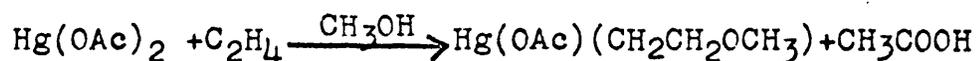
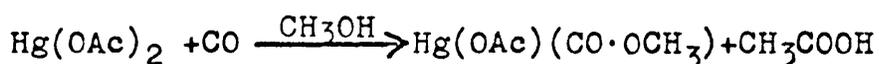
Job, Ch.28 v.28

Holy Bible

Authorised Version

INTRODUCTION

The reaction of mercuric acetate with small organic molecules e.g. carbon monoxide³⁸ and alkenes³⁹, in alcoholic media is well known:



These reactions with olefins have recently been extended to include aprotic solvents⁴⁰. The oxymercuration-deoxymercuration sequence is now a standard tool of the organic chemist for Markovnikov addition of ROH⁴¹ to double bonds. However the details of oxymetalation reactions especially those involving metals other than mercury remain to be investigated.

It was therefore decided to investigate the reactivity of the complexes bis(trifluoroacetato)bis(triphenylphosphine)platinum(II) and diacetato bis(triphenylphosphine)platinum(II) in alcoholic media with alkenes, alkynes, carbon monoxide, acids, alkyl and allyl iodides and sulphur dioxide.

RESULTS AND DISCUSSION

Preparation of Carboxylate Complexes

Bis(trifluoroacetato)bis(triphenylphosphine)platinum (II), $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$; bis(trifluoroacetato)bis(dimethylphenylphosphine)platinum(II), $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$, and diacetato bis(triphenylphosphine)platinum(II), $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ were most easily prepared by the reaction of the appropriate silver salt with the appropriate cis - dichloro bis(phosphine)platinum(II) complex in dichloromethane. The triphenylphosphine complexes may also be prepared by the action of the parent acid on a benzene solution of tetrakis(triphenylphosphine)platinum(0). This method of preparation is, however, not very convenient as it involves isolation of the carboxylate complexes from oils. These latter complexes have also been prepared independently by the action of the parent carboxylic acid on carbonato bis(triphenylphosphine)platinum(II)⁴². The action of silver salts of carboxylic acids on the complexes cis- $\text{PtCl}_2(\text{PR}_3)_2$ does not always give the desired complex. Thus silver acetate does not react with cis - $\text{PtCl}_2(\text{PMe}_2\text{Ph})_2$ and the complex diacetato bis(dimethylphenylphosphine)platinum(II) has not been prepared. Analytical, melting point and molecular weight data for the carboxylate complexes are given in Table 1.1.

TABLE 1.1.

Analytical, molecular weight and melting point data for carboxylate complexes

<u>Compound</u>	<u>Analytical Data</u>			<u>Molecular Weight</u>		<u>Melting Point</u>
	<u>C</u>	<u>H</u>	<u>F</u>	<u>Found</u>	<u>Required</u>	
Pt(O ₂ CCH ₃) ₂ (PPh ₃) ₂	57.37	4.37	-	847	847	210-220°C
	57.39	4.39	-	838	838	
Pt(O ₂ CCF ₃) ₂ (PPh ₃) ₂	50.70	3.09	12.23	937	937	220-225°C
	50.78	3.19	12.05	946	946	
Pt(O ₂ CCF ₃) ₂ (PMe ₂ Ph) ₂	34.44	3.14	16.30	690	690	120-122°C
	34.43	3.16	16.36	697	697	

Molecular weight data were determined from chloroform solution.

Structure of Carboxylate Complexes

Molecular weight determinations in chloroform indicate that complexes are monomeric in solution. I.r. spectral data for these and related complexes is shown in Table 1.2. Curtis⁴³ has correlated the carboxyl stretching frequencies in acetate complexes with the type of acetate coordination. He suggests that for unidentate coordination of the acetate ion to a bivalent metal ion values close to those for ionic acetate (for sodium acetate $\nu_{as}(OCO)$ is at 1578cm.^{-1} and $\nu_{sym}(OCO)$ is at 1414cm.^{-1}) but shifted slightly towards the covalent ester values ($\nu(C=O)$ is about 1740cm.^{-1} and $\nu(C-O)$ is about 1240cm.^{-1}) would be expected. For symmetric bidentate coordination the separation between $\nu_{as}(OCO)$ and $\nu_{sym}(OCO)$ will be reduced compared with ionic values and for asymmetric bidentate coordination a situation midway between that of unidentate and symmetric bidentate coordination is proposed.

⁴⁴ Nakamoto et al. have shown that the effect of changing the metal on $\nu_{as}(OCO)$ and $\nu_{sym}(OCO)$ is different for each structural type and that for a series of α -amino acid complexes bonded through one oxygen $\nu_{as}(OCO)$ increased and $\nu_{sym}(OCO)$ decreased as the metal - oxygen bond becomes stronger. It was also shown that both $\nu_{as}(OCO)$ and $\nu_{sym}(OCO)$ shifted in the same direction for symmetric coordination of the

carboxylate group. Complexes of the type $\text{Pd}(\text{OCOR})_2\text{L}_2$ ($\text{R}=\text{CH}_3, \text{C}_2\text{H}_5, \text{CF}_3$ $\text{L}=\text{PPh}_3$) and $[\text{Pd}(\text{OCOCH}_3)_2\text{L}]_2$ ($\text{L}=\text{PPh}_3, \text{AsPh}_3$) have been prepared by Wilkinson et al., and on the basis of reference 11 i.r. spectral data was interpreted to indicate unidentate carboxylate coordination in the monomeric complexes and both bidentate and unidentate coordination in the dimeric complexes. The structural assignments made by Wilkinson^{45,46} are in accord with the correlations laid down by Curtis⁴³. Comparison of $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ for sodium acetate and sodium trifluoroacetate with $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ of the platinum carboxylate complexes $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$, $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$, $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ indicates unidentate carboxylate coordination in each case (See Table 1.2.). It should be noted that Edwards and Hayward⁴⁷ have indicated that care should be exercised in the use of $\nu_{\text{as}}(\text{OCO})$ - $\nu_{\text{sym}}(\text{OCO})$ separation as a means of assessing the mode of coordination of acetate groups to metals.

^1H n.m.r. and ^{19}F n.m.r. spectral data for the platinum carboxylate complexes are shown in Table 1.3. The stereochemistry of $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ was determined via the ^1H n.m.r. spectrum. This showed three doublets, intensity 1:4:1, centred on 8.43(τ), $J_{(\text{Pt}-\text{H})} = 36$ c.p.s. and $J_{(\text{P}-\text{H})} = 12$ c.p.s., which is typical of a cis configuration⁴⁸. The ^{19}F n.m.r. spectrum of

TABLE 1.2.

Symmetric and Asymmetric Carboxylate Infrared Absorptions (cm.⁻¹).

Complex	Ref.	Ionic		Unidentate		Bidentate	
		$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{sym}}(\text{OCO})$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{sym}}(\text{OCO})$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{sym}}(\text{OCO})$
NaO_2CCH_3	10	1578	1414	-	-	-	-
NaO_2CCF_3	18	1685	1445	-	-	-	-
$\text{Pt}(\text{O}_2\text{CCH}_3)_2(\text{PPh}_3)_2$	-	-	-	1634, 1597	1308, 1299	-	-
$\text{Pt}(\text{O}_2\text{CCF}_3)_2(\text{PPh}_3)_2$	-	-	-	1727, 1700	1400	-	-
$\text{Pt}(\text{O}_2\text{CCF}_3)_2(\text{PMe}_2\text{Ph})_2$	-	-	-	1712, 1690	1436	-	-
$\text{Pd}(\text{O}_2\text{CCH}_3)_2(\text{PPh}_3)_2$	12	-	-	1634	1353, 1307 and/or 1297	-	-
$\text{Pd}(\text{O}_2\text{CCF}_3)_2(\text{PPh}_3)_2$	12	-	-	1684	1397	-	-
$[\text{Pd}(\text{O}_2\text{CCH}_3)_2(\text{PPh}_3)]_2$	13	-	-	1629	1314	1580	1411
$[\text{Pd}(\text{O}_2\text{CCH}_3)_2(\text{AsPh}_3)]_2$	13	-	-	1631	1314	1582	1410

Infrared spectra were recorded from Nujol mulls using KBr windows.

TABLE 1.3.

^1H n.m.r. and ^{19}F n.m.r. data for Carboxylate Complexes

<u>Complex</u>	<u>^{19}F n.m.r. data</u>		<u>^1H n.m.r. data</u>	
	<u>$\delta(\text{CF}_3)$ relative to PhCF_3 (p.p.m.)</u>		<u>Carboxylate $\delta(\text{CH}_3)$</u>	<u>Phosphine $\delta(\text{C}_6\text{H}_5)$</u>
$\text{Pt}(\text{O}_2\text{CCH}_3)_2(\text{PPh}_3)_2$	-	-	8.62(s)	- ~ 2.6(m)
$\text{Pt}(\text{O}_2\text{CCF}_3)_2(\text{PPh}_3)_2$	+9.77(s)	-	-	- ~ 2.5(m)
$\text{Pt}(\text{O}_2\text{CCF}_3)_2(\text{PMe}_2\text{Ph})_2$	+11.80(s)	-	-	8.43(t) ~ 2.6(m) $J(\text{Pt-H}) = 36\text{cps.}$ $J(\text{P-H}) = 12\text{cps.}$

-31-

^1H n.m.r. spectra were recorded from deuteriochloroform solution.

^{19}F n.m.r. spectra were recorded from dichloromethane solution.

s = singlet, t = triplet, m = multiplet.

$\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ showed a singlet at +11.80p.p.m. relative to benzotrifluoride. The ^{19}F n.m.r. spectrum of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ shows a singlet at +9.77p.p.m. relative to benzotrifluoride.

⁴⁹ King has discussed the position of CF_3 resonance for the complexes $\text{Fe}(\text{OAc}_F)(\text{C}_5\text{H}_5)(\text{CO})(\text{PR}_3)$, $\text{R}=\text{C}_6\text{H}_5$, OC_6H_5 ; $\text{Fe}(\text{OAc}_F)(\text{C}_5\text{H}_5)[\text{P}(\text{OMe})_3]_2$ and $\text{Fe}(\text{OAc}_F)(\text{C}_5\text{H}_5)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ in terms of the π acceptor strength of the phosphine ligands. Since triphenylphosphine is probably a better π acceptor than dimethylphenylphosphine, a CF_3 group trans to triphenylphosphine would be less shielded than one trans to dimethylphenylphosphine. Hence in the complexes cis- $\text{Pt}(\text{OAc}_F)_2(\text{PR}_2\text{R}^1)_2$ ($\text{R}=\text{R}^1=\text{Ph}$; $\text{R}=\text{Me}$, $\text{R}^1=\text{Ph}$) CF_3 resonance for the dimethylphenylphosphine complex will appear at a higher field than CF_3 resonance for the triphenylphosphine complex whereas in trans complexes of this type CF_3 resonances will appear at similar fields. Thus the complex $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ is assigned a cis configuration. By analogy the complex $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ is also assigned a cis configuration.

Reactions of Carboxylate Complexes in Alcohols

Preliminary experiments with carbon monoxide showed the complex $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ to be less reactive than its triphenylphosphine analogue. Thus the chemistry of this complex was not investigated in great detail.

TABLE 1.4.

Analytical, molecular weight and melting point data.

<u>Complex</u>	<u>Analytical data</u>			<u>Molecular Weight</u> <u>Found</u>	<u>Melting Point</u> <u>(°C)</u>
	<u>C</u>	<u>H</u>	<u>(Other)</u>		
Pt(COOCH ₃)(O ₂ CCF ₃)(PPh ₃) ₂	53.95 53.88	3.84 3.73	6.50(F) 6.39(F)	986 892	188-195
Pt(COOC ₂ H ₅)(O ₂ CCF ₃)(PPh ₃) ₂	54.52 54.38	3.84 3.89	8.12(F) 6.29(F)	925 906	185-187
Pt(COOCH ₃)(O ₂ CCH ₃)(PPh ₃) ₂	56.40 57.39	4.13 4.33	- -	830 838	224-227
Pt(COOCH ₃)Cl(PPh ₃) ₂	56.73 56.06	4.02 4.09	4.50(Cl) 4.36(Cl)	- 814	235-236
Pt(COOC ₂ H ₅)Cl(PPh ₃) ₂	56.06 56.56	4.06 4.26	4.95(Cl) 4.28(Cl)	- 828	213-217
Pt[PhC=C(H)Ph](O ₂ CCF ₃)(PPh ₃) ₂	61.82 61.74	4.00 4.09	5.72(F) 5.63(F)	1011 1012	218-221
Pt[PhC=C(H)Ph]Cl(PPh ₃) ₂	64.44 64.30	4.47 4.91	3.90(Cl) 3.80(Cl)	- 935	240-242
Pt[CF ₃ C=C(H)CF ₃](O ₂ CCF ₃)(PPh ₃) ₂	50.64 50.61	3.01 3.11	17.30(F) 17.17(F)	1000 996	205-209

Contd....

TABLE 1.4. Contd....

<u>Complex</u>	<u>Analytical data</u>		<u>Molecular Weight</u>	<u>Melting Point</u>
	<u>Found (%)</u>	<u>Required (%)</u>		
	<u>C</u>	<u>H</u>	<u>Found</u>	<u>(°C)</u>
Pt [CF ₃ C=C(H)CF ₃]Cl(PPh ₃) ₂	52.32	3.41	910	242-245
	52.29	3.38	918	
Pt(SO ₂ OCH ₃) ₂ (PPh ₃) ₂	49.88	3.97	-	183-185
	49.08	3.90	920	
[Pt(O ₂ CCF ₃)(PPh ₃) ₂] ₂	56.42	3.99	1640	163-164
	55.44	3.65	1645	
PtI(O ₂ CCF ₃)(PPh ₃) ₂	47.07	3.42	-	-
	47.60	3.13	960	

Molecular Weight data were recorded from chloroform solution.

TABLE 1.5.

Characteristic Infrared Absorptions of Complexes (cm.⁻¹).

Complex	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{sym}}(\text{OCO})$	$\nu(\text{C=O})$ Solid Solution	$\nu(\text{C-O})$	$\nu(\text{C=C})$	$\nu(\text{Pt-Cl})$
Pt(COOCH ₃)(O ₂ CCH ₃)(PPh ₃) ₂	1620(s)	1312(m)	1645(s) 1630(s)	1190	-	-
Pt(COOCH ₃)(O ₂ CCF ₃)(PPh ₃) ₂	1710(s) 1692(s)	1408(m)	1652(s) 1638(s)	Obscured ^b	-	-
Pt(COCC ₂ H ₅)(O ₂ CCF ₃)(PPh ₃) ₂	1708(m) 1695(s)	1406(m)	1645(s) 1640(s)	Obscured ^b	-	-
Pt(COOCH ₃)Cl(PPh ₃) ₂	-	-	1663(s) 1645(s)	1185(m)	-	278(m) 351
Pt(COCC ₂ H ₅)Cl(PPh ₃) ₂	-	-	1665(s) 1640(s)	1185(m)	-	275(m)
Pt[PhC=C(H)Ph](O ₂ CCF ₃)(PPh ₃) ₂	1715(sh) 1695(s)	1415(m)	-	-	1574(w)	-
Pt[PhC=C(H)Ph]Cl(PPh ₃) ₂	-	-	-	-	1550(w)	280(m)
Pt[CF ₃ C=C(H)CF ₃](O ₂ CCF ₃)(PPh ₃) ₂	1720(sh) 1698(s)	1414(m)	-	-	1615(m)	-
Pt[CF ₃ C=C(H)CF ₃]Cl(PPh ₃) ₂	-	-	-	-	1625(m)	300(m)
PtI(O ₂ CCF ₃)(PPh ₃) ₂	1680(s)	1436(m)	-	-	-	-

Infrared spectra were recorded from Nujol mulls or chloroform solution using KBr (3000-400cm.⁻¹) and polythene (400-200cm.⁻¹) windows. s = strong, sh = sharp, m = medium, w = weak.

a. Bands due to coordinated phosphines omitted.

b. Strong absorptions assigned to $\nu(\text{C-F})$ occur in this region.

TABLE 1.6.
¹H n.m.r. data for Alkoxy Carbonyl Complexes

<u>Complex</u>	<u>Chemical Shift of Alkoxy Protons</u>	<u>Coupling Constants (c.p.s.)</u>
	$\overline{\text{CH}_3(\tau)}$ $\overline{\text{CH}_2(\tau)}$	$\overline{J(\text{Pt} - \text{H})}$ $\overline{J(\text{P} - \text{H})}$
Pt(COOCH ₃)(O ₂ CCF ₃)(PPh ₃) ₂	7.5(t) -	6.5 -
Pt(COOCH ₃)Cl(PPh ₃) ₂ ^a	7.6(t) -	15 -
Pt(COCC ₂ H ₅)(O ₂ CCF ₃)(PPh ₃) ₂	9.7(t) 7.1(m)	1 15 Obscured Obscured
Pt(COCC ₂ H ₅)Cl(PPh ₃) ₂ ^a	9.5(t) 7.3(m)	1 15 15 15

N.m.r. spectra were recorded from deuteriochloroform solution.

t = triplet, m = multiplet

a. data from ref. 16.

Reactions of Carboxylate Complexes with Carbon Monoxide

Both $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ and $\text{Pt}(\text{OAc}_\text{F})_2(\text{PPh}_3)_2$ react with carbon monoxide in alcoholic media in a manner analogous to that of mercuric acetate³⁸. The carboxylate alkoxycarbonyl complexes crystallise from the reaction mixture.

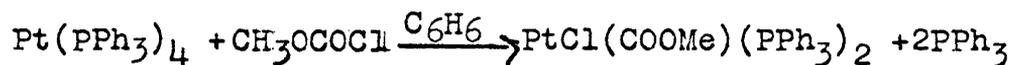


For $\text{R}=\text{CH}_3$, $\text{R}^1=\text{CH}_3$; for $\text{R}=\text{CF}_3$, $\text{R}^1=\text{CH}_3$, C_2H_5

Side reactions occur however and the yield of these complexes is only in the range 30-50%. No other pure complexes could be isolated from the reaction solution.

The carboxylate alkoxycarbonyl complexes are white crystalline solids, soluble in chloroform, dichloromethane and acetone; and insoluble in alcohols, ether and petroleum. They may be converted to the known⁵⁰ chloroalkoxycarbonyl complexes by treatment with lithium chloride in a dichloromethane - methanol (4:1) mixture. Analytical, melting point and molecular weight data for these complexes are given in Table 1.4. I.r. and ¹H n.m.r spectral data are given in Tables 1.5. and 1.6. respectively.

The complex $\text{PtCl}(\text{COOMe})(\text{PPh}_3)_2$ may also be prepared by the reaction of methyl chloroformate with $\text{Pt}(\text{PPh}_3)_4$ in benzene:



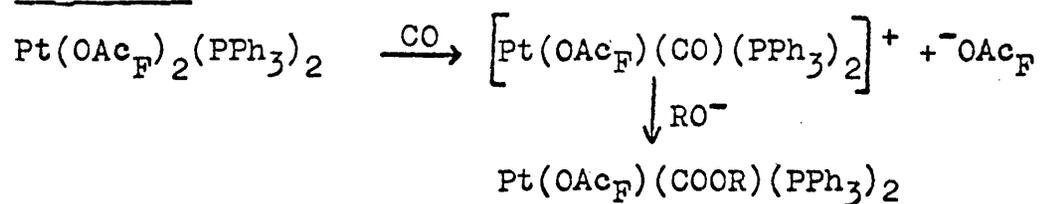
or by the reaction of carbon monoxide at high tempera-

ture and pressure with a methanolic suspension of cis - $\text{PtCl}_2(\text{PPh}_3)_2$.

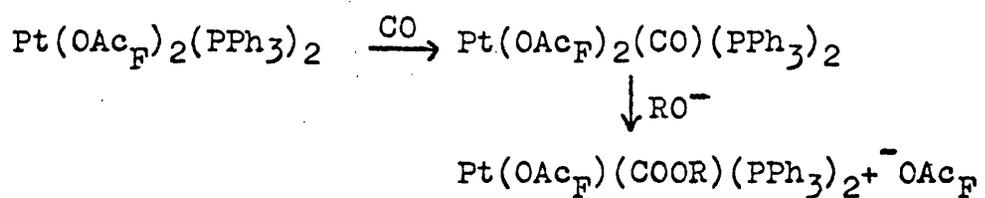
The bands assigned to $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ in the carboxylate alkoxy carbonyl complexes are absent from the i.r. spectra of the chloroalkoxy carbonyl complexes and also from that of cis - $\text{PtCl}_2(\text{PPh}_3)_2$. $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ are assigned by comparison with the i.r. spectra of $\text{Hg}(\text{COOMe})(\text{OAc})$ and $\text{HgCl}(\text{COOMe})$ which show $\nu(\text{C}=\text{O})$ at 1670cm.^{-1} and 1645cm.^{-1} respectively and $\nu(\text{C}-\text{O})$ in the region characteristic of the C-O stretching frequency of formate esters about 1190cm.^{-1} . The i.r. spectral data is consistent with unidentate carboxylate coordination and the presence of an alkoxy carbonyl group bonded via the carbon atom of the carbonyl to platinum. Clark⁵⁰ has obtained the complexes $\text{PtCl}(\text{COOR})(\text{PPh}_3)_2$ via the reaction of alcohols with the cationic carbonyl trans - $[\text{PtCl}(\text{CO})(\text{PPh}_3)_2]^+[\text{BF}_4]^-$. The structure of this complex has been established by an X-ray crystal structure determination⁵¹. Thus the chloroalkoxy carbonyl complexes were assigned a trans configuration.

The ^1H n.m.r. spectral data are consistent with the presence of alkoxy carbonyl groups. The complexes are only sparingly soluble and the multiplet resulting from CH_2 resonances split by both CH_3 -protons and ^{195}Pt in the ethoxy carbonyl complex could not be

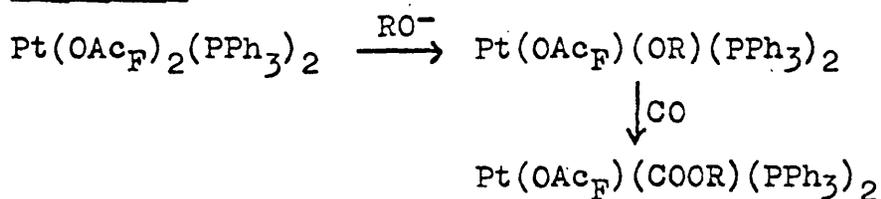
Scheme 1.



Scheme 2.



Scheme 3.



Possible mechanisms for the reaction of carbon monoxide with $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ in alcoholic media.

Fig.1.1.

resolved. The ^{19}F n.m.r. spectra of the complexes $\text{Pt}(\text{COOR})(\text{OAc}_{\text{F}})(\text{PPh}_3)_2$ ($\text{R}=\text{Me}, \text{Et}$) show resonance at +12.00p.p.m. relative to benzotrifluoride. No platinum-fluorine coupling was observed. The position of CF_3 resonance indicates a trans configuration because 1) trifluoroacetate groups trans to triphenylphosphine in cis - $\text{Pt}(\text{OAc}_{\text{F}})_2(\text{PPh}_3)_2$ exhibit CF_3 resonance at 9.77p.p.m.

2) both the methoxycarbonyl and the ethoxycarbonyl complexes show CF_3 resonance at the same field strength .

The complex $\text{Pt}(\text{OAc})(\text{COOMe})(\text{PPh}_3)_2$ was too insoluble for ^1H n.m.r. studies.

A possible mechanism for the formation of the carboxylate alkoxycarbonyl complexes is the nucleophilic attack of an alkoxide ion on the $\text{C}\equiv\text{O}$ bond of a cationic metal carbonyl (See Fig.1.1. scheme 1.). An alternative mechanism would be nucleophilic attack of alkoxide ion on the $\text{C}\equiv\text{O}$ bond of a neutral metal carbonyl complex with loss of a carboxylate group. (Fig.1.1. scheme 2.). The possibility of alkoxide coordination to the central metal atom followed by alkoxide migration or carbonyl insertion however cannot be discounted (Fig.1.1. scheme 3.).

Alcoholic solution of cis - $\text{Pt}(\text{OAc}_{\text{F}})_2(\text{PMe}_2\text{Ph})_2$ did not react with carbon monoxide in alcoholic media even under pressure (100 atmospheres). From the brown

reaction solutions only starting material, about 90%, could be isolated and no traces of alkoxy carbonyl complexes were detected.

This lack of reactivity indicates that in the complex $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ the trifluoroacetate group is less labile than in the complex $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$. It is noteworthy here that trans - $[\text{PtCl}(\text{CO})(\text{PEt}_3)]^+[\text{BF}_4]^-$

gives an unstable alkoxy carbonyl complex on treatment with methanol⁵⁰, and that all other stable alkoxy carbonyl complexes so far discovered contain strong acceptor ligands such as carbon monoxide or triphenylphosphine⁵²⁻⁵⁹.

Clark⁵⁰ has noted that the formation of chloro-alkoxy carbonyl complex from $[\text{PtCl}(\text{CO})(\text{PPh}_3)_2]^+[\text{BF}_4]^-$ is reversible in acid conditions. Alkoxy carbonyls are known for several other transition metals: Mn⁵²,
Re^{52,53}, Fe⁵⁴, Os⁵⁵, Co⁵⁶, Rh⁵⁷, Ir^{57,58,59} and the action of acids has been investigated. Elimination of an alcohol is usually the first step, leaving a cationic carbonyl which, in most cases, has been isolated. The reactions of the carboxylate alkoxy carbonyl platinum complexes with acids were however disappointing in this respect. Reaction with aqueous fluoboric acid yielded no pure isolatable complexes and the reactions with halogeno acids in dichloromethane solution gave cis - $\text{PtX}_2(\text{PPh}_3)_2$ (X=Cl, Br). It would appear that

both the alkoxycarbonyl group and the carboxylate group are susceptible to acid attack. This is further illustrated by the reaction of halogeno acids in dichloromethane solution with the parent bis(carboxylate) complexes, which also yields the corresponding dihalo complexes plus the parent carboxylic acid (detected by their characteristic i.r. spectra).

A series of complexes $\text{RuH}(\text{OCOR})(\text{PPh}_3)_3$ ($\text{R}=\text{Me}, \text{CH}_2\text{Cl}, \text{CF}_3, \text{Et}, \underline{n}\text{-Pr}, \underline{i}\text{-Pr}, \text{Me}_3\text{C}, \text{Ph}.$) have been prepared and the reaction of the acetate and trifluoroacetate with carbon monoxide in methanol has been investigated⁶⁰. In neither case was an alkoxycarbonyl complex isolated; the acetate gave $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ and the trifluoroacetate gave $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ plus $\text{Ru}(\text{C}_2\text{CCF}_2)(\text{CO})_2(\text{PPh}_3)_2$. It was postulated that the latter was formed by the action of liberated trifluoroacetic acid on $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$. This does not however eliminate alkoxycarbonyl formation during the reaction as attempts to prepare ruthenium alkoxycarbonyls by the reaction of alkoxide ion with cationic carbonyls of ruthenium have shown that they are extremely unstable⁵⁵. The complex $\text{RuCl}(\text{COOMe})(\text{CO})_2(\text{PPh}_3)_2$ was stable only at -70°C and was detected spectroscopically. Furthermore complexes of the type $[\text{RuX}(\text{CO})_3\text{L}_2]^+[\text{AlCl}_3\text{X}]^-$ where $\text{X}=\text{I}$, $\text{L}=\text{PPh}_3, \text{PPhEt}_2, \text{P}(\text{C}_6\text{H}_{11})_3$ react with a methanolic KOH-solution to produce $\text{Ru}(\text{CO})_3\text{L}_2$.

Reaction of Carboxylate Complexes with diphenyl acetylene and hexafluorobut -2- yne

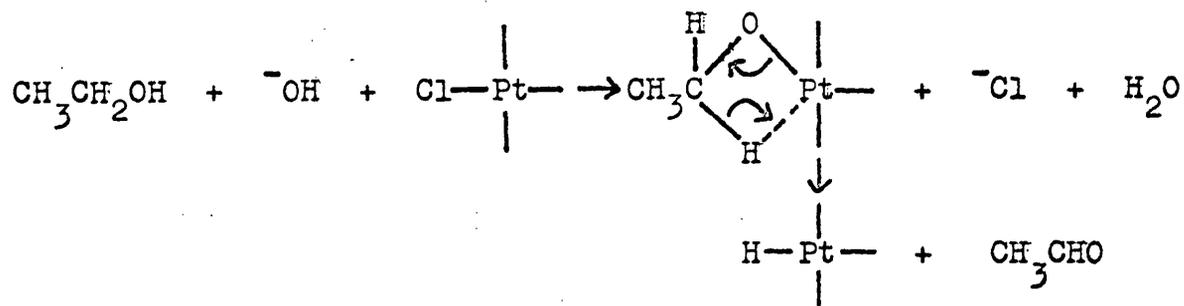
$\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ reacts with diphenylacetylene to give the vinyl complex $\text{Pt}(\text{OAc}_F)[\text{PhC}=\text{C}(\text{H})\text{Ph}](\text{PPh}_3)_2$ as pale orange crystals. Analytical, melting point and molecular weight data are given in Table 1.4. and i.r. spectral data in Table 1.5. The yields of the vinyl complex are solvent dependent: CH_3OH - 92%, $\text{C}_2\text{H}_5\text{OH}$ - 77% $n\text{C}_3\text{H}_7\text{OH}$ - 56%. No other pure complexes could be isolated. I.r. spectral data are consistent with the presence of a vinyl group, $\nu(\text{C}=\text{C})$ is at 1547cm.^{-1} and a unidentate carboxylate group; $\nu_{\text{as}}(\text{OCO})$ is at 1695cm.^{-1} and $\nu_{\text{sym}}(\text{OCO})$ is at 1415cm.^{-1} . Treatment of $\text{Pt}(\text{OAc}_F)[\text{PhC}=\text{C}(\text{H})\text{Ph}](\text{PPh}_3)_2$ with lithium chloride yielded the chloro complex $\text{PtCl}[\text{PhC}=\text{C}(\text{H})\text{Ph}](\text{PPh}_3)_2$ as a white crystalline solid. Analytical and melting point data are given in Table 1.4. and i.r. spectral data in Table 1.5. The i.r. spectrum of this complex showed $\nu(\text{Pt}-\text{Cl})$ at 280cm.^{-1} , $\nu(\text{C}=\text{C})$ at 1550cm.^{-1} and blank in the region assigned to $\nu_{\text{as}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ for the carboxylate vinyl complex. Both the vinyl complexes were too insoluble for ^1H and ^{19}F n.m.r. spectral studies.

By analogy with the reactions of olefins with ⁴¹mercuric acetate in alcohols . a vinyl complex of the type $\text{Pt}[\text{PhC}=\text{C}(\text{OR})\text{Ph}](\text{OAc}_F)(\text{PPh}_3)_2$ would be expected.

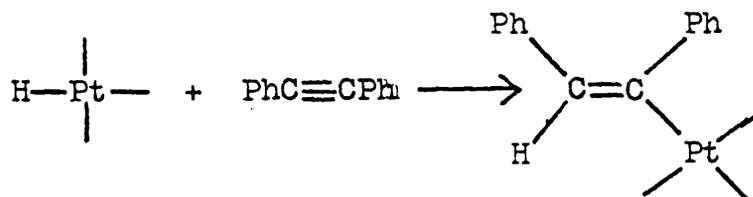
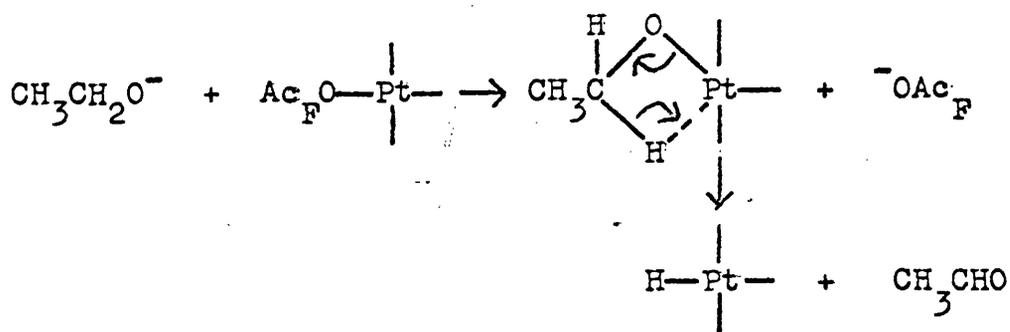
The presence of a Pt $\left[\text{PhC}=\text{C}(\text{H})\text{Ph}\right]$ vinyl group was demonstrated by the action of trifluoroacetic acid on a dichloromethane solution of the carboxylate vinyl complex at room temperature. This yielded trans - stilbene and $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ quantitatively. The source of the vinyl proton is thought to be the methylene proton of the solvent alcohol. In the preparation of the vinyl complex in ethanol, acetaldehyde was detected qualitatively by trapping out as acetaldehyde -2:4 - dinitrophenylhydrazone. Similarly in propanol, propionaldehyde was detected quantitatively as propionaldehyde -2:4 - dinitrophenylhydrazone. (See Experimental Section for details) When the reaction is repeated in CH_3OD no deuterium is incorporated into the product. When CD_3OD is used as the solvent deuterium is incorporated into the product; as shown by the i.r. spectrum of the product, which exhibits an absorption at 2240cm.^{-1} which may be assigned to ν (C-D) for a vinyl complex and is absent from the i.r. spectrum of the non deuterated product.

It is known³¹ that cis $\text{PtCl}_2(\text{PEt}_3)_2$ reacts with ethanolic KOH solution to give trans - $\text{PtHCl}(\text{PEt}_3)_2$ and the source of the hydride is thought to be the α -methylene group of ethanol. This has been confirmed by tracer studies and aldehyde produced during the course of the reaction was detected quantitatively³¹.

A hydride ion transfer promoted by base has been postulated as a mechanism for this reaction:

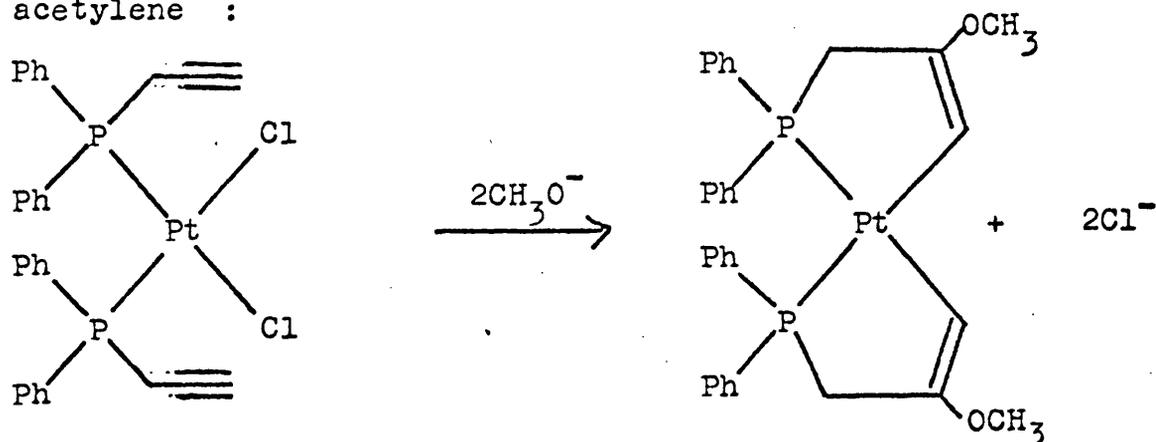


Thus the formation of a metal hydride intermediate followed by insertion of diphenyl acetylene into the metal-hydride, or hydride migration to coordinated diphenyl acetylene, is a reasonable mechanism for the formation of the carboxylate vinyl complex:



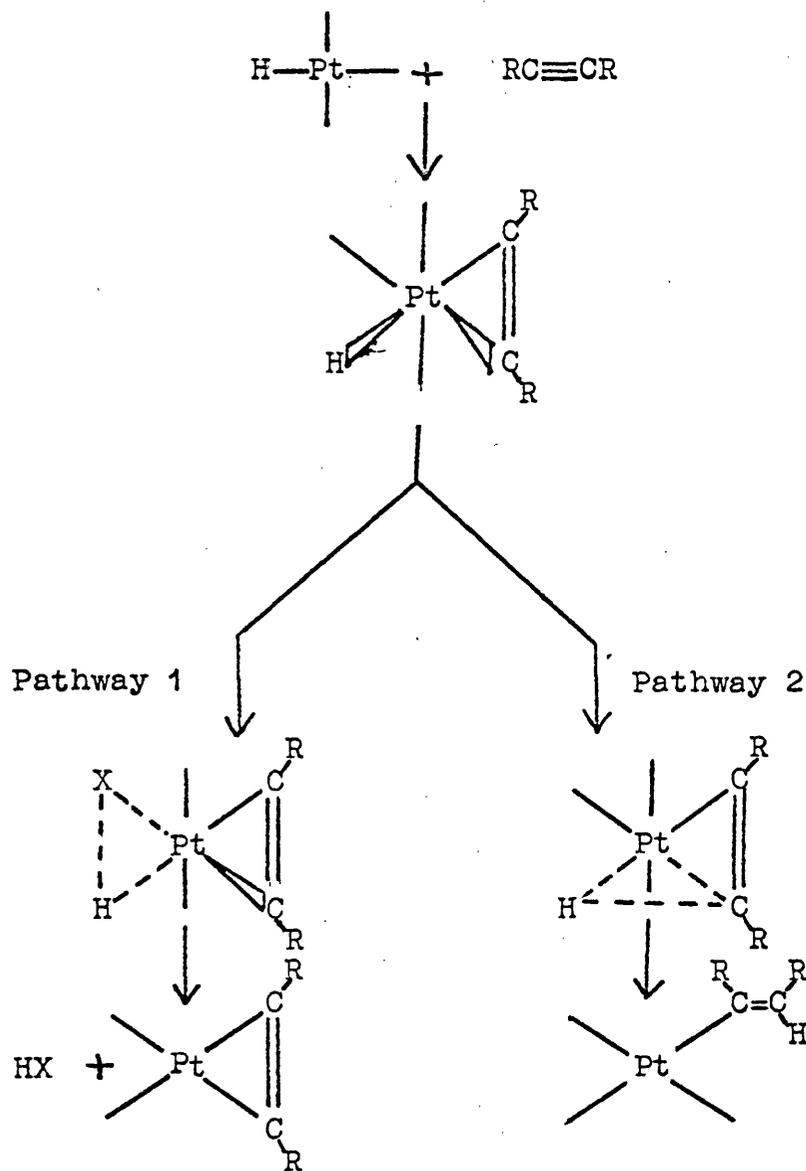
In the absence of alcoholic solvents, no reaction between diphenylacetylene and $\text{Pt}(\text{OAc}_\text{F})_2(\text{PPh}_3)_2$ occurs. Thus even after vigorous reflux of diphenylacetylene and the trifluoroacetate complex in acetone, chloroform

or benzene for 24 hours, starting materials are recovered quantitatively. It is interesting to note that the reaction of methoxide ion with platinum complexes containing free acetylene groups does in fact give complexes containing vinyl ether groups via nucleophilic attack of the methoxide ion on the acetylene :



The reaction of equimolar quantities of tri-fluoroacetic acid and the complex $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$ in dichloromethane solution at room temperature yields a yellow carboxylate vinyl complex which analyses as $\text{Pt}[\text{PhC}=\text{C}(\text{H})\text{Ph}](\text{OAc}_F)(\text{PPh}_3)_2$ but has a different i.r. spectrum to the carboxylate vinyl complex described above . The chloro analogue has been prepared by treatment of this complex with lithium chloride . The i.r. spectral data is consistent with unidentate carboxylate coordination, but $\nu(\text{C}=\text{C})$ is obscured by absorptions due to coordinated phosphines in both

62



R = Ph, X = OAc Pathway 1 operative
 R = Ph, X = OAc_F Pathway 2 operative
 R = CF₃, X = OAc_F Pathways 1 and 2 operative

Possible mechanisms for the reaction of acetylenes with carboxylate complexes.

Fig.1.2.

the chloro and the carboxylate vinyl complexes. These complexes and those vinyl complexes discussed earlier may be cis - trans isomers about platinum and this is the most obvious explanation of these observations but the possibility of isomers due to the cis or trans configuration of the vinyl group cannot be discounted.

In contrast to this the complex $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ reacts with diphenyl acetylene in alcohols to give the known ⁶⁷ complex $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$ in about 50% yields. No other pure complexes could be isolated. The presence of acetyldehyde was detected by trapping out as acetaldehyde-2:4-trinitrophenylhydrazone when the reaction solvent was ethanol. Similarly, when the reaction solvent was n-propanol, propionaldehyde was detected by trapping out as propionaldehyde-2:4-dinitrophenylhydrazone.

No reaction occurs between diphenylacetylene and $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ when the reaction solvent is acetone, chloroform, or benzene. Attempts to prepare the complex $\text{Pt}(\text{OAc})[\text{PhC}=\text{C}(\text{H})\text{Ph}](\text{PPh}_3)_2$ by treating the complex $\text{PtCl}[\text{PhC}=\text{C}(\text{H})\text{Ph}](\text{PPh}_3)_2$ with silver and potassium acetate failed.

The reaction of the complexes $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ and $\text{Pt}(\text{OAc}_\text{F})_2(\text{PPh}_3)_2$ with diphenylacetylene may be considered in terms of the reactions of a six coordinate metal hydride intermediate as shown in Fig.1.2. Pathway 1 involves the elimination of a carboxylic

acid and hence the formation of a metal-acetylene complex.

Pathway 2 involves hydride migration (or acetylene insertion) to give a vinyl complex.

The reason for the reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with diphenylacetylene following pathway 1 while the reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ follows pathway 2 is to be found in the differing strength of acetic and trifluoroacetic acid. The elimination of acetic acid is much more favoured than the elimination of trifluoroacetic acid. It is noteworthy that ^1H n.m.r. and i.r. spectral studies⁶⁹ on the complexes trans - $\text{PtHL}(\text{PEt}_3)_2$ where $\text{L}=\text{CF}_3\text{COO}, \text{CHCl}_2\text{COO}, \text{CH}_2\text{ClCOO}$ have shown that the Pt-H bond strength increases as the pKa of the carboxylic acid decreases.

$\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ reacts with hexafluorobut -2- yne in methanol in a Carius tube at 70°C to give a mixture of the known⁶³ complex $\text{Pt}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$ (30%) and $\text{Pt}(\text{OAc}_F)[\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3](\text{PPh}_3)_2$ (30%), a white crystalline solid characterised by analysis and melting point (Table 1.4.), i.r. (Table 1.5.) and ^{19}F n.m.r. spectral data. There is no apparent reaction between $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ and hexafluorobut -2- yne at room temperature. The complex $\text{Pt}(\text{OAc}_F)[\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3](\text{PPh}_3)_2$ may also be obtained by the reaction of equimolar quantities of trifluoroacetic acid and $\text{Pt}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$

in dichloromethane at room temperature . The i.r. spectrum is consistent with unidentate carboxylate coordination, $\nu_{as}(\text{OCO})$ is at 1695cm.^{-1} and $\nu_{sym}(\text{OCO})$ at 1415cm.^{-1} , and the presence of a vinyl group, $\nu(\text{C}=\text{C})$ is at 1615cm.^{-1} . The ^{19}F n.m.r. spectrum shows a broad multiplet at -5.00p.p.m. and a quartet at -9.30p.p.m. relative to benzotrifluoride. The quartet is further split into two smaller quartets due to coupling with ^{195}Pt , $J(\text{Pt}-\text{F}) = 130\text{Hz}$. This spectrum is consistent with the group $\text{Pt}[\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3]$ and the value of 11Hz for $J_{65}(\text{CF}_3-\text{CF}_3)$ indicates a cis arrangement of CF_3 groups .

The complex $\text{Pt}(\text{OAc}_F)[\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3](\text{PPh}_3)_2$ may be converted to the chloro analogue by treatment with lithium chloride. This complex is identical to that obtained by the reaction of hydrogen chloride with a dichloromethane solution of $\text{Pt}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$. I.r. spectral data (Table 1.5.) for this complex is consistent with the presence of a vinyl group, $\nu(\text{C}=\text{C})$ is at 1625cm.^{-1} and $\nu(\text{Pt}-\text{Cl})$ is observed at 300cm.^{-1} . Bands assigned to $\nu_{as}(\text{OCO})$ and $\nu_{sym}(\text{OCO})$ in $\text{Pt}(\text{OAc}_F)[\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3](\text{PPh}_3)_2$ are not present. Analytical and melting point data for $\text{PtCl}[\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3](\text{PPh}_3)_2$ is given in Table 1.4.

This reaction may be discussed in terms of the mechanism shown in Fig.1.2. The formation of a strong

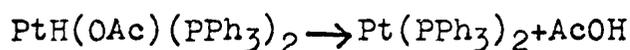
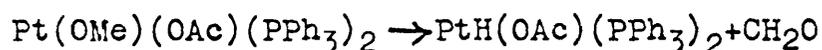
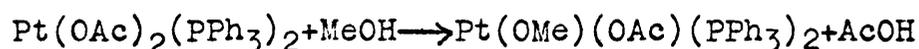
metal-acetylene bond will favour pathway 1. It is known that acetylenes having electron-withdrawing substituents form more stable acetylene complexes than those with electron releasing substituents⁶⁶. Thus in the reaction of $\text{Pt}(\text{OAcF})_2(\text{PPh}_3)_2$ with diphenyl acetylene in methanol pathway 2 is in operation exclusively, while in the reaction with hexafluorobut-2-yne pathway 1 becomes operational. Trifluoroacetic acid is known to react with $\text{Pt}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{PPh}_3)_2$ at room temperature to give the vinyl complex⁶⁴. Why the complex formed via pathway 1 is not attacked by the trifluoroacetic acid also formed via pathway 1 is not clear. The reaction is however not clean; at 70°C there is some metal deposition while at 100°C total decomposition takes place.

The reaction between hexafluorobut-2-yne and $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ in methanol yielded intractible oils.

Reaction of Carboxylate Complexes with Alcohols

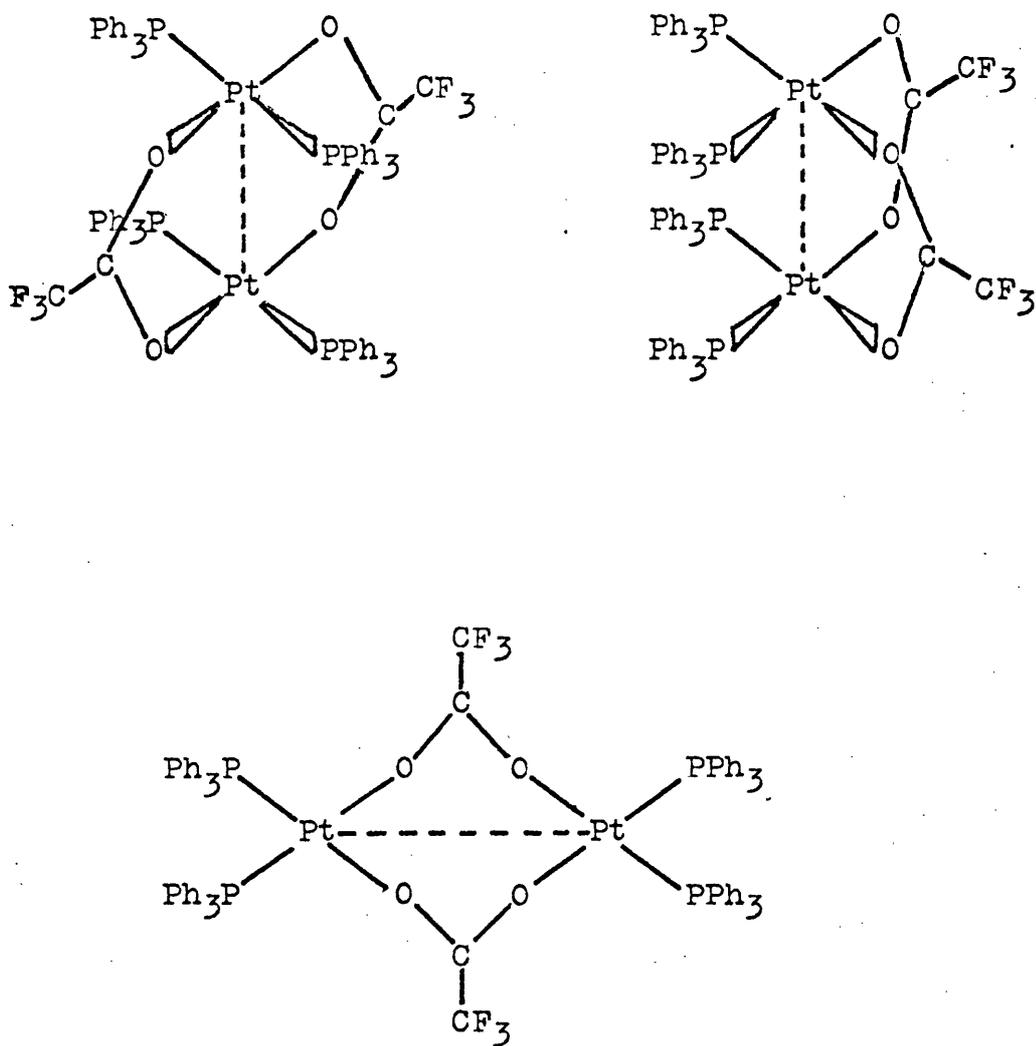
$\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ reacted with both methanol and ethanol to yield a dark red solution. In both reactions the alcohol is oxidised. The presence of formaldehyde was detected, by trapping out as formaldehyde-2:4-dinitro phenyl hydrazone, when the reaction solvent was methanol. Similarly, when the reaction solvent was ethanol, acetaldehyde was detected by trapping out as acetaldehyde-2:4-dinitro phenylhydrazone. However on

work up starting material is recovered almost quantitatively. This is in accord with the formation of $\text{PtH(OAc)(PPh}_3)_2$ which eliminates acetic acid to give $\text{Pt(PPh}_3)_2$ and acetic acid.



The complex $\text{Pt(OAc)}_2(\text{PPh}_3)_2$ may be prepared by the reaction of acetic acid on a benzene solution of $\text{Pt(PPh}_3)_4$.

The reaction of $\text{Pt(OAc)}_2(\text{PPh}_3)_2$ with alcohols is however different. On refluxing with methanol or ethanol under nitrogen an orange solution is obtained. Evaporation to dryness yields an oil from which may be obtained, in the absence of chlorinated solvents, a white crystalline solid (m.p. $183-184^\circ\text{C}$). This compound changes slowly to a yellow crystalline complex (m.p. $163-164^\circ\text{C}$) which may also be obtained from the original oil by treatment with chlorinated solvents. In both reactions the alcohol is oxidised. The presence of formaldehyde was detected, by trapping out as formaldehyde-2:4-dinitro phenylhydrazone, when the reaction solvent is methanol. Similarly, when the reaction solvent is ethanol, acetaldehyde was detected by trapping



Possible structures for the complex

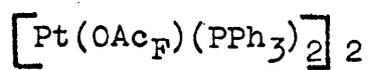
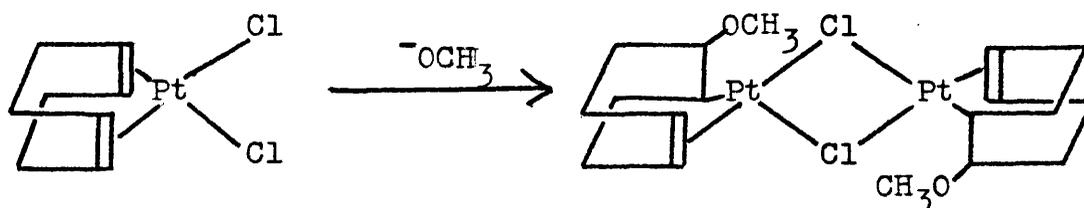


Fig. 1.3.

out as acetaldehyde-2:4-dinitrophenylhydrazone. The i.r. spectrum of this yellow complex, which indicates the presence of a carboxylate group is not consistent with unidentate coordination. $\nu_{\text{as}}(\text{OCO})$ is at 1690cm.^{-1} but $\nu_{\text{sym}}(\text{OCO})$ is not in the region associated with unidentate coordination about 1400cm.^{-1} $\nu_{\text{sym}}(\text{OCO})$ for bidentate or bridging coordination would be expected above 1445cm.^{-1} but the presence of absorptions due to coordinated phosphine about 1480cm.^{-1} probably obscure it. The ^{19}F n.m.r. spectrum shows a singlet at +10.00 p.p.m. relative to benzotrifluoride and the ^1H n.m.r. spectrum exhibits a complex resonance about 2.6 τ . This also indicates that the complex is diamagnetic. Analysis indicates a formula $[\text{Pt}(\text{OAc}_F)(\text{PPh}_3)_2]_2$ and molecular weight determinations from chloroform solution indicates a dimer. Three possible structures for this Pt(I) complex are shown in Fig. 1.3.

Reaction of Carboxylate Complexes with Olefins

Nucleophilic attack on an olefin coordinated to a metal with the formation of a carbon-metal σ bond is well known ⁴¹. The first platinum complex reported to undergo such a reaction was dichlorocycloocta-1,5-⁷⁰diene platinum(II) :



The structure of this complex was confirmed by X ray crystallography⁷¹. This reaction has been extended to include palladium different olefins⁷³ e.g. dicyclopentadiene and different nucleophiles⁷⁴ e.g. $^-CHYCOOR$ where $Y=CO_2CH_3$, $CO_2C_2H_5$, $COCH_3$ and $R=CH_3$, C_2H_5 . The analogous reactions of mercuric acetate has long been known and exploited⁴¹. Thus the reactions of simple olefins with the carboxylate complexes were investigated.

$Pt(OAc_F)_2(PPh_3)_2$ does not react with tetrachloroethylene in methanol at room temperature. At $100^\circ C$ in a Carius tube the known⁷⁵ complex trans - chloro-(trichlorovinyl)bis(triphenylphosphine)platinum(II) is formed. At lower temperatures about $80^\circ C$ the yield of the vinyl complex is diminished and the dimeric trifluoroacetate complex may be isolated. There is no reaction between tetrachloroethylene and $Pt(OAc)_2(PPh_3)_2$ in methanol at room temperature. At $80^\circ C$ in a Carius tube a mixture of trans - chloro-(trichlorovinyl)bis(triphenylphosphine)platinum(II) and cis - dichloro bis(triphenylphosphine)platinum(II) is

obtained.

Tetrachloroethylene is known⁷⁵ to react with a benzene solution of $\text{Pt}(\text{PPh}_3)_4$ at 80°C to give the complex $\text{Pt}(\text{C}_2\text{Cl}_4)(\text{PPh}_3)_2$. In the presence of methanol this complex rapidly isomerises to the complex trans - $\text{PtCl}(\text{C}_2\text{Cl}_3)(\text{PPh}_3)_2$ ⁷⁵. A mechanism for the reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ with tetrachloroethylene may be postulated (See Fig.1.4. pathway 1.). There is no evidence to suggest that pathway 2 occurs even to a slight extent. It is suggested here that the dominance of pathway 1 is due to the rapid isomerisation of the π complex to the vinyl complex, and this may occur (not shown in Fig.1.4.) before trifluoroacetic acid is eliminated. The lack of reactivity of tetrachloroethylene is illustrated by the formation of the dimeric trifluoroacetate complex at low temperatures.

Trichloroethylene reacted with both $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ and $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ in methanol at 80°C to give cis - $\text{PtCl}_2(\text{PPh}_3)_2$ ⁷⁶ quantitatively.

Tetracyanoethylene is known⁷⁶ to react with $\text{PtHCl}(\text{PPh}_3)_2$ to give $\text{Pt}[\text{C}_2(\text{CN})_4](\text{PPh}_3)_2$. Thus both the acetate and trifluoroacetate complexes might be expected to react similarly with tetracyanoethylene in methanol. However the complex $\text{Pt}(\text{CN})_2(\text{PPh}_3)_2$ was isolated from the reaction mixture in very high yield. The reaction of tetracyanoethylene with methanol to give hydrogen cyanide which reacts with the carboxylate complexes to

give the dicyano complex cannot be discounted but it is noted that $\text{Pt}(\text{PPh}_3)_4$ in benzene reacts with tetra-
cyanoethylene to give $\text{Pt}(\text{CN})_2(\text{PPh}_3)_2$ ⁷⁷.

Tetrafluoroethylene reacted with both $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ and $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ in methanol at 100°C to give a mixture of the complex $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$ and an orange carbonyl complex ($\nu(\text{C}\equiv\text{O})$ is at 2000 cm.^{-1}) which could not be characterised. The formation of carbonyls in the reactions of platinum complexes with tetrafluoroethylene has been reported⁷⁸.

The reaction of both the acetate and trifluoroacetate complexes with ethylene in methanol at about 70°C in Carius tubes gave dark red solutions from which no pure complexes could be isolated.

The complex $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ in methanol reacts with tetrafluoroethylene at 100°C to yield an orange intractible oil. Reaction with tetrachloroethylene under similar conditions yielded a colourless oil from which a few crystals could be isolated. The i.r. spectrum of these crystals indicated a vinyl complex; $\nu(\text{C}=\text{C})$ is at 1536 cm.^{-1} , and $\nu(\text{Pt}-\text{Cl})$ at 372 cm.^{-1} , 307 cm.^{-1} , 293 cm.^{-1} , the last two bands indicating the presence of cis - $\text{PtCl}_2(\text{PMe}_2\text{Ph})_2$; but the complex could not be obtained analytically pure in sufficient amount to permit further characterisation.

Reaction of Carboxylate Complexes with alkyl and allyl iodides

Both $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ and $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ react readily with alkyl and allyl iodides in refluxing methanol to give the known ⁷⁹ complex $\text{PtI}_2(\text{PPh}_3)_2$ quantitatively. $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ reacts similarly to give the known ⁴⁸ complex trans - $\text{PtI}_2(\text{PMe}_2\text{Ph})_2$ quantitatively. The stereochemistry was confirmed by ¹H n.m.r. spectroscopy. Under reflux conditions in methanol the methanolysis of an alkyl or allyl iodide to give a methyl ether and hydriodic acid will occur. Hence the reaction of the carboxylate complexes with alkyl or allyl iodide in methanol is in fact the reaction of hydriodic acid with these complexes. As discussed earlier, halogeno acids react with the carboxylate complexes to give the corresponding dihalo bis(phosphine)platinum(II) complexes.

Reactions of the Carboxylate Complexes with Sulphur Dioxide

No pure complexes could be isolated from the reaction of sulphur dioxide with $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ in methanol at 80°C in a Carius tube, and although a methanolic solution of sulphur dioxide will dissolve the trifluoroacetate complex at room temperature. ($\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ is insoluble in methanol at room temperature.) work up of the solution yields starting material only. Reversible reaction of sulphur dioxide with transition metal complexes e.g. trans- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ ⁸⁰ has been reported, but the above observation may

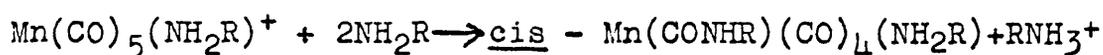
merely be a solubility effect and not involve coordination of sulphur dioxide to platinum.

$\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ reacts with sulphur dioxide in methanol at room temperature to give a high yield of the complex bis(methylsulphonate)bis(triphenylphosphine)platinum(II), $\text{Pt}(\text{SO}_3\text{Me})_2(\text{PPh}_3)_2$. Analytical and melting point data is given in Table 1.4. The i.r. spectrum of the complex is blank in the carboxylate region and shows bands at 1270cm.^{-1} , 1100cm.^{-1} and 990cm.^{-1} . The bands at 1270cm.^{-1} and 1110cm.^{-1} may be assigned to $\nu_{\text{as}}(\text{SO}_2)$ and $\nu_{\text{sym}}(\text{SO}_2)$ respectively. They are about 100cm.^{-1} lower than values quoted for covalent sulphonates viz. $1370\text{--}1350\text{cm.}^{-1}$ and $1192\text{--}1170\text{cm.}^{-1}$ ⁸¹. A similar phenomena is observed for the complexes $\text{PtCl}(\text{p-SO}_2\text{C}_6\text{H}_4\text{CH}_3)(\text{PPh}_3)_2$ ⁸²; $\nu_{\text{as}}(\text{SO}_2)$ is at 1205cm.^{-1} and $\nu_{\text{sym}}(\text{SO}_2)$ is at 1043cm.^{-1} and $\text{IrCl}_2(\text{SO}_2\text{CH}_3)(\text{PPh}_3)_2$ ⁸³; $\nu_{\text{as}}(\text{SO}_2)$ is at 1220cm.^{-1} and $\nu_{\text{sym}}(\text{SO}_2)$ is at 1070cm.^{-1} compared with $1350\text{--}1300\text{cm.}^{-1}$ and $1160\text{--}1120\text{cm.}^{-1}$ for sulphones⁸¹. The lowering of $\nu(\text{SO}_2)$ is due to π -back bonding between the central metal atom and sulphur. The band at 990cm.^{-1} is assigned to $\nu(\text{S-O})$ ⁴⁴. A band at 306cm.^{-1} may be tentatively assigned to $\nu(\text{Pt-S})$ ⁸⁴ and the known⁸⁵ tendency of Pt(II) to coordinate to sulphur in preference to oxygen supports this assignation. Since the complex shows no oxidising properties towards potassium iodide a peroxy

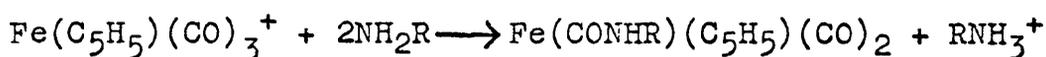
complex containing the group Pt-SO₂O-OR is eliminated. Thus the complex is formulated as containing methyl sulphonate ligands. The simplest mechanism for the formation of Pt(SO₂OCH₃)₂(PPh₃)₂ is displacement of acetate by methoxide followed by sulphur dioxide insertion or methoxide migration to give the methyl sulphonate ligand.

Reactions of Carboxylate Complexes in Amines

The reaction of cationic metal carbonyls with primary and secondary amines to form complexes containing the carboxamido group have been reported^{86,87} :



R= Me, Et, iPr



R= Me, Et, iPr

The structure of cis - Mn(CO)₄(CONHCH₃)(NH₂CH₃) has been established by an X ray structural investigation⁸⁸ .

Amine mercuration reactions of mercuric acetate with olefins in the presence of secondary amines have been reported⁸⁹ . Thus the reactions of Pt(OAc)₂(PPh₃)₂ and Pt(OAc)_F₂(PPh₃)₂ with carbon monoxide in diethylamine were investigated. However only air sensitive, deep purple oils could be isolated. It was observed that in the absence of oxygen the carboxylate complexes reacted with diethyl amine to give yellow oils

which decomposed rapidly on exposure to air. No further investigations were pursued.

Reactions of Carboxylate Complexes in Aprotic Solvents.

Reactions of Carboxylate Complexes with Acids

Both $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ and $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ in dichloromethane solution reacted with halogeno acids to give the dihalo complexes cis - $\text{PtX}_2(\text{PPh}_3)_2$ ($\text{X}=\text{Cl}$, Br .) and the corresponding carboxylic acid (detected by i.r. spectroscopy). Oxidative addition of hydrogen chloride to the complex cis - $\text{Pt}(\text{Me})_2(\text{PEt}_3)_2$ gives cis - $\text{Pt}(\text{Me})\text{Cl}(\text{PEt}_3)_2$ and methane via the Pt(IV) intermediate $\text{PtHCl}(\text{Me})_2(\text{PEt}_3)_2$ ³². However attempts to trap out a Pt(IV) intermediate, such as $\text{PtHCl}(\text{OAc}_F)_2(\text{PPh}_3)_2$ at -78°C were unsuccessful. Treatment of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ in dichloromethane solution with trifluoroacetic acid at room temperature yields the complex $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ while acetic acid does not react with $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ in dichloromethane solution even under reflux conditions.

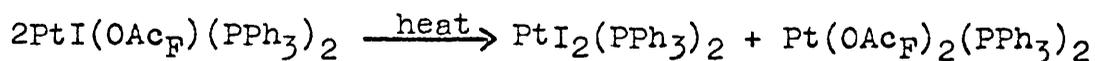
Reactions of Carboxylate Complexes with acetyl chloride

Both $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ and $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ in benzene solution reacted with acetyl chloride to give the complex cis - $\text{PtCl}_2(\text{PPh}_3)_2$.

Reactions of Carboxylate Complexes with methyl iodide

The complex $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ in chloroform solution reacted with methyl iodide on reflux to give a pink solution from which no pure complexes could be isolated.

The complex $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ in both chloroform and benzene solutions reacted with methyl iodide on reflux to give an orange solution, from which was isolated the orange crystalline complex trifluoroacetato iodo bis(triphenylphosphine)platinum(II), $\text{PtI}(\text{OAc}_F)(\text{PPh}_3)_2$. Analytical and melting point data are given in Table 1.4. and i.r. spectral data are given in Table 1.5. The i.r. spectrum is consistent with unidentate carboxylate coordination ($\nu_{\text{as}}(\text{OCO})$ is at 1680cm.^{-1} and $\nu_{\text{sym}}(\text{OCO})$ is at 1436cm.^{-1}). The reaction of the complex $\text{Au}(\text{OAc})(\text{PPh}_3)$ with alkyl halides to give $\text{AuI}(\text{PPh}_3)$ and alkyl acetate has been reported⁹⁰. The ultimate fate of the methyl and trifluoroacetate groups in the reaction of methyl iodide with $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ is presumably similar. Whether the reaction is an oxidative addition of methyl iodide to $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ to give a Pt(IV) complex followed by reductive elimination, or a simple displacement reaction is not known. Attempts to determine the melting point of the complex indicated that double decomposition occurred; melting occurred at both 225°C and 275°C .



Reaction of Carboxylate Complexes with chlorine

When chlorine was bubbled through a dichloromethane

solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ or $\text{Pt}(\text{OAc}_\text{F})_2(\text{PPh}_3)_2$ a yellow colouration, which was not removed by bubbling nitrogen through the solution, resulted. However only intractible oils could be obtained from such solutions.

Reaction of Carboxylate Complexes with carbon monoxide

When carbon monoxide was bubbled through a dichloromethane solution of either $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ or $\text{Pt}(\text{OAc}_\text{F})_2(\text{PPh}_3)_2$ a dark brown solution was formed from which no pure complexes could be isolated.

Reactions of cis - dichloro bis(triphenylphosphine)
platinum(II) in alcoholic media

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King has noted on the basis of force constant calculations for $\nu(\text{CO})$ frequencies in the complexes $\text{M}(\text{OAc}_F)(\text{CO})_5$ ($\text{M}=\text{Mn}$ and Re) and also by comparison of $\Delta\sigma$ and $\Delta\pi$ parameters of Graham⁹² for chloro and trifluoroacetato complexes of the type $\text{MnX}(\text{CO})_5$, that the bonding properties of trifluoroacetate and chloride ligands are similar. Thus some reactions of cis - $\text{PtCl}_2(\text{PPh}_3)_2$ have been investigated. As this complex is very insoluble in alcohols the conditions employed were much more vigorous than those for the corresponding reactions of the trifluoroacetate complex.

Reaction of cis - $\text{PtCl}_2(\text{PPh}_3)_2$ with carbon monoxide

cis - $\text{PtCl}_2(\text{PPh}_3)_2$ suspended in methanol reacted with carbon monoxide at 100°C and 1500 p.s.i. over 24 hours to give a low yield of the complex trans - $\text{PtCl}(\text{COOMe})(\text{PPh}_3)_2$. In ethanol under similar conditions the ethoxycarbonyl complex was not isolated but trans - $\text{PtHCl}(\text{PPh}_3)_2$ was detected spectroscopically. This is consistent with Clark's observation⁵⁰ that the complexes $\text{PtCl}(\text{COOR})(\text{PPh}_3)_2$ ($\text{R}=\text{Me}, \text{Et}$), in the presence of chloride ion and water at 100°C decompose to give trans - $\text{PtHCl}(\text{PPh}_3)_2$, carbon dioxide and the alcohol ROH. It is noteworthy that cis- $\text{PtCl}_2(\text{PPh}_3)_2$ does not give trans - $\text{PtHCl}(\text{PPh}_3)_2$ on treatment with methanol or ethanol at 100°C .

Reaction of cis - PtCl₂(PPh₃)₂ with tetrachloroethylene

Tetrachloroethylene did not react with cis - PtCl₂(PPh₃)₂ in methanol below 100° C. Above 100° C. a yellow solution was obtained from which was isolated an amorphous yellow powder. The i.r. spectrum of this powder showed no bands attributable to $\nu(\text{C}=\text{C})$ and a single $\nu(\text{Pt}-\text{Cl})$ stretching frequency at 300cm.⁻¹. This compound is not trans - PtCl₂(PPh₃)₂ which shows $\nu(\text{Pt}-\text{Cl})$ at 345cm.⁻¹. No further characterisation was possible.

Reaction of cis - PtCl₂(PPh₃)₂ with tetrafluoroethylene

Tetrafluoroethylene did not react with cis - PtCl₂(PPh₃)₂ in methanol below 100° C. but at 100 C. over seven days a suspension containing equal quantities of the known complexes trans - PtCl(CF=CF₂)(PPh₃)₂ and trans - PtCl[(CF₂H)C=CF₂](PPh₃)₂ was formed. As the solvent is changed from methanol to ethanol to propanol to cyclohexanol the yield of trans - PtCl[(CF₂H)C=CF₂](PPh₃)₂ decreased and a mixture of starting material and only trans - PtCl(CF=CF₂)(PPh₃)₂ is obtained from the reaction in cyclohexanol. The two vinyl complexes have previously been isolated from the reaction of trans -PtHCl(PPh₃)₂ and tetrafluoroethylene in benzene and it would seem probable that this complex is formed initially in the reactions of cis - PtCl₂(PPh₃)₂ in alcohols and then reacts further to give the observed products.

TABLE 1.7.

Summary of the reactions between some d⁸ metal complexes and tetrafluoroethylene in methanol.

<u>Complex</u>	<u>Temperature</u>	<u>Product</u>
PtCl ₂ (COD)	140°C	Decomposition of starting material, polytetrafluoroethylene produced.
PdCl ₂ (PPh ₃) ₂	110°C	Decomposition of starting material, polytetrafluoroethylene produced.
RhCl(CO)(PPh ₃) ₂	110°C	Starting material unchanged, polytetrafluoroethylene produced.

$[\text{PtCl}(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$ is produced in the reaction of trans - $\text{PtHCl}(\text{PPh}_3)_2$ with tetrafluoroethylene in benzene. This complex would not be isolated from a reaction mixture containing an alcohol as it is known to react with alcohols to give complexes of the type trans - $\text{PtCl}(\text{COOR})(\text{PPh}_3)_2$. Under the conditions of the reaction these complexes are known to decompose to give trans - $\text{PtHCl}(\text{PPh}_3)_2$. Hence the only complexes isolated are trans - $\text{PtCl}(\text{CF}=\text{CF}_2)(\text{PPh}_3)_2$ and trans - $\text{PtCl}[(\text{CF}_2\text{H})\text{C}=\text{CF}_2](\text{PPh}_3)_2$.

Investigations of the reactions of tetrafluoroethylene with other d^8 square planar complexes in methanol were however disappointing. The results are summarised in Table 1.7.

EXPERIMENTAL

Analytical, melting point and molecular weight data are shown in Tables 1.1. and 1.4. and in this section. Melting points are uncorrected and were recorded on a Reichert hot-stage apparatus. ^1H n.m.r. spectra were recorded on a Varian Associates Spectrometer at 60 MC/S. ^{19}F n.m.r. spectra were recorded on a Varian Associates D.A.60 Spectrometer at 56.4 MC/S. Results are shown in Tables 1.3. and 1.6. I.r. spectra were recorded from Nujol mulls or chloroform solution (unless otherwise stated) on a Perkin-Elmer 225 Spectrophotometer, using KBr ($5000-400\text{ cm.}^{-1}$) and polythene ($400-200\text{ cm.}^{-1}$) windows. Results are shown in Tables 1.2. and 1.5.

AnalaR benzene and AnalaR diethylether were dried over sodium wire before use. AnalaR methanol and absolute ethanol were used. Other solvents were of reagent grade unless otherwise stated. Light petroleum b.p. $40-60^\circ\text{C}$ was used throughout.

Triphenylphosphine was supplied by Albright and Wilson Ltd. and recrystallised from ethanol before use. Organo iodide compounds were supplied by B.D.H. Ltd. and redistilled under nitrogen and stored at 0°C before use. Acetyl chloride was supplied by B.D.H. Ltd. and redistilled under nitrogen in anhydrous conditions directly into reaction mixtures. Tetrachloroethylene and trichloroethylene were supplied by B.D.H. Ltd. and

redistilled under nitrogen and stored over molecular sieves before use. Tetrafluoroethylene was prepared by thermal decomposition of polytetrafluoroethylene (supplied by I.C.I. Ltd.) under vacuum in a silica tube. Tetracyanoethylene and diphenylacetylene were supplied by Koch Light Chemicals Ltd. and used without further purification. Hexafluorobut -2- yne was supplied by Cambrian Chemicals Ltd. Platinum, palladium and iridium salts were obtained on loan from Johnson Matthey Ltd.

Preparation of Starting Materials

Preparation of bis(trifluoroacetato)bis(triphenylphosphine)platinum(II)

A solution of cis - dichlorobis(triphenylphosphine) platinum(II) (2.00g.) in dichloromethane (30ml.) was refluxed with silver trifluoroacetate (1.20g.) for 8 hours. The reaction mixture was filtered and evaporated to half volume under reduced pressure. On addition of light petroleum (30ml.) crystals of the complex were deposited. The complex was filtered off, washed with light petroleum and air dried. The complex was recrystallised from a dichloromethane - light petroleum mixture for analysis. (Found: C, 50.70; H, 3.09; F, 12.23; M(CHCl₃), 937; C₄₀H₃₀F₆O₄P₂Pt requires C, 50.78; H, 3.19; F, 12.05%; M, 946.) Yield 100% (2.52g.) m.p. 220-225°C decomp.

Preparation of diacetato bis(triphenylphosphine)platinum
(II)

A solution of cis - dichloro bis(triphenylphosphine) platinum(II) (2.00g.) in dichloromethane (30ml.) was refluxed with silver acetate (1.00g.) for 8 hours. The reaction mixture was filtered and evaporated to half volume under reduced pressure. On addition of light petroleum (30ml.) crystals of the complex were deposited. The complex was filtered off, washed with light petroleum and air dried. The complex was recrystallised from a dichloromethane - light petroleum mixture for analysis. (Found: C, 57.43; H, 4.37; M(CHCl₃), 847; C₄₀H₃₆O₄P₂Pt requires: C, 57.39; H, 4.39%; M, 838) Yield 100% (2.12g.) m.p. 210-220°C decomp.

Preparation of bis(trifluoroacetate)bis(dimethylphenyl-
phosphine)platinum(II)

A solution of cis - dichloro bis(dimethylphenylphosphine)platinum(II) (2.00g.) in dichloromethane (30ml.) was refluxed with silver trifluoroacetate(1.70g.) for 8 hours. The reaction mixture was filtered and evaporated to one quarter volume under reduced pressure. On addition of diethyl ether (20ml.) crystals of the complex were deposited. The complex was filtered off, washed with diethyl ether and air dried. The complex was recrystallised from a dichloromethane - diethyl ether mixture for analysis. (Found: C, 34.44; H, 3.14;

F, 16.30; M(CHCl₃), 690; C₂₀H₂₂F₆O₄P₂Pt requires: C, 34.43; H, 3.16; F, 16.36%, M, 697.) Yield 100% (2.60g.) m.p. 120-122°C decomp.

Reactions of Carboxylate Complexes

Reactions with carbon monoxide:

Preparation of trifluoroacetato(methoxycarbonyl)bis-(triphenylphosphine)platinum(II)

Carbon monoxide was passed through a stirred suspension of Pt(OAc_F)₂(PPh₃)₂ (0.50g.) in methanol (25ml.) for 30 minutes at room temperature. The resultant orange solution was filtered and the filtrate allowed to stand overnight. The complex crystallised out and was filtered off, washed with cold methanol and air dried. The complex was recrystallised for analysis from an acetone- light petroleum mixture. (Found: C, 53.95; H, 3.84; F, 6.50; M(CHCl₃), 986; C₄₀H₃₃F₃O₄P₂Pt requires: C, 53.88; H, 3.73; F, 6.39%; M, 892) Yield 47% (0.22g.) m.p. 188-195°C decomp.

Preparation of trifluoroacetato(ethoxycarbonyl)bis-(triphenylphosphine)platinum(II)

Carbon monoxide was passed through a stirred suspension of Pt(OAc_F)₂(PPh₃)₂ (0.50g.) in ethanol(25ml.) for 30 minutes at room temperature. The resultant orange solution was filtered and the filtrate allowed to stand overnight. The complex crystallised out and was filtered off, washed with cold ethanol and air dried. The

complex was recrystallised for analysis from an acetone - light petroleum mixture. (Found: C, 54.52; H, 3.84; F, 8.12; $M(\text{CHCl}_3)$ 925; $\text{C}_{41}\text{H}_{35}\text{F}_3\text{O}_4\text{P}_2\text{Pt}$ requires: C, 54.38; H, 3.89; F, 6.29%; M, 906.) Yield 31% (0.18g.) m.p. 185-187°C decomp.

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ with carbon monoxide in dichloromethane

Carbon monoxide was passed through a stirred solution of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.50g.) in dichloromethane (20ml.) for 5 minutes. The solution rapidly darkened to a deep brown colour. No pure complexes could be isolated.

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ with carbon monoxide in methanol

A solution of $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ (0.50g.) in methanol (25ml.) contained in a steel bomb was subjected to 700 atmospheres of carbon monoxide overnight at room temperature. Evaporation under reduced pressure of the resulting brown solution to dryness yielded an oil which on treatment with diethyl ether gave crystals of starting material (0.45g., 90% recovery).

Preparation of acetato(methoxycarbonyl)bis(triphenylphosphine)platinum(II)

Carbon monoxide was passed through a stirred solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.50g.) in methanol (25ml.) for 30 minutes at room temperature. The resultant

orange solution was filtered and the filtrate allowed to stand overnight. The complex crystallised out and was filtered off, washed with cold methanol and air dried. The complex was recrystallised for analysis from an acetone - light petroleum mixture. (Found: C, 56.40; H, 4.13; M(CHCl₃), 830; C₄₀H₃₆O₄P₂Pt requires C, 57.39; H, 4.33%; M, 838) Yield 40% (0.20g.) m.p. 224-227°C decomp.

Reaction of Pt(OAc)₂(PPh₃)₂ with carbon monoxide in dichloromethane

Carbon monoxide was passed through a solution of Pt(OAc)₂(PPh₃)₂ (0.50g.) in dichloromethane (20ml.) for 5 minutes. The solution rapidly darkened to a deep brown colour. No pure complexes could be isolated.

Preparation of chloro(alkoxycarbonyl)bis(triphenylphosphine)platinum(II)

A solution of the complex Pt(COOR)(O₂CR¹)(PPh₃)₂ (R=CH₃, C₂H₅, R¹=CF₃; R=CH₃, R¹=CH₃) in a 1:1 dichloromethane - methanol mixture (40ml.) was refluxed with excess lithium chloride for 2 hours. The solution was evaporated to dryness and the residue extracted with water. The remaining insoluble portion was recrystallised from a dichloromethane - methanol mixture.

Chloro(methoxycarbonyl)bis(triphenylphosphine)platinum(II):

(Found: C, 56.73; H, 4.02; Cl, 4.50; calculated for C₃₈H₃₃ClO₂P₂Pt C, 56.06; H, 4.09; Cl, 4.3%) Yield 100% m.p. 235-236°C decomp.

Chloro(ethoxycarbonyl)bis(triphenylphosphine)platinum(II):

(Found: C, 56.06; H, 4.06; Cl, 4.95; calculated for $C_{39}H_{35}$

ClO_2P_2Pt C, 56.56; H, 4.26; Cl, 4.28%) Yield 100% m.p.

213-217°C decomp.

Reactions with diphenylacetylene

Preparation of trifluoroacetato(1,2 - diphenylvinyl)bis
(triphenylphosphine)platinum(II)

$Pt(OAc_F)_2(PPh_3)_2$ (0.50g.) and diphenylacetylene (0.10g.) were refluxed in methanol (25ml.) for 8 hours to give a yellow solution and pale orange crystals. The crystals were filtered off, washed with cold alcohol and recrystallised for analysis from a dichloromethane - methanol mixture. (Found: C, 61.82; H, 4.00; F, 5.72; $M(CHCl_3)$, 1011; $C_{52}H_{41}F_3O_2P_2Pt$ requires C, 61.74; H, 4.09; F, 5.63% M , 1012) Yield 92% (0.49g.) m.p. 218-221°C decomp.

Ethanol gave the same complex in 77% yield and n-propanol in 56% yield.

Preparation of chloro(1,2 - diphenylvinyl)bis(tri-
phenylphosphine)platinum(II)

$Pt(OAc_F)[PhC=C(H)Ph](PPh_3)_2$ (0.30g.) in a dichloromethane - methanol mixture (40ml.) was refluxed with excess lithium chloride for 2 hours. The solution was evaporated to dryness and the residue extracted with water. The remaining insoluble portion was recrystallised for analysis from a dichloromethane - methanol mixture. (Found: C, 64.44; H, 4.47; Cl, 3.90; $C_{50}H_{41}$

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ClPt_2 requires C, 64.30; H, 4.91; Cl, 3.80%) Yield 100%
(0.28g.) m.p. 240-242°C decomp.

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ with diphenylacetylene in
non-alcoholic solvents

$\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.50g.) and diphenylacetylene
(0.10g.) were refluxed in acetone, benzene or chloro-
form (25ml.) for 8 hours. Evaporation to half volume
under reduced pressure followed by addition of light
petroleum (15ml.) lead to quantitative precipitation
of the starting complex $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ identified
by the i.r. spectrum and m.p.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with diphenylacetylene

$\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.50g.) and diphenylacetylene
(0.10g.) were refluxed in methanol (25ml.) for 8 hours
to give a yellow solution and yellow crystals. The
crystals were filtered off, washed with cold methanol,
air dried and identified as diphenylacetylene bis-
(triphenylphosphine)platinum(0) from the i.r. spectrum
and m.p. which were identical to those of an authentic
sample. Yield 51%(0.27g.) Identical yields are obtained
in both ethanol and n - propanol.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with diphenylacetylene in
non-alcoholic solvents

$\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.50g.) and diphenylacetylene
(0.10g.) were refluxed in acetone, benzene or chloro-
form (25ml.) for 8 hours. Evaporation to half volume under

reduced pressure followed by addition of light petroleum (15ml.) lead to quantitative precipitation of the starting complex $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$; identified by the i.r. spectrum and m.p.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PMe}_2\text{Ph})_2$ with diphenylacetylene

$\text{Pt}(\text{OAc})_2(\text{PMe}_2\text{Ph})_2$ (0.50g.) and diphenylacetylene (0.1 g.) were refluxed in methanol (25ml.) for 48 hours. Evaporation to quarter volume under reduced pressure followed by addition of diethyl ether (20ml.) lead to the quantitative precipitation of the starting complex $\text{Pt}(\text{OAc})_2(\text{PMe}_2\text{Ph})_2$; identified by the i.r. spectrum and m.p.

Reactions with hexafluorobut -2- yne

Preparation of trifluoroacetate [1,2-bis(trifluoromethyl) vinyl]bis(triphenylphosphine)platinum(II)

Hexafluorobut -2- yne (2ml.) was condensed onto a suspension of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.50g.) in methanol (20ml.) contained in a Carius tube. The sealed tube was kept at 70°C for 2 hours. The resultant solution was filtered and evaporated to dryness to give a colourless oil. This oil was taken up in a minimum of dichloromethane and the resulting solution chromatographed on an alumina-hexane column. Two complexes were isolated: hexafluorobut -2- yne bis(triphenylphosphine)platinum (0), identified by the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield

30%(0.14g.) and trifluoroacetato $[1,2 - \text{bis}(\text{trifluoromethyl vinyl})]$ bis(triphenylphosphine)platinum(II).

(Found: C, 50.64; H, 3.01; F, 17.30; $\text{C}_{42}\text{H}_{31}\text{F}_9\text{O}_2\text{P}_2\text{Pt}$ requires C, 50.61; H, 3.11; F, 17.17;%) Yield 30%(0.15g.) m.p. 205-209°C.

Preparation of chloro $[1,2 - \text{bis}(\text{trifluoromethyl vinyl})]$ -bis(triphenylphosphine)platinum(II)

$\text{Pt}(\text{OAc}_F) [\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3] (\text{PPh}_3)_2$ (0.30g.) in a 1:1 dichloromethane - methanol mixture (40ml.) was refluxed with excess lithium chloride for 2 hours. The solution was evaporated to dryness and the residue extracted with water. The remaining insoluble portion was recrystallised for analysis from a dichloromethane - methanol mixture. (Found: C, 52.32; H, 3.41; Cl, 3.90; F, 12.45; $\text{C}_{40}\text{H}_{31}\text{ClF}_6\text{P}_2\text{Pt}$ requires C, 52.29; H, 3.38; Cl, 3.87; F, 12.34;%) Yield 100% (0.46g.) m.p. 242-245°C.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with hexafluorobut -2- yne

Hexafluorobut -2- yne (2ml.) was condensed onto a solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ in methanol (20ml.) contained in a Carius tube. The sealed tube was kept at 70°C for 2 hours. The resultant solution was filtered and evaporated to dryness under reduced pressure to give a green oil. No pure complexes could be isolated.

Reactions with alcohols

Preparation of $[\text{Pt}(\text{OAc}_F)(\text{PPh}_3)_2]$ -2-

$\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.50g.) was refluxed in methanol or ethanol (50ml.) in an atmosphere of nitrogen for 8 hours. The resulting yellow solution was evaporated to dryness under reduced pressure to yield a yellow oil. This was taken up in a minimum of methanol and on addition of diethyl ether a white microcrystalline precipitate was obtained. This was filtered off, washed with diethyl ether and air dried. Yield 0.33g. m.p. 188-189°C. On exposure to light over one week this substance becomes yellow. This same yellow substance was isolated from the initial yellow oil in a highly crystalline form by taking up the oil in a minimum of dichloromethane followed by addition of diethyl ether. The crystals were filtered off, washed with diethyl ether, air dried and recrystallised for analysis from a dichloromethane - diethyl ether mixture. (Found: C, 56.42; H, 3.99 ; F, 4.20 ; P, 7.55 ; M, 1640 ; $\text{C}_{76}\text{H}_{60}\text{F}_6\text{O}_4\text{P}_4\text{Pt}_2$ requires C, 55.44; H, 3.65 ; F, 4.37 ; P, 7.54 ; M, 1645 (CHCl_3)) Yield 75% (0.33g.) m.p. 163-164°C

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with alcohols

$\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.50g.) was refluxed in methanol or ethanol (50ml.) in an atmosphere of nitrogen for 8 hours. The resulting dark red solution was evaporated to dryness under reduced pressure to yield a colourless oil. Treatment of this oil with diethyl ether led to almost quantitative recovery of the starting

complex $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ identified by the i.r. spectrum and m.p.

Detection of aldehydes formed during reactions with alcohols.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with methanol

A stream of nitrogen was bubbled through the reaction mixture and then through a solution of Brady's reagent for the entire course of the reaction. The resultant yellow precipitate was filtered off, washed with ethanol, air dried and recrystallised from ethanol. m.p. 166°C Lit. m.p. 166°C

This proved the formation of formaldehyde during the reaction. An identical procedure proved the formation of acetaldehyde during the reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with ethanol. m.p. 168°C Lit. m.p. 168°C

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with alcohols.

The above procedure was repeated for the reactions of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with alcohols and the presence of formaldehyde and acetaldehyde was detected for the reaction media methanol and ethanol.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with diphenylacetylene in alcohols

The above procedure was repeated and the presence of acetaldehyde and propionaldehyde was detected for the reaction media ethanol and n - propanol.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with diphenylacetylene in alcohols

The above procedure was repeated and the presence of acetaldehyde and propionaldehyde was detected for the reaction media ethanol and n - propanol.

Reactions with Olefins

Reactions with Tetrafluoroethylene

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ with tetrafluoroethylene

Tetrafluoroethylene (3ml.) was condensed onto a suspension of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.50g.) in methanol (20ml.) in a Carius tube. The sealed tube was kept at 100°C for 8 hours. An orange solution was formed and on cooling colourless crystals were deposited. These were filtered off, washed with methanol, air dried and identified as tetrafluoroethylene bis(triphenylphosphine) platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 41.5% (0.18g.). The orange filtrate was evaporated to dryness under reduced pressure and on treatment with diethyl ether an orange solid was obtained which could not be further characterised. Yield 0.27g.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with tetrafluoroethylene

Tetrafluoroethylene (3ml.) was condensed onto a solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.50g.) in methanol (20ml.) in a Carius tube. The sealed tube was kept at 100°C for 8 hours. An orange solution was formed and on cooling colourless crystals were deposited. These were filtered off, washed with methanol, air dried and identified as tetrafluoroethylene bis(triphenylphosphine)platinum(o)

from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 8.2% (0.04g.). The orange filtrate was evaporated to dryness under reduced pressure and on treatment with diethyl ether an orange solid was obtained which could not be further characterised. Yield (0.30g.)

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ with tetrafluoroethylene

Tetrafluoroethylene (3ml.) was condensed onto a solution of $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ (0.50g.) in methanol (20ml.) in a Carius tube. The sealed tube was kept at 100°C for 8 hours. An orange solution was formed. On evaporation to dryness under reduced pressure an intrac-
-tible orange oil was produced from which no complexes could be isolated.

Reactions with Tetrachloroethylene

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ with tetrachloroethylene

Redistilled tetrachloroethylene (1ml.) and $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.50g.) in methanol (20ml.) were sealed in a Carius tube and kept at 80°C for 8 hours. A yellow solution was formed and on cooling white crystals were deposited. These were filtered off, washed with methanol, air dried and identified as chloro-trichlorovinyl bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 32% (0.15g.). The yellow filtrate was evaporated to dryness under reduced

pressure, taken up in a minimum of dichloromethane and on addition of diethyl ether yellow crystals were deposited. These were identified as $[\text{Pt}(\text{OAc}_F)(\text{PPh}_3)_2]_2$ from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 30% (0.13g.)

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with tetrachloroethylene

Redistilled tetrachloroethylene (1ml.) and $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.50g.) in methanol were sealed in a Carius tube and kept at 80°C for 8 hours. White crystals and a yellow solution were formed. No pure compounds could be isolated from the solution. The solid product was filtered off, washed with methanol, air dried and shown by the i.r. spectrum to be a mixture of cis - di - chloro bis(triphenylphosphine)platinum(II) and trans - chlorotrichlorovinyl bis(triphenylphosphine)platinum(II). Yield (0.67g.).

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ with tetrachloroethylene

Redistilled tetrachloroethylene (1ml.) and $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ (0.50g.) in methanol (20ml.) were sealed in a Carius tube and kept at 80°C for 8 hours. The resultant colourless solution was evaporated to dryness under reduced pressure to yield a colourless oil which on shaking with diethyl ether yielded a few colourless crystals. The i.r. spectrum indicated that these consisted of a mixture of cis - dichloro bis -

(dimethylphenylphosphine)platinum(II) and chloro trichlorovinyl(dimethylphenylphosphine)platinum(II).

Reactions with Trichloroethylene

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ with trichloroethylene

Redistilled trichloroethylene (1ml.) and $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.30g.) in methanol (20ml.) was sealed in a Carius tube and kept at 80°C for 8 hours. White crystals were deposited, filtered off, washed with methanol, air dried and identified as cis - dichloro-bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.25g.).

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with trichloroethylene

Redistilled trichloroethylene (1ml.) and $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.30g.) in methanol (20ml.) were sealed in a Carius tube and kept at 80°C for 8 hours. White crystals were deposited, filtered off, washed with methanol, air dried and identified as cis - dichloro bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.28g.)

Reactions with Tetracyanoethylene

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ with tetracyanoethylene

$\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.30g.) and tetracyanoethylene (0.1g.) in methanol (30ml.) were refluxed for 8 hours. The resultant white crystalline precipitate was filtered off,

washed with methanol, air dried and identified as dicyano bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.25g.).

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with tetracyanoethylene

$\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.30g.) and tetracyanoethylene (0.10g.) in methanol were refluxed for 8 hours. The resultant white crystalline precipitate was filtered off, washed with methanol, air dried and identified as dicyano bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.29g.).

Reactions with Acids

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ with hydrogenchloride

1. Dry hydrogen chloride was bubbled through a stirred suspension of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.30g.) in methanol (20ml.). A white precipitate was formed, filtered off, washed with methanol, air dried and identified as cis - dichloro bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.25g.).
2. Dry hydrogen chloride was bubbled through a solution of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.30g.) in dichloromethane (20ml.). The solution was evaporated to half volume under reduced pressure and on addition of light petroleum (20ml.) a white precipitate was formed, filtered off, washed

with light petroleum, air dried and identified as cis - dichloro bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.25g.).

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with hydrogenchloride

1. Dry hydrogen chloride was bubbled through a solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.30g.) in methanol (20ml.). A white precipitate was formed, filtered off, washed with methanol, air dried and identified as cis - dichloro-bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.28g.).

2. Dry hydrogen chloride was bubbled through a solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ in dichloromethane (20ml.). The solution was evaporated to half volume under reduced pressure and on addition of light petroleum (20ml.) a white precipitate was formed, filtered off, washed with light petroleum, air dried and identified as cis - dichloro bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.28g.).

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ with hydrogenchloride

1. Dry hydrogen chloride was bubbled through a solution of $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ (0.30g.) in methanol (40ml.). The solution was evaporated to half volume under reduced pressure and on the addition of diethyl ether (20ml.) a white crystalline precipitate was formed,

filtered off, washed with diethyl ether, air dried and identified as cis - dichloro bis(dimethylphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.23g.).

2. Dry hydrogen chloride was bubbled through a solution of $\text{Pt}(\text{OAc}_F)_2(\text{PMe}_2\text{Ph})_2$ (0.30g.) in dichloromethane (20ml.). The solution was evaporated to half volume under reduced pressure and on addition of diethyl ether (20ml.) a white crystalline precipitate was formed, filtered off, washed with diethyl ether, air dried and identified as cis - dichloro bis(dimethylphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.23g.).

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ with acetic acid

Acetic acid (1ml.) was added to a solution of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.30g.) in dichloromethane (30ml.) and the mixture refluxed for 8 hours. Evaporation to half volume under reduced pressure followed by addition of light petroleum (20ml.) led to quantitative recovery of the starting complex identified as $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ from the i.r. spectrum and m.p.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with trifluoroacetic acid

Trifluoroacetic acid was added to a solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.30g.) in dichloromethane (30ml.) and the mixture refluxed for 8 hours. On evaporation to

half volume under reduced pressure and addition of light petroleum (20ml.) a white crystalline precipitate was formed, filtered off, washed with light petroleum, air dried and identified as $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ from the i.r. spectrum and m.p. Yield 100% (0.34g.).

Reaction with Organo-iodine Compounds

Reactions of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$

1. Methyl iodide, ethyl iodide or alkyl iodide (1ml.) was added to a suspension of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.30g.) in methanol (30ml.) and the mixture refluxed for 2 hours. The resulting yellow crystalline precipitate was filtered off, washed with methanol, air dried and identified as diiodo bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.31g.).

2. Preparation of iodo trifluoroacetato bis(triphenylphosphine)platinum(II)

Methyl iodide was added to a solution of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.30g.) in benzene (30ml.) and the mixture refluxed for 8 hours. The resulting yellow solution was evaporated to half volume under reduced pressure and on addition of light petroleum (30ml.) a yellow crystalline precipitate was formed. This was filtered off, washed with light petroleum, air dried and recrystallised from a benzene - light petroleum mixture for analysis. (Found: C, 47.07; H, 3.42 ; F, 6.10 ; I, 14.02; $\text{C}_{38}\text{H}_{30}\text{F}_3\text{IO}_2\text{P}_2\text{Pt}$ requires C, 47.60 ;

H, 3.13; F, 5.94; I, 13.20%) Yield 100% (0.30g.). m.p. 225 C and 275 C.

Reactions of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with methyl iodide

1. Methyl iodide (1ml.) was added to a solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.30g.) in methanol (30ml.) and the mixture refluxed for 2 hours. The resulting yellow crystalline precipitate was filtered off, washed with methanol, air dried and identified as diiodo bis(tri-phenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.35g.).

2. Methyl iodide (1ml.) was added to a solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.30g.) in chloroform (30ml.) and the mixture refluxed for 8 hours. A red solution resulted but no pure complexes could be isolated.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PMe}_2\text{Ph})_2$ with methyl iodide

Methyl iodide (1ml.) was added to a solution of $\text{Pt}(\text{OAc})_2(\text{PMe}_2\text{Ph})_2$ (0.30g.) in methanol (30ml.) and the mixture refluxed for 8 hours. On cooling the resultant yellow solution a yellow crystalline precipitate was formed. This was filtered off, washed with methanol, air dried and identified as cis - diiodo bis(dimethyl-phenylphosphine)platinum(II) from the i.r. and n.m.r. spectra and m.p. which were identical to those of an authentic sample. Yield 100% (0.31g.).

Reactions with Chlorine

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with chlorine

Dry chlorine was bubbled through a solution of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.30g.) in dichloromethane (30ml.). The solution became yellow but no pure complexes could be isolated.

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with chlorine

Dry chlorine was bubbled through a solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.30g.) in dichloromethane (30ml.). The solution became yellow but no pure complexes could be isolated.

Reactions with Acetyl chloride

Reaction of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ with acetyl chloride

A few drops of acetyl chloride were distilled in the presence of dry nitrogen, directly into a solution of $\text{Pt}(\text{OAc}_F)_2(\text{PPh}_3)_2$ (0.30g.) in benzene (30ml.). The mixture was refluxed in the presence of dry nitrogen for 8 hours. The resulting solution was evaporated to half volume under reduced pressure and on addition of light petroleum (15ml.) a white precipitate was formed. This was filtered off, washed with light petroleum, air dried and identified as cis - dichloro bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.25g.).

Reaction of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ with acetyl chloride

A few drops of acetyl chloride were distilled, in the presence of dry nitrogen, directly into a suspension of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.30g.) in benzene (30ml.). The

mixture was refluxed in the presence of dry nitrogen for 8 hours. The resulting solution was evaporated to half volume under reduced pressure and on addition of light petroleum (15ml.) a white precipitate was formed. This was filtered off, washed with light petroleum, air dried and identified as cis - dichloro bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield 100% (0.28g.).

Reactions with Sulphur Dioxide

Reaction of $Pt(OAc_F)_2(PPh_3)_2$ with sulphur dioxide

1. Dry sulphur dioxide was passed through a stirred suspension of $Pt(OAc_F)_2(PPh_3)_2$ (0.30g.) in methanol (30ml.). The resulting solution was evaporated to half volume and a white crystalline precipitate was formed. This was filtered off, washed with methanol, air dried and identified as the starting complex $Pt(OAc_F)_2(PPh_3)_2$ by the i.r. spectrum and m.p. Recovery of starting material was quantitative.

2. Sulphur dioxide (2ml.) was condensed into a suspension of $Pt(OAc_F)_2(PPh_3)_2$ (0.30g.) in methanol (20ml.) contained in a Carius tube. The sealed tube was kept at 70°C for 2 hours. Orange needle-like crystals were deposited. These were filtered off, washed with methanol and air dried. However no pure complex could be obtained therefrom.

Preparation of bismethylsulphonato bis(triphenylphosphine)platinum(II)

Sulphur dioxide was passed through a stirred solution of $\text{Pt}(\text{OAc})_2(\text{PPh}_3)_2$ (0.50g.) in methanol (30ml.) for 20 minutes. The reaction mixture was filtered and allowed to stand for 1 hour. Pale pink crystals were deposited, filtered off, washed with methanol and air dried. (Found: C, 49.88; H, 3.97; S, 7.03; $\text{C}_{38}\text{H}_{36}\text{O}_6\text{P}_2\text{PtS}_2$ requires C, 49.08; H, 3.90; S, 6.90%) Yield 79.5% (0.43g.) m.p. 183-185°C.

Reactions of cis - dichloro bis(triphenylphosphine)platinum(II)

Reaction of cis - $\text{PtCl}_2(\text{PPh}_3)_2$ with carbon monoxide in methanol

cis - $\text{PtCl}_2(\text{PPh}_3)_2$ (0.30g.) suspended in methanol (15ml.) in a stainless steel bomb was treated with carbon monoxide at 1500 p.s.i. at 100°C for 24 hours. The resulting suspension was filtered and the solid residue washed with methanol and air dried. This residue was extracted with cold benzene (30ml.). The benzene extract was evaporated to half volume under reduced pressure and on addition of light petroleum (15ml.) crystals were deposited. These were identified as trans - chloro(methoxycarbonyl)bis(triphenylphosphine)platinum(II) from the i.r. spectrum and m.p. which were identical to those of an authentic sample. Yield

16% (0.05g.)

Reaction of $\text{cis} - \text{PtCl}_2(\text{PPh}_3)_2$ with carbon monoxide in ethanol

The above procedure was repeated. Only starting material was isolated from the reaction mixture but trans - hydridochochloro bis(triphenylphosphine)platinum(II) was detected from the i.r. spectrum.

Reaction of $\text{cis} - \text{PtCl}_2(\text{PPh}_3)_2$ with tetrachloroethylene

Tetrachloroethylene (1ml.), cis - $\text{PtCl}_2(\text{PPh}_3)_2$ (0.30g.) and methanol (20ml.) were sealed in a Carius tube and maintained at 100°C for 8 hours. The resultant yellow solution was evaporated to dryness under reduced pressure and the resultant oil treated with diethyl ether to give an amorphous yellow powder. No further characterisation was possible. Yield 0.20g.

Reaction of $\text{cis} - \text{PtCl}_2(\text{PPh}_3)_2$ with tetrafluoroethylene

Tetrafluoroethylene (2ml.) was condensed onto a suspension of cis - $\text{PtCl}_2(\text{PPh}_3)_2$ (0.50g.) in methanol (20ml.) contained in a Carius tube and the sealed tube maintained at 100°C for 7 days. The resultant suspension was filtered off, washed with methanol and air dried. The crystalline residue was taken up in a minimum of dichloromethane and the solution chromatographed on an alumina-hexane column. Two pure complexes were isolated: trans - chloro(perfluorovinyl)bis(triphenylphosphine)-platinum(II) Yield 49% (0.26g.) and trans - chloro-

[1-(difluoromethyl) 2-(difluor)vinyl] bis(triphenylphosphine)platinum(II) Yield 49% (0.27g.) . These were identified from the i.r. spectra and m.ps. which were identical to those of authentic samples. The reaction is solvent dependent and the yield of trans-PtCl[(CF₂H)(C=CF₂)](PPh₃)₂ decreases as the solvent is changed from methanol to ethanol to propanol and only starting material and trans - PtCl(CF=CF₂)(PPh₃)₂ are obtained from the reaction in cyclohexanol.

CHAPTER 2

"And he that breaks a thing to find out what
it is has left the path of wisdom." -

Gandalf the Grey

The Fellowship of the Ring

J.R.R. Tolkien

INTRODUCTION

1,2 - dicarbonyl compounds are known to undergo cycloaddition reactions⁹⁵. Both tetrachloro o - quinone and 9,10 - phenanthrenequinone react with sulphur dioxide upon irradiation to give cyclic sulphates⁹⁶ as shown in Fig. 2.1.a. Triphenylphosphine forms 1:1 adducts with o - benzoquinones⁹⁷ and 9,10 - phenanthrene quinone⁹⁸. The products of these reactions were considered to have dipolar structures as shown in Fig.2.1.b.

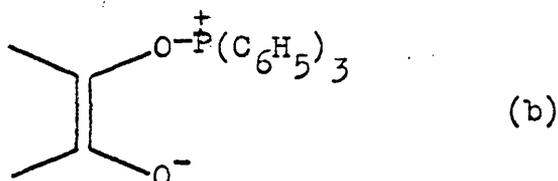
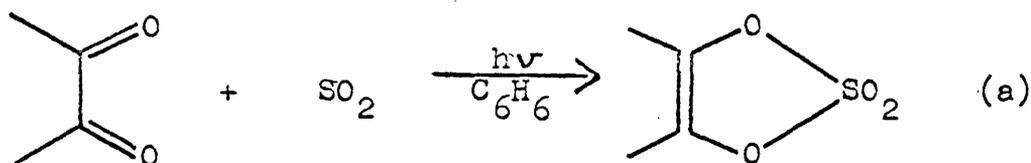


Fig.2.1.

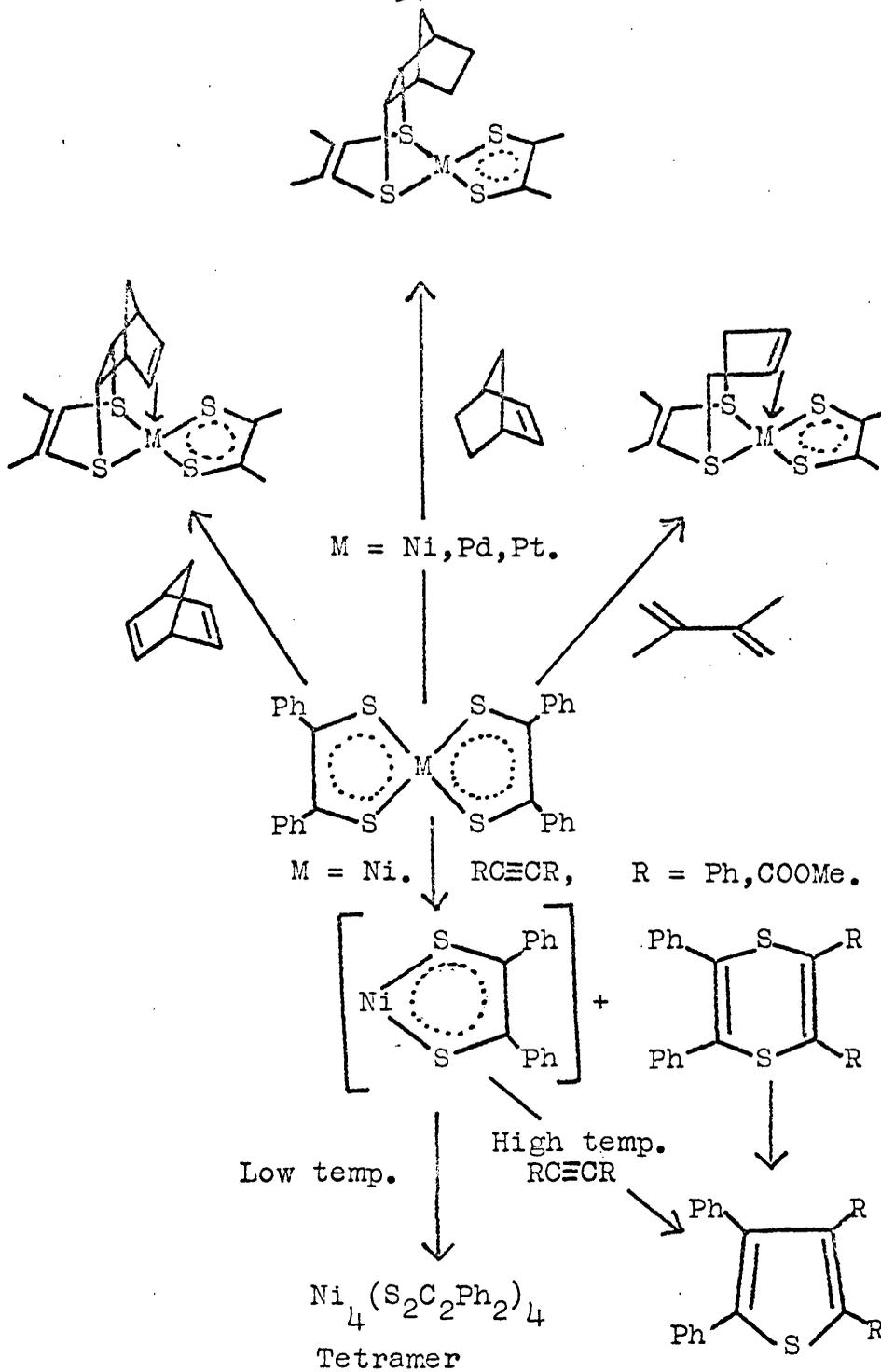
In an attempt to study further d^8 - metal complexes containing metal-oxygen bonds the reactions of the o - quinones tetrachloro o - benzoquinone and 9,10 - phenanthrenequinone with the d^{10} metal complexes tetrakis(triphenylphosphine) platinum (o) and - palladium (o) were investigated. The d^8 - metal complexes

prepared in this manner proved very stable and totally unreactive towards carbon monoxide, alkyl halides and diphenyl acetylene. Thus the reactions of o - quinones with complexes containing organic moieties, e.g. a carbonyl group or π - bonded olefins and acetylenes, which might conceivably be incorporated into a ring system formed by addition of an o - quinone were investigated. The reactions of tetrachloro o - benzoquinone and 9,10 - phenanthrenequinone with the complexes $\text{Ni}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$, trans - $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, $\text{Pt}(\text{trans} - \text{C}_2\text{H}_2\text{Ph}_2)(\text{PPh}_3)_2$, and the reactions of tetrachloro o - benzoquinone with the complexes $\text{Pt}(\text{PhC}_2\text{H})(\text{PPh}_3)_2$ and $\text{Pt}(\text{Ph}_2\text{C}_2)(\text{PPh}_3)_2$ were studied.

Little has been recently reported on metal - 1,2 - dioxylene systems. A series of complexes derived from o - benzoquinone and tetrachloro o - benzoquinone of the $[\text{M} - \text{O}_4]^{2-}$ type have been prepared, $\text{M}=\text{Mg}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$; but research has concentrated on the properties of electron transfer exhibited by such complexes ¹⁰⁰.

1,2 - dithiolene complexes have however been the subject of much research ¹⁰¹. The reactions of some bis(dithiolene) complexes of the nickel group with olefins and acetylenes ¹⁰² have been reported and the results of such investigations are shown in Fig.2.2.

-97-



Reactions of bis(dithiolene) complexes of the nickel group with olefins and acetylenes.

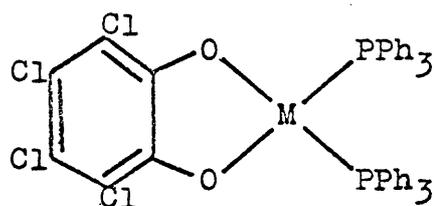
Fig.2.2.

RESULTS AND DISCUSSION

Reactions of quinones with the complexes $\text{Pt}(\text{PPh}_3)_4$
and $\text{Pd}(\text{PPh}_3)_4$

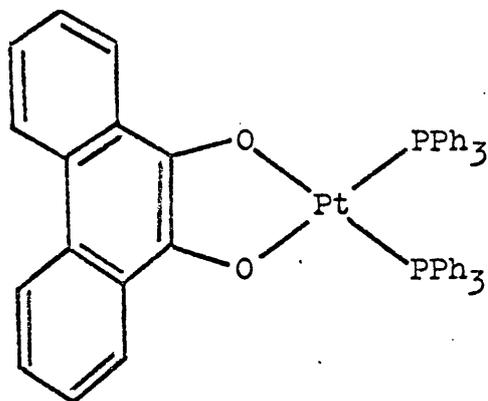
Tetrakis(triphenylphosphine) platinum (0) dissolved in dry benzene reacts readily with both tetrachloro o - benzoquinone and 9,10 - phenanthrenequinone to give the complexes (tetrachlorobenzene 1,2 - dioxylene) bis (triphenylphosphine) platinum (II) and (phenanthrene 1,2 - dioxylene) bis (triphenylphosphine) platinum (II) respectively, in good yield. Analytical, melting point and molecular weight data are shown in Table 2.1. Tetrakis(triphenylphosphine) palladium(0) dissolved in dry benzene reacts readily with tetrachloro o - benzoquinone to give two complexes; a dark blue crystalline complex and a brown crystalline complex. Both complexes analyse as $\text{Pd}(\text{C}_6\text{Cl}_4\text{O}_2)(\text{Ph}_3\text{P})_2$ (see Table 2.1.) and their i.r. spectra are similar. Both complexes may be recrystallised without loss or change in melting point; and both may be stored for several months without apparent change. Thus it would appear that there are two stable crystalline forms of the complex (tetrachlorobenzene 1,2 - dioxylene) bis(triphenylphosphine) palladium (II). No pure complexes could be obtained from the reaction of 9,10 - phenanthrenequinone with tetrakis(triphenylphosphine) palladium (0) in benzene solution.

The structure of these 1,2 - dioxylene complexes



(tetrachlorobenzene-1,2-dioxy)bis(triphenylphosphine)Metal(II).

M = Pd, Pt.



(9,10-phenanthrene-1,2-dioxy)bis(triphenylphosphine)platinum(II).

Fig.2.3.

is thought to be square planar in keeping with the known geometry of four coordinate Pt(II) and Pd(II) and is shown in Fig. 2.3. E.s.r. data obtained from $[\text{Cu}(\text{C}_6\text{H}_4\text{O}_2)_2]^{2-}$ and its tetrachloro analogue have shown that there is some degree of covalence in the copper-oxygen bonds. Thus the representation of these complexes as square planar systems containing Pt - O σ bonds is not unjustified. The possibility of these complexes being metal (O) complexes of o - quinones is thought unlikely considering a) the readiness with which o - quinones undergo cyclo addition and lose their dione character and b) the readiness with which the complexes $\text{M}(\text{PPh}_3)_4$ (M=Pd,Pt) undergo oxidative addition.

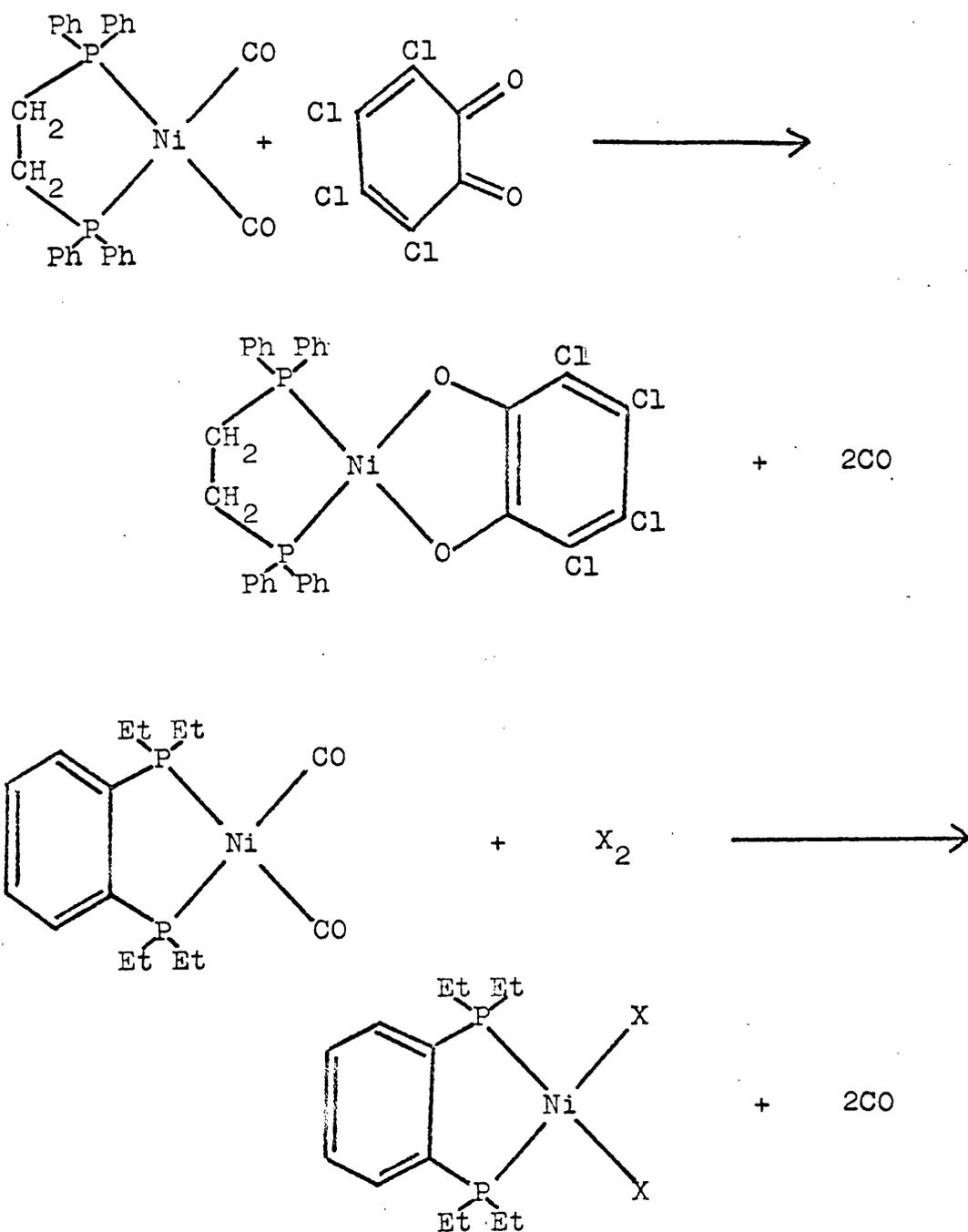
The complex tetrakis(triphenylphosphine) platinum (0) in benzene solution has been shown to be extensively dissociated into tris(triphenylphosphine) platinum (0) and triphenylphosphine and the coordinately unsaturated $\text{Pt}(\text{PPh}_3)_3$ has been shown to be the reactive intermediate in some substitution and oxidative addition reactions. Presumably the reaction of o - quinones with both $\text{Pt}(\text{PPh}_3)_4$ and $\text{Pd}(\text{PPh}_3)_4$ in benzene proceeds via such intermediates. o - quinones are known to react readily with phosphines and in reactions with tetrachloro o - benzoquinone unless excess o - quinones is used a low yield of 1,2 - dioxylene complex is obtained. An excess of quinone in the reaction of 9,10 - phenan-

threnequinone with $\text{Pt}(\text{PPh}_3)_4$ was not necessary and it has been reported that this o-quinone only reacts with triphenylphosphine in wet benzene .
98

Attempts to react the platinum 1,2 - dioxylene complexes with methyl iodide, diphenyl acetylene and carbon monoxide in benzene or dichloromethane failed, even under vigorous conditions. The stability of the platino 1,2 - dioxylene ring system with respect to carbon monoxide compared to that of the bis(acetato) platinum system (in non alcoholic solvents) is probably best understood in terms of the chelate effect; which is completely absent in the bis(acetato) platinum case. It has been established that 5 - membered rings are more stable than comparable 6 - and 7 - membered rings . Any reaction at the metal oxygen bond, the weakest point in the ring system , would lead to loss of the stability associated with the 5 - membered ring either completely if $\text{C}_6\text{Cl}_4\text{O}_2^{2-}$ is displaced, or partially if insertion resulted in a 6 - or 7 - membered ring being formed.
104
85

Reactions of quinones with metal-carbonyl complexes

In an attempt to incorporate a carbonyl into the ring formed upon oxidative addition of an o-quinone to a metal complex the reaction of the complexes $\text{Ni}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$, trans - $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and



Reaction of halogen and o-quinone with nickel carbonyl complexes

Fig.2.4.

trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ with both tetrachloro o - benzoquinone and 9,10 - phenanthrenequinone were investigated.

Dicarbonyl [1,2 - bis(diphenylphosphino)ethane] nickel (0) dissolved in dry benzene reacts instantly with tetrachloro o - benzoquinone; effervescence occurs and a high yield of the complex (tetrachlorobenzene 1,2 - dioxylene) [1,2 - bis(diphenylphosphine)ethane] nickel(II) is obtained as a brown crystalline precipitate. Analytical and melting point data are given in Table 2.1. This reaction is in keeping with the reaction of dicarbonyl [o - phenylene bis(diethylphosphine)]nickel(0), $\text{Ni}(\text{CO})_2[\text{o} - \text{C}_6\text{H}_4(\text{PEt}_2)_2]$, with halogens to give dihalo [o - phenylene bis(diethylphosphine)]nickel(II) , $\text{NiX}_2[\text{o} - \text{C}_6\text{H}_4(\text{PEt}_2)_2]$. These reactions occur very readily at room temperature with the evolution of carbon monoxide ¹⁰⁶. Both these reactions are shown in Fig. 2.4. ^{106a}

Reaction of a benzene solution of $\text{Ni}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ with 9,10 - phenanthrenequinone at room temperature over ten days produces a dark green precipitate. There is no visible evolution of gas. Attempted purification however lead to recovery of quinone only.

A benzene solution of trans - chlorocarbonyl bis (triphenylphosphine) iridium(I), trans - $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ reacts overnight with tetrachloro-o-benzoquinone at

TABLE 2.1.

Analytical, molecular weight and melting point data for 1,2 - dioxylene complexes.

Complex	Analytical Data			Molecular Weight Found	Melting Point
	Found (%)	Required (%)	Other		
	C	H		Required	
Pt(C ₆ Cl ₄ O ₂)(PPh ₃) ₂	52.25 52.19	3.04 3.11	14.63(Cl) 14.70(Cl)	972 966	275-277°C
Pd(C ₆ Cl ₄ O ₂)(PPh ₃) ₂ (Blue form)	57.25 57.52	3.35 3.45	16.37(Cl) 16.17(Cl)	- -	220-222°C
Pd(C ₆ Cl ₄ O ₂)(PPh ₃) ₂ (Brown form)	57.44 57.52	3.44 3.45	14.85(Cl) 16.17(Cl)	- -	226-228°C
Ni(C ₆ Cl ₄ O ₂)(Ph ₂ PCH ₂ PPh ₂)	54.02 54.65	2.95 2.71	19.92(Cl) 20.21(Cl)	- -	247-249°C
Ir(C ₆ Cl ₄ O ₂)Cl(CO)(PPh ₃) ₂	50.24 50.25	2.96 2.92	18.35(Cl) 17.28(Cl)	- -	300°C
Rh(C ₆ Cl ₄ O ₂)Cl(CO)(PPh ₃) ₂	55.33 55.06	3.22 3.20	18.72(Cl) 18.94(Cl)	- -	175°C
Pt(C ₄ H ₈ O ₂)(PPh ₃) ₂	66.13 65.42	4.13 4.17	- -	920 928	200-202°C
Pt(C ₆ Cl ₄ O ₂)(PhC≡CPh)(PPh ₃)	51.61	2.78	16.06(Cl) 3.57(P)	925	232-234°C
	51.06	2.84	16.12(Cl) 3.52(P)	881	

Molecular weight data obtained from chloroform solution.

TABLE 2.2.

Infrared Spectral data concerning $M(C_6Cl_4O_2)Cl(CO)(PPh_3)_2$ and related complexes (cm^{-1}).

Complex	$\nu(C=O)$	$\nu(M-Cl)$	ref.
<u>trans</u> - $IrCl(CO)(PPh_3)_2$	1960st.	312st.	20
$Ir(C_6Cl_4O_2)Cl(CO)(PPh_3)_2$	2060st. 2012w.	367w. 292st.	-
$IrCl_3(CO)(PPh_3)_2$	2080st.	326vst. 302st.	107
$IrClBr_2(CO)(PPh_3)_2$	2088st.	311st. 302sh.	107
$IrClI_2(CO)(PPh_3)_2$	2079st.	304sh. 296st.	107
<u>trans</u> - $RhCl(CO)(PPh_3)_2$	1960st.	311st.	108
$Rh(C_6Cl_4O_2)Cl(CO)(PPh_3)_2$	2020st.	328st.	-
$RhCl_3(CO)(PPh_3)_2$	not reported	341, 316	107
$RhClI_2(CO)(PPh_3)_2$	not reported	308mst.	107

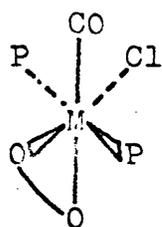
I.r. spectra were recorded from Nujol mulls using KBr windows.

st = strong, m = medium, w = weak, sh = sharp.

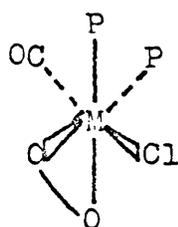
room temperature to give a red crystalline precipitate of the complex (tetrachlorobenzene - 1,2 - dioxylyene) (chloro)(carbonyl)bis(triphenylphosphine) iridium(III), $\text{Ir}(\text{C}_6\text{Cl}_4\text{O}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$, in high yield. Under similar conditions trans - chloro(carbonyl)bis(triphenylphosphine)rhodium(I), trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ reacts readily with tetrachloro-o-quinone to give the dark blue crystalline complex (tetrachlorobenzene -1,2- dioxylyene) (chloro)(carbonyl)bis(triphenylphosphine)rhodium(III); $\text{Rh}(\text{C}_6\text{Cl}_4\text{O}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$, in good yield. Analytical and melting point data for these complexes are given in Table 2.1.

I.r. data concerning these and related complexes are given in Table 2.2. Both complexes show an increased frequency of $\nu(\text{C}\equiv\text{O})$ on going from the starting material. This is due to the smaller back donation of electrons from the central metal atom in the M(III) complex onto the carbon monoxide, due to the increased positive charge; this increasing the carbon - oxygen bond order and increasing the stretching frequency of the carbon - oxygen bond.

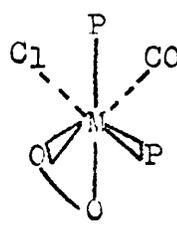
Although the oxidative addition of an o - quinone to a metal complex must always be cis there are six possible geometries for the resultant complex in the reactions considered here. These are illustrated in Fig. 2.5.A-F.



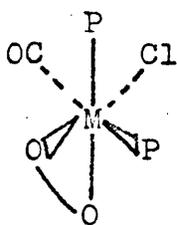
(A)



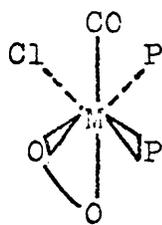
(B)



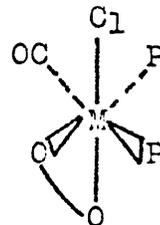
(C)



(D)



(E)



(F)

P = PPh₃, $\begin{matrix} \text{O} \\ | \\ \text{O} \end{matrix}$ = 1,2-dioxylylene system, M = Ir, Rh.

Possible stereochemical isomers from the addition of an o-quinone to trans-MCl(CO)(PPh₃)₂.

Fig.2.5.

From the i.r. data it is possible to elucidate the stereochemistry of the complexes prepared. As there is only one carbonyl group and one metal-halogen bond in the M(III) complexes a single stretching frequency for $\nu(\text{C}\equiv\text{O})$ and a single stretching frequency for $\nu(\text{M}-\text{Cl})$ are to be expected. [The solution spectra of the complexes are identical in the $\nu(\text{C}\equiv\text{O})$ region, to the solid state spectra in that region.] Thus it appears that the complex $\text{Ir}(\text{C}_6\text{Cl}_4\text{O}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ as prepared here consists of a mixture of geometrical isomers. The absorptions at 2012cm.^{-1} and 367cm.^{-1} are assigned to the complex with structure (A) in Fig. 2.5. The increase in the frequency of $\nu(\text{C}\equiv\text{O})$ observed is less than that found when the Cl - Ir - CO system remaining trans undergoes an Ir(I) to Ir(III) oxidation state increase. Structures (D) and (F) in Fig. 2.5., in which a carbonyl group is trans to a phosphine, would exhibit $\nu(\text{C}\equiv\text{O})$ at values higher than those observed for the trans Cl - Ir - CO system; due to competition between the phosphine and carbonyl for electron density at the metal, this leading to a decrease in electron density in the π^* orbitals of the carbonyl. e.g. $\nu(\text{C}\equiv\text{O})$ for the complex $\text{IrCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_2$, in which CO is trans to PMe_2Ph is at 2092cm.^{-1} ¹⁰⁹. Hence structures (D) and (F) may be eliminated. Shaw ¹⁰⁹ has assigned $\nu(\text{Ir}-\text{Cl})$ stretching frequencies into the following groups depending on the ligand in the trans position:

331 - 320 cm.^{-1} (trans - Cl), 315 - 304 cm.^{-1} (trans-CO), 291 - 280 cm.^{-1} (trans - tertiaryphosphine). Hence the absorption at 367 cm.^{-1} is assigned to $\nu(\text{Ir-Cl})$ trans-1,2 - dioxylene. The only structure which fits these i.r. spectra criteria i.e. both carbonyl and chloride ligands trans to 1,2 - dioxylene, is structure (A). Both absorptions associated with isomer (A) are weak indicating that it is present in a small amount relative to the other component.

The absorption at 2060 cm.^{-1} and 290 cm.^{-1} are assigned to isomers (C) or (E). The absorption at 290 cm.^{-1} is assigned to $\nu(\text{Ir-Cl})$ trans to triphenylphosphine. $\nu(\text{C}\equiv\text{O})$ is at a frequency lower than expected for the systems trans OC - Ir - Cl or trans OC - Ir - PPh₃ and hence is assigned a trans - 1,2 - dioxylene position. It is interesting to note the difference in $\nu(\text{C}\equiv\text{O})$ for the isomers (A) and (C) or (E). It would appear that in isomer (A) there is more π -back donation from the central metal atom to the π^* orbitals of the carbon monoxide than in isomer (C) or (E). This implies that there is more back donation from the metal to the oxygen of the 1,2-dioxylene system, in isomer (C) or (E) than in isomer (A). A possible explanation of the difference in the bonding of these isomers is as follows:

Neither the carbon monoxide nor chloride ligand have a strong trans - bond weakening effect; hence the Ir-O bonds in isomer (A) will be equivalent and the metal - 1,2 - dioxylene system will be symmetric.

Triphenylphosphine has a strong trans bond weakening effect¹⁰⁹; hence the Ir - O bond trans to triphenylphosphine in isomer (C) or (E) will be weaker, i.e. longer, than the Ir - O bond trans to CO in isomer (C) or (E). Such assymetry in a chelate group has been observed in the complex $K[Pt(acac)_2Cl]$ ¹⁵¹. It may be postulated that Ir - O trans - CO bond of isomer (C) or (E) will become shorter than the Ir - O trans - CO bond of isomer (A) to retain the metal - 1,2 - dioxylene ring stability. Such a shortening may be considered to increase π - back donation from the metal to the oxygen trans to CO with the result that $\nu(C\equiv O)$ for isomer (C) or (E) is higher than $\nu(C\equiv O)$ for isomer (A), where such Ir - O trans - CO bond shortening does not occur.

The complex $Rh(C_6Cl_4O_2)Cl(CO)(PPh_3)_2$ exhibits only one $\nu(C\equiv O)$ stretching frequency and one $\nu(Rh - Cl)$ stretching frequency. Thus only one geometrical isomer is present. From Table 2.2. it is apparent that $\nu(Rh(III) - Cl)$ occurs at frequencies between 10 and 20 cm^{-1} higher than $\nu(Ir(III) - Cl)$ frequencies for equivalent environments. Thus Shaw's¹⁰⁹ $\nu(Ir - Cl)$ trans - ligand groupings may be converted to $\nu(Rh - Cl)$ trans - ligand groups. This is of course only a rough guide but a paucity of i.r. spectral data for Rh(III) complexes containing the $RhCl(CO)(PPh_3)_2$ system in a

variety of configurations make this necessary. Thus the absorption at 328 cm.^{-1} is assigned to $\nu(\text{Rh} - \text{Cl})$ trans to carbon monoxide. Hence the complex $\text{Rh}(\text{C}_6\text{Cl}_4\text{O}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ is assigned structure (B) in Fig. 2.5.

It is interesting to note that during the formation of $\text{Ir}(\text{C}_6\text{Cl}_4\text{O}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$, isomers (C) or (E), the tertiary phosphines and the carbon monoxide and chloride ligands have become cis when they were originally trans in the starting material. In the formation of $\text{Rh}(\text{C}_6\text{Cl}_4\text{O}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ the triphenylphosphine ligands have become cis when they were originally trans in the starting material. Such substantial rearrangements of ligands upon oxidative addition have, in the past, been considered unlikely^{107,110}. A similar rearrangement is encountered in the formation of the complexes $\text{IrBr}(\text{CO})(\text{PPh}_3)_2(\text{C}_2(\text{CN})_4)^5$ and $\text{IrCl}(\text{CO})(\text{PPhMe}_2)(\text{C}_2(\text{CN})_4)^6$ from trans $\text{IrX}(\text{CO})\text{L}_2$. Baddley¹¹¹ has argued that although the trans configuration would appear sterically preferable the strong π acidity of $\text{C}_2(\text{CN})_4$ forces a cis configuration. In a trans configuration $\text{C}_2(\text{CN})_4$ would be trans to CO and there would be competition between the two strong π acids for electron density. However trans - $\text{RhCl}(\text{CO})_2(\text{PPh}_3)$ reacts with $\text{C}_2(\text{CN})_4$ to give the complex $\text{RhCl}(\text{CO})_2(\text{PPh}_3)(\text{C}_2(\text{CN})_4)$ in which the carbonyl groups are thought to be cis yet cis $\text{RhCl}(\text{CO})_2\text{L}$

(L = pyridine or *p* - toluidine) reacts with $C_2(CN)_4$ to give the complex $RhCl(CO)_2L(C_2(CN)_4)$ in which the carbonyl groups are trans. Thus it is apparent that the factors controlling the resultant geometry of a complex formed via an oxidative addition reaction are more complex than has been supposed, and that considerable rearrangement of ligands may take place under mild conditions.

9,10 - phenanthrenequinone does not react with trans $RhCl(CO)(PPh_3)_2$ even on vigorous reflux in benzene for one week, and only undergoes incomplete reaction with trans - $IrCl(CO)(PPh_3)_2$ under similar conditions. This is in keeping with the known trend of the tendency to undergo oxidative addition to increase on descending a triad. Careful chromatography could not separate the 9,10 - phenanthrene 1,2. dioxylene adduct from the starting material. The i.r. spectrum of the mixture shows $\nu(C\equiv O)$ at 2020 cm^{-1} and $\nu(Ir - Cl)$ at 328 cm^{-1} for the adduct which may be assigned structure (A) in Fig. 2.5.

I.r. absorptions of the metal -1,2 - dioxylene system.

The i.r. absorptions associated with the tetra-chlorobenzene 1,2 - dioxylene - metal system will now be discussed. A simple group theory treatment of

TABLE 2.3.

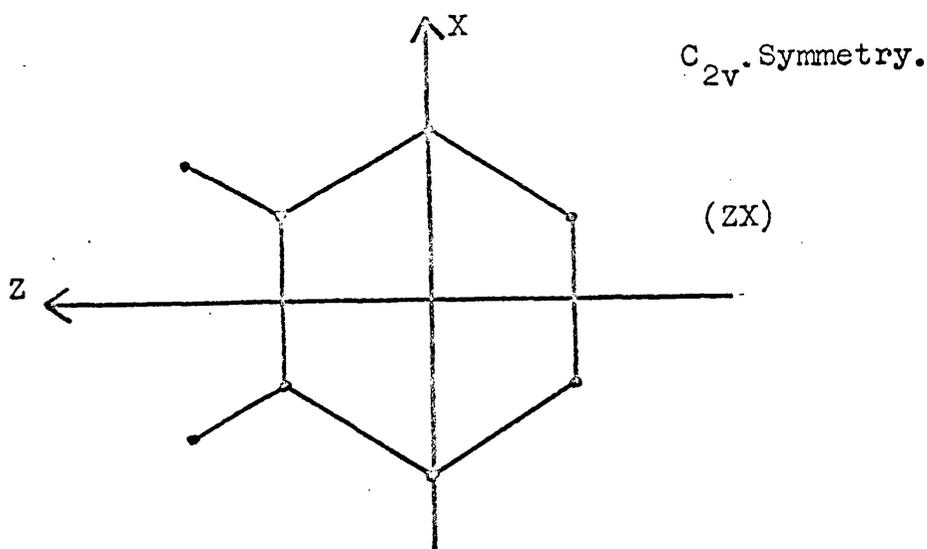
Infrared absorptions associated with metal -1,2- dioxylene system (cm.⁻¹).

<u>Complex</u>	<u>I.r. absorption</u>
Pt(C ₆ Cl ₄ O ₂)(PPh ₃) ₂	1527w 1433s 1262s 1221msh 974s 808s 796s 584s
Pd(C ₆ Cl ₄ O ₂)(PPh ₃) ₂ Blue form	1520w 1430s 1260s 1216msh 970s 805s 791s 563m
Brown form	1520w 1433s 1260s 1218msh 970s 804s 790s 563m
Ni(C ₆ Cl ₄ O ₂)(Ph ₂ PCH ₂ CH ₂ PPh ₂)	1525w 1437s 1259s 1224ssh 977s 808s 796s 590s 583m
Ir(C ₆ Cl ₄ O ₂)Cl(CO)(PPh ₃) ₂	1525w 1425s 1253s 1212msh 971s 808s 795s 596s
Rh(C ₆ Cl ₄ O ₂)Cl(CO)(PPh ₃) ₂	1530w 1433s 1260s 1210msh 972s 809s 794sh 578s
Pt(C ₁₄ H ₈ O ₂)(PPh ₃) ₂	1509w 1416s 1338m 1221s 936s - 791s 554s others 1052s 601s
Ir(C ₁₄ H ₈ O ₂)Cl(CO)(PPh ₃) ₂	1512w - 1339m 1220w 940w - 789w others 1051s

I.r. spectra recorded from Nujol mulls using KBr widdows.

s = strong, w = weak, sh = sharp, m = medium.

the system shown in Fig. 2.6. indicates that there are thirteen in plane (σ_{zx}) i.r. active vibrations and deformations; viz. $7A_1$ and $6B_1$. Of these $4A_1$ and $4B_1$ are basically $\nu(C=C)$ and $\nu(C-O)$. Hence eight absorptions, in the $900 - 1800 \text{ cm}^{-1}$ region, should be observed. As seen from Table 2.3. only five absorptions are observed. This is most probably due to accidental coincidence of some of these bands with bands associated with coordinated phosphine. Thus it is possible to use these i.r. absorptions only as a fingerprint for the tetrachlorobenzene -1,2 - dioxylene metal system. It is seen, from Table 2.3. that a similar, though not quite so well defined, pattern is observed for the phenanthrene - 1,2 - dioxylene - metal system.



Model system used in the group theory treatment of the metal - 1,2 - dioxylene system.

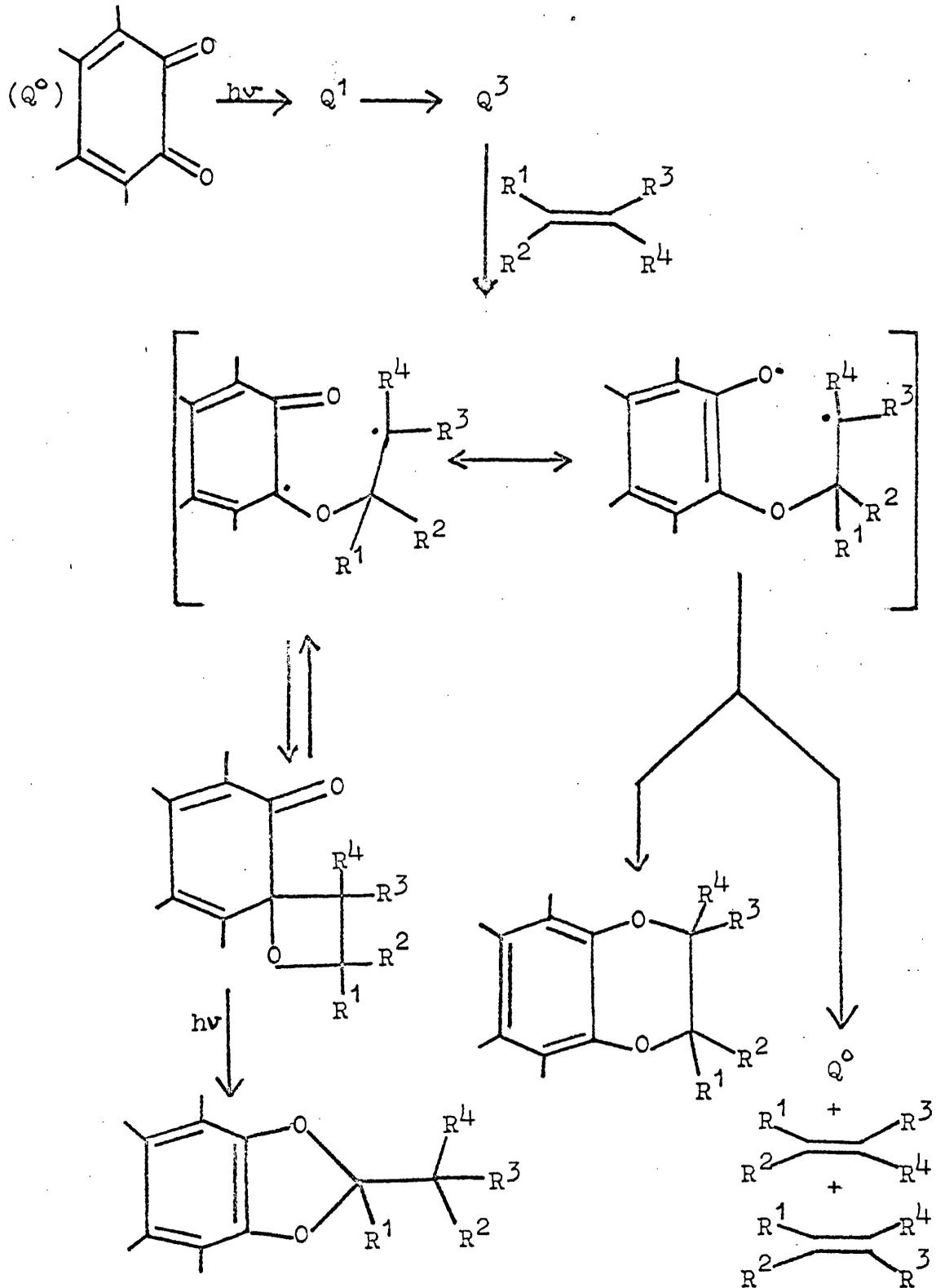
Fig.2.6.

It is interesting to note that, whilst unreactive towards carbon monoxide, methyl iodide and diphenyl acetylene, the metal - 1,2 - dioxylene system is, in most cases, extremely acid labile. Treatment of the complexes $M(C_6Cl_4O_2)(PPh_3)_2$ ($M = Pt, Pd$) in dichloromethane solution with hydrogen chloride leads to instant formation of the complexes $MCl_2(PPh_3)_2$ ($M = Pt, Pd$) and tetrachlorocatechol quantitatively. Attempts to detect Pt(IV) metal hydride intermediates at low temperatures failed. Similarly the complex $Ni(C_6Cl_4O_2)(Ph_2PCH_2CH_2PPh_2)$ in dichloromethane solution reacts with hydrogen chloride to give the complex $NiCl_2(Ph_2PCH_2CH_2PPh_2)$ and tetrachlorocatechol quantitatively. The reaction of the complex $Pt(C_{14}H_8O_2)(PPh_3)_2$ in dichloromethane solution gives a quantitative yield of the complex cis - $PtCl_2(PPh_3)_2$ and 9,10-phenanthrenequinone. This is consistent with the known chemistry of 9,10 - dihydroxyphenanthrene, which rapidly oxidises to 9,10 - phenanthrenequinone. The complex $Ir(C_6Cl_4O_2)Cl(CO)(PPh_3)_2$ in dichloromethane solution does not react with hydrogen chloride at room temperature. This complex is coordinately saturated, unlike the 1,2 - dioxylene complexes of the nickel group elements; and steric hindrance provides a ready explanation for the lack of reactivity of the complex, especially if proton attack at the central metal atom is considered to be the first step.

Reaction of the complex $\text{Pt}(\text{trans } \text{C}_2\text{H}_2\text{Ph}_2)(\text{PPh}_3)_2$

with o - quinones

The photocycloaddition of olefins to o - quinones is well known⁹⁵. Recent work¹¹⁴ has shown that 1,4 - dioxenes are only one of several possible types of products. A scheme, into which these recent results are incorporated, for the various photoreactions of 9,10 - phenanthrenequinone with olefins is shown in Fig. 2.7. The reaction of both cis and trans stilbene¹¹⁵ with 9,10 - phenanthrenequinone has been reported and a temperature dependent loss of stereochemical integrity in the products (diphenyl dioxenes) has been noted. A lesser degree of loss of configuration was observed in the reaction of cis¹¹⁶ and trans¹¹⁷ stilbene with tetrachloro o - benzoquinone to give dioxenes. The reaction of the complex (trans - stilbene) bis(triphenylphosphine)platinum(o) in benzene solution with 9,10 phenanthrenequinone and tetrachloro o - benzoquinone was investigated. High yields of the complexes $\text{Pt}(\text{C}_{14}\text{H}_8\text{O}_2)(\text{PPh}_3)_2$ and $\text{Pt}(\text{C}_6\text{Cl}_4\text{O}_2)(\text{PPh}_3)_2$ were obtained and no reaction between the displaced olefin and o - quinone was detected. In recent discussions of the bonding of molecular oxygen to transition metals the coordinated molecule has been likened to the excited state of oxygen gas¹¹⁸ and Orgel¹¹⁹ has noted the similarity of a simple



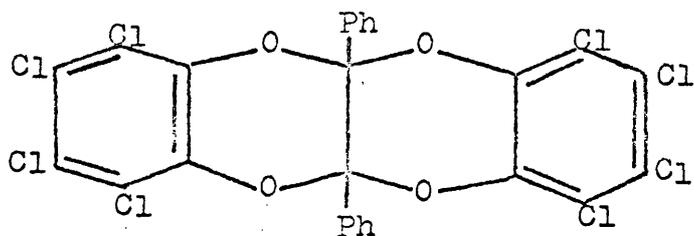
Photoreactions of 9,10-phenanthrenequinone with olefins.

Fig.2.7.

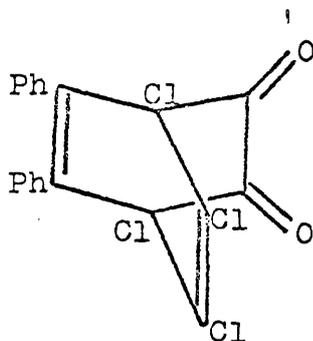
molecule bonded to a transition metal to the molecule in an excited state. Thus trans - stilbene while bonded to platinum may be regarded as being in an excited state. The lack of reaction between this "excited" trans - stilbene and the o - quinones is consistent with the scheme shown in Fig. 2.7. The essential feature of this scheme is quinone excitation; direct excitation of olefin does not lead to cycloaddition¹¹⁴.

The reaction of acetylene complexes with tetrachloro o - benzoquinone

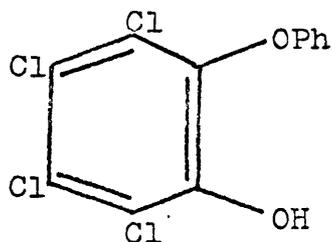
The reaction of diphenylacetylene with tetrachloro o - benzoquinone is complex and gives a mixture of products¹¹⁶ shown in Fig. 2.8. The reaction of the complex (diphenylacetylene)bis(triphenylphosphine) platinum(0) with tetrachloro-o-quinone was investigated and predictably a complex mixture of products is obtained. Upon addition of the quinone to a benzene solution of the complex, the solution rapidly turns dark brown and a yellow crystalline precipitate is formed. This yellow complex has an analysis consistent with the formulation $Pt(C_6Cl_4O_2)(Ph_2C_2)(PPh_3)$ and is formed in moderate yield (46%). Analytical, melting point and molecular weight data are shown in Table 2.1. i.r. spectral data for this and related complexes



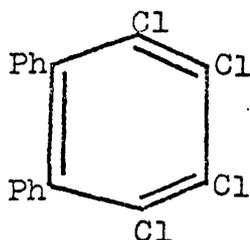
(a) From photoreaction; detected mass spectrometrically.



(b) Isolated in up to 70% yield from thermal reaction.



(c) Major product from photoreaction.

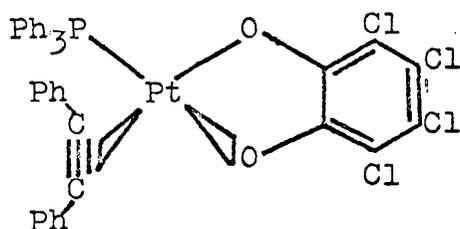


(d) Formed by irradiation of (b) with visible light.

Products from the reaction of diphenylacetylene and tetrachloro-*q*-benzoquinone.

Fig.2.8.

is shown in Table 2.4. From the i.r. spectrum it is apparent that the platinum - 1,2 - dioxylene ring system is present in the complex. The absorption at 1961 cm.^{-1} is similar to values for $\nu(\text{C}\equiv\text{C})$ obtained when an acetylene is bonded weakly to a metal in a manner similar to that of ethylene in Zeise's Salt i.e. perpendicular to the coordination plane ¹²⁰. (See Table 2.4.) Such an absorption is not consistent with the acetylene bonding to platinum as in the complex (diphenylacetylene)bis(triphenylphosphine) platinum(0) ; such complexes exhibit i.r. absorptions about 1800 cm.^{-1} ¹²⁰. From molecular weight data the complex is known to be monomeric; and thus the structure shown in Fig.2.9. is assigned to this complex.



Structure assigned to the complex (tetrachlorobenzene -1,2-dioxylene) (diphenylacetylene) (triphenylphosphine) platinum(II).

Fig.2.9.

TABLE 2.4.

Infrared spectral data concerning acetylene and acetylide complexes (cm.⁻¹).

<u>Complex</u>	<u>ref.</u>	<u>$\nu(\text{C}\equiv\text{C})$</u>	<u>Absorptions associated with metal - 1,2 - dioxylyene system</u>
<u>trans - Pt(C\equivCPh)₂(PPh₃)₂</u>	121	2110	-
<u>cis - Pt(C\equivCPh)₂(PPh₃)₂</u>	122	2125	-
<u>Pt(C\equivCPh)Cl(PPh₃)₂</u>	122	2125	-
<u>Pt(C₆Cl₄O₂)(PPh₃)₂</u>	-	-	1527w, 1433s, 1262s, 1221sh, 974s, 808, 796s, 584s.
<u>Pt(C₆Cl₄O₂)(PhC\equivCPh)(PPh₃)</u>	-	1961	1538w, 1526w, 1423s, 1257s, 1208sh, 962s, 812s, 801s, 596s.
<u>K PtCl₃(RC\equivCR)</u>	120	1994	-
<u>K PtCl₃(R¹C\equivCR¹)</u>	120	2004	-
<u>K PtCl₃(R¹C\equivCR²)</u>	120	2004	-

I.r. spectra were recorded from Nujol mulls using KBr windows.

s = strong, w = weak, sh = sharp.

The only pure complex which could be isolated from the dark brown solution was (tetrachlorobenzene-1,2-dioxylyene)bis(triphenylphosphine)platinum(II) (18%).

The reaction of the complex (phenylacetylene)bis(triphenylphosphine)platinum(0) in benzene solution with tetrachloro-o-quinone was also investigated. A complex reaction takes place giving a dark brown solution from which precipitates a yellow crystalline solid. This complex was identified as

$\text{Pt}(\text{C}_6\text{Cl}_4\text{O}_2)(\text{PPh}_3)_2$ (24%). Careful chromatography of the reaction solution lead to isolation of a very low yield (3%) of the known ¹²¹ complex trans- $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_3)_2$.

With the exception of those diones which undergo cleavage because of special structural features all diones participate in hydrogen abstraction; but at present it is difficult to establish the factors determining the ease of hydrogen donation by various species ¹¹⁴. However it is reasonable to suppose that the acetylide moiety is formed via hydrogen abstraction from phenylacetylene.

EXPERIMENTAL

Analytical, melting point and molecular weight data are shown in Table 2.1. and in this section. Melting points are uncorrected and were recorded on a Reichart hot-stage apparatus. Infrared spectra were recorded from Nujol mulls or chloroform solution on a Perkin - Elmer 225 spectrophotometer, using KBr(5000-400cm.⁻¹) and polythene (400-200cm.⁻¹) windows. Results are shown in Tables 2.2.,2.3. and 2.4.

AnalaR benzene was dried over sodium wire before use. Other solvents used were of reagent grade unless otherwise stated. Light petroleum b.p. 40-60°C was used throughout. All solvents used in reactions were saturated with nitrogen before use. All reactions were performed in an atmosphere of nitrogen. Triphenylphosphine was supplied by Albright and Wilson Ltd., and recrystallised from ethanol before use. Platinum, rhodium and iridium salts were obtained, on loan, from Johnson Matthey Ltd.

The complexes $\text{Pt}(\text{PPh}_3)_4$ ⁷⁹, $\text{Pd}(\text{PPh}_3)_4$ ¹²³, $\text{Pt trans} - (\text{PhHC}=\text{CHPh})(\text{PPh}_3)_2$ ⁶⁷, $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$ ⁶⁷, $\text{Pt}(\text{PhC}\equiv\text{CH})(\text{PPh}_3)_2$ ⁶⁷, $\text{trans} - \text{IrCl}(\text{CO})(\text{PPh}_3)_2$ ¹²⁴ and $\text{trans} - \text{RhCl}(\text{CO})(\text{PPh}_3)_2$ ¹⁰⁸ were prepared by literature methods.

The complex $\text{Ni}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ was prepared by the following method:

Carbon monoxide was bubbled through a stirred suspension of the complex $\text{NiCl}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (0.53 g.) in absolute ethanol (25 ml.) for ten minutes while a solution of NaBH_4 (0.10 g.) in absolute ethanol (100 ml.) was slowly added dropwise. A pale yellow solution resulted. This was evaporated to one quarter volume and a white crystalline precipitate was formed. This precipitate was filtered off, washed rapidly with cold ethanol, air dried and identified as

$\text{Ni}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ from the m.p. and i.r. spectrum which were identical to those of an authentic sample ¹⁰⁶.
Yield 82% (0.42 g.) m.p. 138-140°C.

1. Preparation of (tetrachlorobenzene 1,2-dioxy)bis(triphenylphosphine)platinum(II):

a) Reaction of tetrakis(triphenylphosphine)platinum(0) with tetrachloro o-benzoquinone

To a solution of $\text{Pt}(\text{PPh}_3)_4$ (1.00g.) in benzene (40ml.) was added tetrachloro o-benzoquinone (0.20g.) and the resulting orange yellow solution was refluxed overnight. On cooling a yellow crystalline precipitate was formed. Evaporation to half volume completed the precipitation; the precipitate was filtered off, washed with light petroleum and recrystallised for analysis from a dichloromethane - light petroleum mixture. (Found C, 52.25; H, 3.04; Cl, 14.63; $\text{M}(\text{CHCl}_3)$, 972; $\text{C}_{42}\text{H}_{30}\text{Cl}_4\text{O}_2\text{P}_2\text{Pt}$ requires C, 52.19; H, 3.11;

Cl, 14.70 %, M, 966.) Yield 80% (0.62g.) m.p. 275 - 277 C. (decomp.)

b) Reaction of trans - stilbenebis(triphenylphosphine) platinum(o) with tetrachloro o - benzoquinone

To a solution of Pt(trans - PhHC=CHPh)(PPh₃)₂ (0.50g.) in chloroform (30ml.) was added tetrachloro o - benzoquinone (0.01g.) and the mixture stood at room temperature overnight. The resulting yellow solution was evaporated to half volume under reduced pressure and light petroleum (15ml.) was added. The resulting yellow crystalline precipitate was filtered off, washed with light petroleum, air dried and identified as (tetrachlorobenzene 1,2-dioxylyene)bis(triphenylphosphine)platinum(II) from its m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 84% (0.45g.) m.p. 275-277^o C. (decomp.)

2. Preparation of (phenanthrene 9,10 - dioxylyene)bis (triphenylphosphine)platinum(II):

a) Reaction of tetrakis(triphenylphosphine)platinum (o) with 9,10-phenanthrenequinone

To a solution of Pt(PPh₃)₄ (1.00g.) in benzene (40ml.) was added 9,10-phenanthrenequinone (0.17g.). The resulting dark red solution was refluxed gently overnight and then evaporated to half volume under reduced pressure. Addition of light petroleum (20ml.) gave rise to a dark red crystalline precipitate which

was filtered off, washed with light petroleum, air dried and recrystallised for analysis from a benzene-light petroleum mixture. (Found C, 66.13; H, 4.13; $M(\text{CHCl}_3)=920$, $\text{C}_{50}\text{H}_{38}\text{O}_2\text{P}_2\text{Pt}$ requires C, 65.42; H, 4.17%; $M=928$) Yield 77% (0.58g.) m.p. 200-202° C. (decomp.).

b) Reaction of trans-stilbenebis(triphenylphosphine) platinum(o) with 9,10-phenanthrenequinone

To a solution of $\text{Pt}(\text{trans PhHC=CHPh})(\text{PPh}_3)_2$ (0.50g.) in benzene (40ml.) was added 9,10-phenanthrenequinone (0.12g.). A dark red solution was formed immediately and this was refluxed gently for 30 minutes. The solution was evaporated to half volume under reduced pressure. Addition of light petroleum (20ml.) led to the deposition of dark red crystals which were filtered off, washed with light petroleum, air dried and identified as (phenanthrene 9,10-dioxylene)bis(triphenylphosphine)platinum(II) from its m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 77% (0.39g.) m.p. 200-202° C (decomp.)

3. Preparation of (tetrachlorobenzene 1,2-dioxylene) bis(triphenylphosphine)palladium(II):

Reaction of tetrakis(triphenylphosphine)palladium(o) with tetrachloro o - benzoquinone

To a solution of $\text{Pd}(\text{PPh}_3)_4$ (1.00g.) in benzene (40ml.) was added tetrachloro o - benzoquinone (0.22g.).

The mixture was refluxed overnight and the resultant dark coloured solution evaporated to a quarter volume under reduced pressure. A pale blue solid was deposited. This was filtered off, the filtrate being retained, washed with light petroleum, air dried and recrystallised for analysis from a dichloromethane-light petroleum mixture to give dark blue crystals, which were filtered off, washed with light petroleum and air dried. (Found: C, 57.25; H, 3.35; Cl, 16.37; $C_{40}H_{30}Cl_4O_2P_2Pd$ requires C, 57.52; H, 3.45; Cl, 16.17%.) Yield 37% (0.28g.) m.p. 220-222°C. (decomp.).

To the retained filtrate was added light petroleum (10ml.). Brown crystals were deposited, filtered off, washed with light petroleum, air dried and recrystallised from a dichloromethane-light petroleum mixture for analysis. (Found: C, 57.44; H, 3.44; Cl, 14.85; $C_{40}H_{30}Cl_4O_2P_2Pd$ requires C, 57.52; H, 3.45; Cl, 16.17) Yield 13% (0.10g.) m.p. 226-228°C (decomp.)

4. Reaction of tetrakis(triphenylphosphine)palladium (o) with 9,10-phenanthrenequinone:

To a solution of $Pd(PPh_3)_4$ (1.00g.) in benzene (40ml.) was added 9,10 - phenanthrenequinone (0.19g.). The mixture was refluxed overnight. Evaporation of the reaction mixture to half volume under reduced pressure and the addition of light petroleum (20ml.) gave a brown precipitate which was filtered off, washed with light petroleum and air dried. No pure complexes were obtain-

ed from this brown powder. Yield 0.51g.

5. Preparation of (tetrachlorobenzene 1,2 - dioxylyene)

1,2 - bis(diphenylphosphine)ethane nickel(II):

Reaction of dicarbonyl 1,2 - bis(diphenylphosphine)
ethane nickel(o) with tetrachloro o - benzoquinone

To a solution of $\text{Ni}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (0.40g.) in benzene (40ml.) was added to tetrachloro o - benzoquinone (0.20g.). Effervescence occurred and a dark coloured solution was formed. The mixture was stood overnight during which time dark brown needle-like crystals were deposited. These were filtered off, washed with benzene and air dried. Evaporation of the filtrate to a small volume yielded a further crop of these crystals. (Found: C, 54.02; H, 2.95; Cl, 19.92; $\text{C}_{32}\text{H}_{24}\text{Cl}_4\text{NiO}_2\text{P}_2$ requires C, 54.65; H, 2.71; Cl, 20.21. %) Yield 91% (0.50g.) m.p. 247-249° C. (decomp.)

6. Reaction of dicarbonyl 1,2 - bis(diphenylphosphine)
ethane nickel(o) with 9,10 - phenanthrenequinone:

To a solution of $\text{Ni}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (0.40g.) in benzene (40ml.) was added 9,10 phenanthrenequinone (0.17g.). No effervescence occurred and the reaction mixture was stirred at room temperature for 5 days to give a green suspension. This was filtered and the green precipitate washed with benzene and air dried. Attempts to purify this precipitate by recrystallisation or sublimation failed and only the starting quinone could be isolated from such attempts.

7. Preparation of (tetrachlorobenzene 1,2 - dioxylyene) chlorocarbonyl bis(triphenylphosphine)iridium(III):

Reaction of trans - chlorocarbonyl bis(triphenylphosphine)iridium(I) with tetrachloro o - benzoquinone

To a solution of trans - $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (0.50g.) in benzene (40ml.) was added tetrachloro o - benzoquinone (0.16g.). The mixture was refluxed overnight to give a dark red solution which on standing for 8 hours deposited an orange crystalline solid. This was filtered off, washed with benzene, air dried and recrystallised for analysis from a dichloromethane - light petroleum mixture. (Found: C, 50.24; H, 2.96; Cl, 18.35; $\text{C}_{43}\text{H}_{30}\text{Cl}_5\text{O}_3\text{P}_2\text{Ir}$ requires C, 50.25; H, 2.92; Cl, 17.28.%). Yield 64% (0.42g.) m.p. darkens at 270°C . decomposes at 300°C .

8. Reaction of trans - chlorocarbonyl bis(triphenylphosphine)iridium(I) with 9,10 - phenanthrenequinone:

To a solution of trans - $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ (0.50g.) in benzene (40ml.) was added 9,10 - phenanthrenequinone (0.14g.). The mixture was refluxed vigorously for 6 days to give a dark brown solution. This solution was evaporated to quarter. Addition of diethyl ether (20ml.) gave rise to the deposition of brown crystals. These were filtered off, washed with diethyl ether and air dried. The i.r. spectrum of the sample showed that the Ir(I) complex was still present and neither successive recrystallisations from dichloromethane - diethyl ether

mixtures nor chromatography over fluorosil using chloroform as an eluent could free the Ir(III) complex from the starting material.

9. Preparation of (tetrachlorobenzene 1,2 - dioxylyene) chlorocarbonyl bis (triphenylphosphine)rhodium(III):

Reaction of trans - chlorocarbonyl bis(triphenylphosphine) rhodium(I) with tetrachloro o - benzoquinone

To a solution of trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (0.40g.) in benzene (40ml.) was added tetrachloro o - benzoquinone (0.15g.). The resulting dark blue solution was stood at room temperature overnight and evaporated to half volume under reduced pressure. Addition of light petroleum (20ml.) led to the deposition of a blue crystalline precipitate which was filtered off, washed with light petroleum, air dried and recrystallised from a benzene - light petroleum mixture for analysis. (Found: C, 55.33; H, 3.22; Cl, 18.72; $\text{C}_{43}\text{H}_{30}\text{Cl}_5\text{O}_3\text{P}_2\text{Rh}$, requires C, 55.06; H, 3.20; Cl, 18.94. %) Yield 87% (0.47g.) m.p. 175^o C. (decomp.).

10. Reaction of trans - chlorocarbonyl bis(triphenylphosphine)rhodium(I) with 9,10 - phenanthrenequinone:

To a solution of trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (0.40g.) in benzene (40ml.) was added 9,10 - phenanthrenequinone (0.13g.). The mixture was vigorously refluxed for 3 days. No colour change was observed. The reaction solution was evaporated to quarter volume under reduced pressure. Addition of ethanol (20ml.) lead to the formation of a

yellow crystalline precipitate which was filtered off, washed with ethanol, air dried and identified as trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ from its m.p. and i.r. spectrum which were both identical to those of an authentic sample. The recovery of trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ was quantitative.

11. Reaction of (tetrachlorobenzene 1,2 - dioxylene) bis (triphenylphosphine)platinum(II) with hydrogen chloride:

Dry hydrogen chloride was bubbled through a solution of $\text{Pt}(\text{C}_6\text{Cl}_4\text{O}_2)(\text{PPh}_3)_2$ (0.19g.) in dichloromethane (10ml.). The yellow solution became colourless instantly. The solution was evaporated to half volume under reduced pressure and addition of ethanol (15ml.) gave rise to a white crystalline precipitate. This was filtered off, the filtrate being retained, washed with ethanol, air dried and identified as cis - dichloro bis(triphenylphosphine)platinum(II) from its m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 96% (0.15g.) m.p. 310°C . The retained filtrate was evaporated to half volume, ethanol (5ml.) was added and on slow addition of water (5ml.) needle-like crystals were precipitated. These were filtered off, washed with water, air dried and identified as tetrachlorocatechol from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 100% (0.05g.) m.p. $194-195^\circ\text{C}$.

12. Reaction of (phenanthrene 9,10 - dioxylene)bis
(triphenylphosphine)platinum(II) with hydrogen chloride:

Dry hydrogen chloride was bubbled through a solution of $\text{Pt}(\text{C}_{14}\text{H}_8\text{O}_2)(\text{PPh}_3)_2$ (0.15g.) in dichloromethane (10ml.). The red solution turned yellow instantly. The solution was evaporated to half volume under reduced pressure and addition of ethanol (15ml.) gave rise to a white crystalline precipitate. This was filtered off, the filtrate being retained, washed with ethanol, air dried and identified as cis - dichlorobis(triphenylphosphine) platinum(II) from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 86% (0.11g.) m.p. 310°C . The retained filtrate was evaporated to half volume, ethanol (10ml.) was added and the resulting solution evaporated to half volume. The solution was stored at 0 C overnight and yellow crystals were deposited. These were filtered off, washed with ethanol at -78°C , air dried and identified as 9,10 - phenanthrenequinone from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 90% (0.03g.) m.p. $208-210^\circ\text{C}$.

13. Reaction of tetrachlorobenzene 1,2 - dioxylene bis
(triphenylphosphine)palladium(II) with hydrogen chloride:

Blue Form: Dry hydrogen chloride was bubbled through a solution of $\text{Pd}(\text{C}_6\text{Cl}_4\text{O}_2)(\text{PPh}_3)_2$ (0.20g.) in dichloromethane (10ml.). The solution turned from blue to yell-

ow instantly. The solution was evaporated to half volume under reduced pressure. Addition of ethanol (15ml.) gave rise to a yellow crystalline precipitate. This was filtered off, the filtrate being retained, washed with ethanol, air dried and identified as trans - dichloro bis (triphenylphosphine)palladium(II) from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 94% (0.15g.) m.p. 210°C . The colourless filtrate was evaporated to half volume under reduced pressure; ethanol (5ml.) was added and on slow addition of water (5ml.) white needle-like crystals were precipitated. These were filtered off, washed with water, air dried and identified as tetrachlorocatechal from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 88% (0.05g.) m.p. 194-195°C.

Brown Form: Dry hydrogen chloride was bubbled through a solution of $\text{Pd}(\text{C}_6\text{Cl}_4\text{O}_2)(\text{PPh}_3)_2$ (0.20g.) in dichloromethane (10ml.). The brown solution turned yellow instantly. The solution was evaporated to half volume under reduced pressure. Addition of ethanol (15ml.) gave rise to a yellow crystalline precipitate. This was filtered off, the filtrate being retained, washed with ethanol, air dried and identified as trans - dichloro bis (triphenylphosphine)palladium(II) from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 94% m.p. 210°C . The colourless

filtrate was evaporated to half volume under reduced pressure; ethanol (5ml.) was added and on slow addition of water (5ml.) white needle-like crystals were precipitated. These were filtered off, washed with water, air dried and identified as tetrachlorocatechol from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 88% (0.05g.) m.p. 194-195^o C.

14. Reaction of (tetrachlorobenzene 1,2 - dioxylene)
1,2 - bis(diphenylphosphino)ethane nickel(II) with
hydrogen chloride:

Dry hydrogen chloride was bubbled through a solution of $\text{Ni}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (0.20g.) in dichloromethane (10ml.). The dark solution became orange instantly. Ethanol was added (20ml.) and the mixture evaporated to half volume under reduced pressure. The mixture was cooled to 0^o C and orange crystals were deposited. These were filtered off, the filtrate being retained, washed with ice-cold ethanol, air dried and identified as dichloro 1,2 - bis(diphenylphosphino)ethane nickel(II) from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 93% (0.14g.) m.p. 160^o C . The colourless filtrate was evaporated to half volume under reduced pressure. Ethanol (5ml.) was added and on slow addition of water (5ml.) white needle-like crystals were deposited. These were filtered off, washed with water, air dried and identified as tetra-

chlorocatechal from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 71% (0.05g.) m.p. 194-195^o C.

15. Reaction of (tetrachlorobenzene 1,2 - dioxylene) chlorocarbonyl bis(triphenylphosphine) iridium(III) with hydrogen chloride:

Dry hydrogen chloride was bubbled through a solution of $\text{Ir}(\text{C}_6\text{Cl}_4\text{O}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (0.20g.) in dichloromethane (15ml.) for 10 minutes. No colour change was observed. The orange solution was evaporated to half volume under reduced pressure. Addition of light petroleum (15ml.) lead to the precipitation of an orange crystalline solid which was filtered off, washed with light petroleum, air dried and identified as starting material from the m.p. and i.r. spectrum which were identical to those of an authentic sample. The recovery of $\text{Ir}(\text{C}_6\text{Cl}_4\text{O}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ was quantitative.

16. Preparation of (tetrachlorobenzene 1,2 - dioxylene) (diphenylacetylene)(triphenylphosphine)platinum(II):
Reaction of diphenylacetylene bis(triphenylphosphine) platinum(o) with tetrachloro o - benzoquinone :

To a solution of $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$ (1.00g.) in benzene (30ml.) was added tetrachloro o - benzoquinone (0.28g.). The mixture was shaken vigorously for 30 seconds and stood overnight. A yellow crystalline precipitate was formed. This was filtered off, the filtrate being retained, washed with benzene, air dried

and recrystallised for analysis from a dichloromethane - light petroleum mixture (Found: C, 51.61; H, 2.78; Cl, 16.06 P. 3.57 M(CHCl₃)=925 C₄₀H₃₉Cl₄O₂Ppt requires C, 51.06; H, 2.84; Cl, 16.12 ; P, 3.52%. M=881) Yield 46% (0.45g.) m.p. 232-234^o C decomp. The retained filtrate was evaporated to dryness to give a dark brown oil which was taken up in a minimum of dichloromethane and chromatographed over fluorosil. Elution with diethylether gave an orange fraction which on addition of light petroleum gave crystals of the complex Pt(C₅Cl₄O₂)(PPh₃)₂ identified as such from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield (0.19g.) m.p. 275-277^o C.

17. Reaction of phenylacetylene bis(triphenylphosphine) platinum(o) with tetrachloro o - benzoquinone:

To a solution of Pt(PhC≡CH)(PPh₃)₂ (0.60g.) in benzene (30ml.) was added tetrachloro o - benzoquinone (0.18g.). The mixture was shaken vigorously for 30 seconds and stood overnight. A yellow crystalline precipitate was formed. This was filtered off, the brown coloured filtrate being retained, washed with benzene, air dried, recrystallised from a dichloromethane - light petroleum mixture and identified as the complex Pt(C₆Cl₄O₂)(PPh₃)₂ from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 24% (0.27g.) m.p. 277-275^o C decomp. The retained filtrate was evaporated to dryness, under reduced pressure, to

-137-

give a dark brown oil which was taken up in a minimum of dichloromethane and chromatographed over fluorosil. Elution with dichloromethane gave a yellow fraction which on addition of light petroleum gave crystals of the complex trans - $\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_3)_2$; identified from the m.p. and i.r. spectrum which were identical to those of an authentic sample ¹²¹. Yield 3% (0.025g.) m.p. 220-222°C decomp.

CHAPTER 3

If the stone falls on the egg, alas for the egg.

If the egg falls on the stone, alas for the egg.

. Proverb .

INTRODUCTION

As a further study of d^8 metal complexes containing metal-oxygen bonds the chemistry of some rhodium(I) acetylacetonate complexes has been investigated. The stereochemistry of such systems is indicated by the CH_3 - resonances of the acetylacetonate moiety in the 1H n.m.r. spectrum and this has proved useful in determining the final stereochemistry of the complexes formed via oxidative addition reactions. Some work has been done on such systems. Parshall¹²⁵ has investigated the chemistry of the complex (acetylacetonato)(ethylene)(tetrafluoroethylene)rhodium(I), $Rh(acac)(C_2H_4)(C_2F_4)$. The properties of the transition metal - acetylacetonate ring have been investigated, principally by Collman¹²⁶, with specific regard to electrophilic substitution at the C-3 position in such systems. Lewis et al¹²⁷ have provided a series of investigations into the reaction of both C- and O- bonded transition metal acetylacetonates.

The complexes studied in this work are (acetylacetonato) cyclo octa- 1,5- diene rhodium(I), $Rh(acac)(COD)$; (acetyl acetonato)(triphenylphosphine)(carbonyl) rhodium(I), $Rh(acac)(CO)(PPh_3)$ ^{128,129}; both known complexes, and a new complex acetylacetonato bis(triphenylphosphine)rhodium(I), $Rh(acac)(PPh_3)_2$. Rh(I) complexes although not as reactive towards oxidative addition as their Ir(I) analogues¹¹², are known to

undergo oxidative addition with a variety of reagents: acids, alkyl halides, olefins and acetylenes. Thus the reactions of the rhodium acetylacetonate complexes, mentioned above, with such reagents have been investigated.

RESULTS AND DISCUSSION

Preparation of Starting Materials

Rh(acac)(COD) was prepared by the literature method .
Rh(acac)(PPh₃)₂ was prepared by treating Rh(acac)(COD) in diethyl ether solution with excess triphenylphosphine. Gentle reflux resulted in quantitative precipitation of the complex. Analytical, melting point and molecular weight data are given in Table 3.5. Rh(acac)(CO)(PPh₃) was prepared by bubbling carbon monoxide through a stirred suspension of Rh(acac)(PPh₃)₂ in diethyl ether at room temperature.

Structure of Starting Materials

One of the C-3 protons in acetylacetonone is labile with the result that a keto-enol tautomerism may occur (See Fig. 3.1.). At room temperature acetylacetonone is 81% enol form ¹³⁰. Under appropriate conditions with various ligands the enol or potential enol proton may be removed and replaced by a metal to give a complex in which the metal is bonded either to two oxygen

Keto - Enol Tautomerism in Acetylacetone.

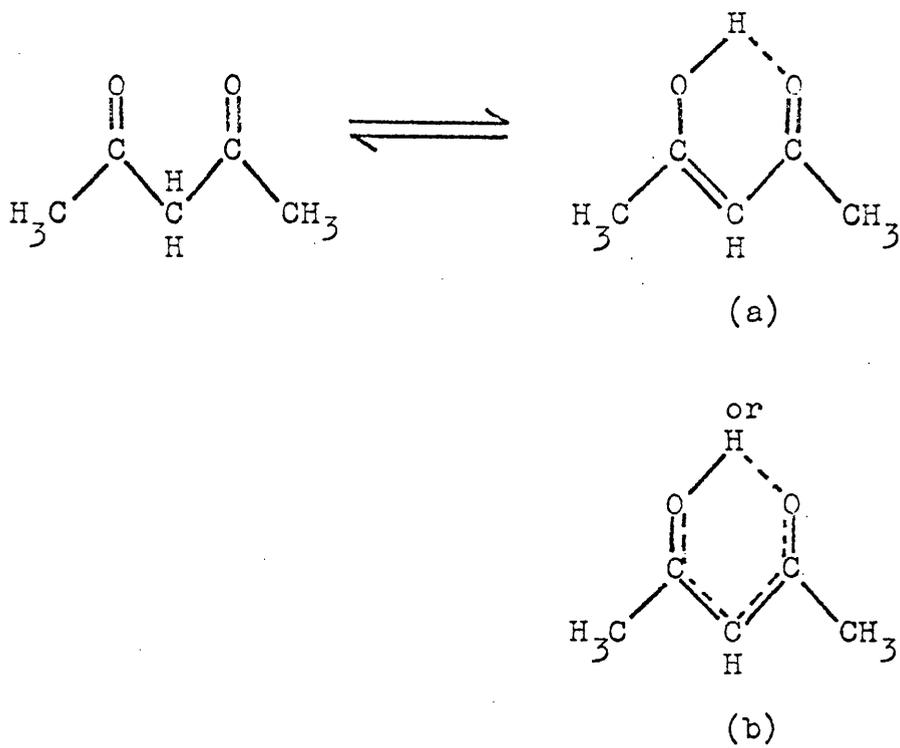
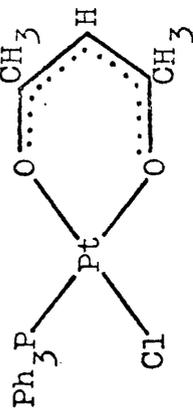
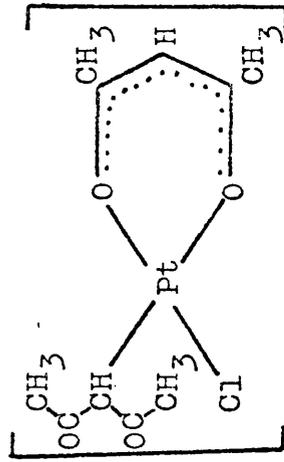


Fig.3.1.

O - bonded.

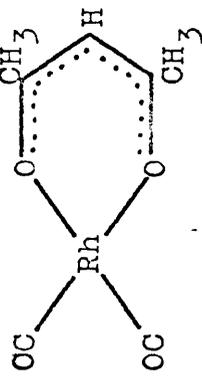


C - bonded.



Ref.

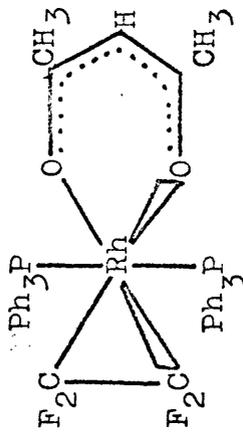
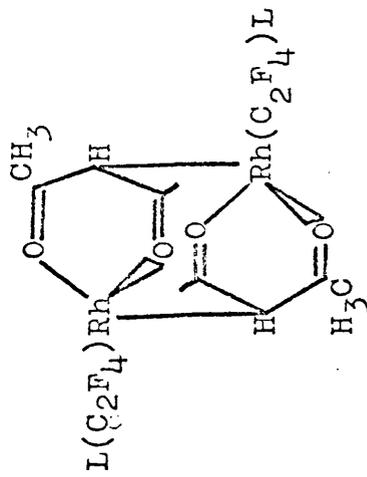
Ref.



Ref.

-141-

125



O - bonded and C - bonded coordination of the acetylacetonate ligand.

Fig. 3.2.

atoms, or to the C-3 atom. Examples of both types of coordination are known and shown in Fig.3.2.

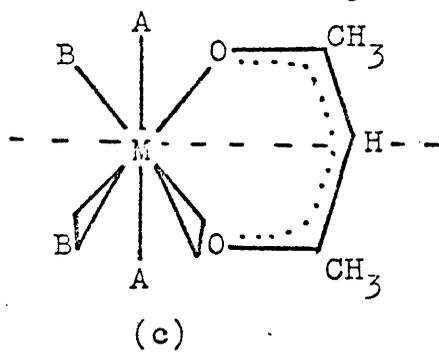
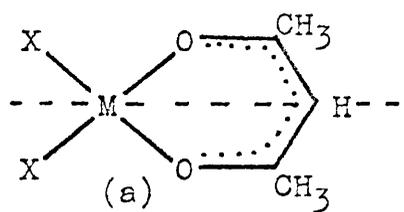
I.r. Spectral Data

The manner of coordination of a β -diketone to a metal in a complex may be discerned by the i.r. spectrum of such a complex. Strong absorptions in the regions $1500-1600\text{ cm.}^{-1}$ are indicative of an O-bonded chelating group. Such absorptions are considered to be mainly a mixture of $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$ modes, (See localised bonding representation of acetylacetonate enol form; Fig.3.1(a)). although some $\delta(\text{C}-\text{H})$ contribution has been observed ¹³¹. Absorptions above 1600 cm.^{-1} are indicative of a C-bonded β -diketone and such absorptions are composed almost exclusively of $\nu(\text{C}=\text{O})$ contributions. Table 3.1. shows i.r. spectral data for known O-bonded and C-bonded acetylacetonate complexes. I.r. spectral data for the complexes $\text{Rh}(\text{acac})(\text{COD})$, $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ and $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ are shown in Table 3.2. and indicate that in the solid state and in solution the acetylacetonate moiety is O-bonded to the rhodium in all three complexes.

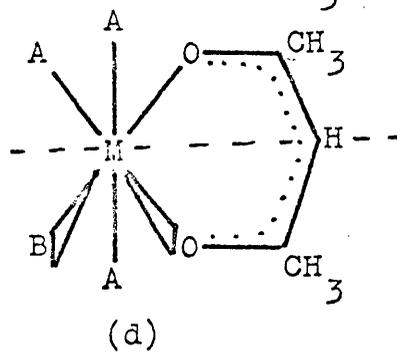
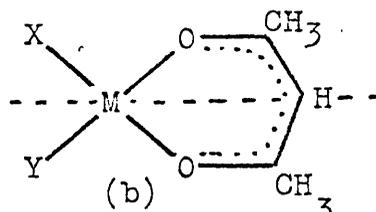
¹H n.m.r. Spectral Data

Complexes which have a plane of symmetry perpen-

Methyl Groups
Equivalent.



Methyl Groups
Non - Equivalent.



Symmetrical and asymmetrical acetylacetonate -
metal rings.

Fig.3.3.

dicular to the plane of the metal-acetylacetonate ring (See Fig.3.3(a) and (c)) may be expected to exhibit a single resonance in the methyl proton region. Those complexes in which the methyl groups on a single acetylacetonate moiety are nonequivalent (See Fig.3.3 (b) and (d)) will show two resonances in the methyl proton region, each resonance corresponding to one methyl group. Examples of this are shown in Table 3.3.

^1H n.m.r. spectral data for the complexes $\text{Rh}(\text{acac})(\text{COD})$, $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ and $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ are shown in Table 3.4.

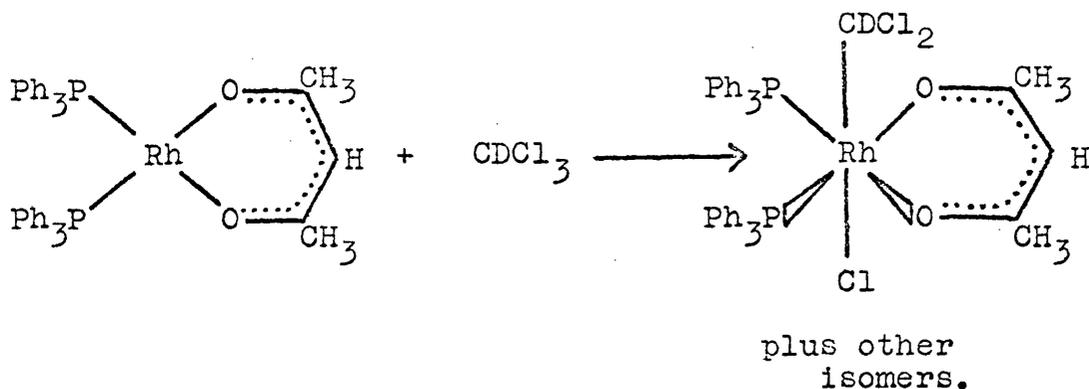
As reported ¹³² $\text{Rh}(\text{acac})(\text{COD})$ exhibits a single resonance corresponding to two equivalent methyl groups at room temperature and the spectrum does not change on cooling to -50°C .

From symmetry arguments $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ should exhibit methyl resonance as a doublet. This has been observed ^{132a}, and the spectrum is independent of temperature. However on addition of triphenylphosphine the doublet associated with methyl resonance collapses to a singlet. This spectrum is however temperature dependent. On cooling to -10°C the singlet has broadened considerably and at -50°C a sharp doublet is again observed. Thus at room temperature in the presence of free triphenylphosphine an exchange process, which relieves molecular asymmetry is occurring. On cooling this exchange process is slowed down sufficiently for

the n.m.r. phenomena to observe the assymetry in the molecule.

On the basis of symmetry arguements the methyl groups in $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ are equivalent and a single resonance is to be expected. However in degassed deuterio-chloroform a complex pattern of bands assignable to methyl resonance is observed. The spectrum is unchanged by lowering the temperature. There are two possible explanations:

1. Reaction between the complex and solvent:



Attempts to isolate such a Rh(III) complex failed. From i.r. spectral data the complex appears to be stable in benzene. However attempts to record the ^1H n.m.r. spectrum of the complex in benzene were not successful as the complex is only sparingly soluble in this solvent.

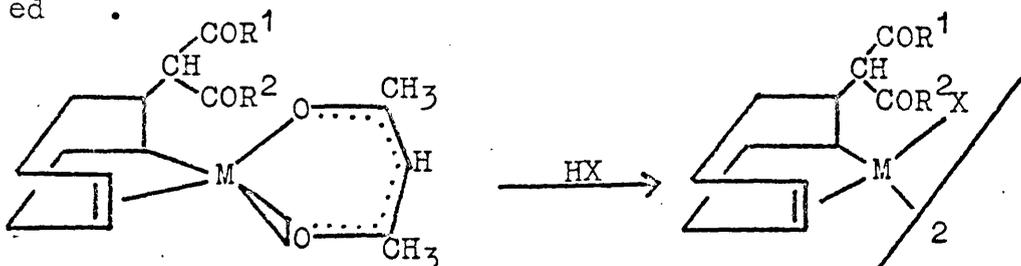
2. The complex dissociates or decomposes in solution. The molecular weight of the complex in chloroform is 571 (required 727) and this indicates dissociation or decomposition.

Reactions of Rhodium(I) Acetylacetonato Complexes

Reactions with Acids

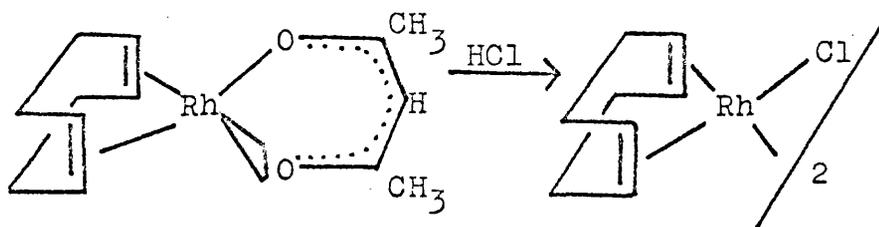
Reactions with Hydrogen Chloride:

There are several examples of the reaction of metal-ketoenolates with halogeno acids already reported ¹³³



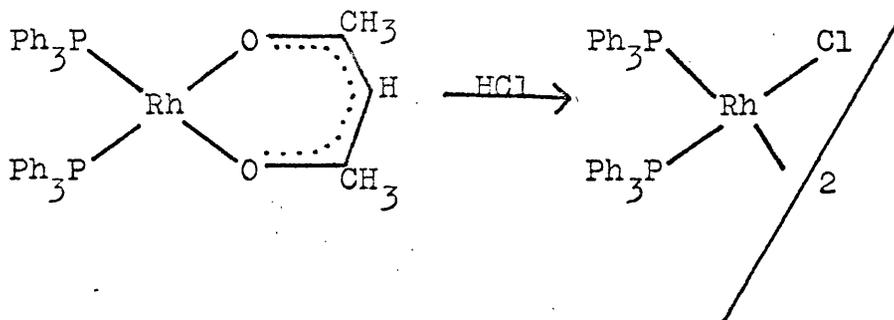
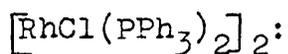
$M = \text{Pd, Pt}; R^1 = \text{Me, Ph}; R^2 = \text{Me, Ph}; X = \text{Cl, Br, I}.$

In this work Rh(acac)(COD) has been found to react similarly with hydrogen chloride in diethyl ether to give the known ¹²⁸ complex $\mu\mu'$ -dichloro bis(cycloocta-1,5-diene)dirhodium(I), $[\text{RhCl}(\text{COD})]_2$:



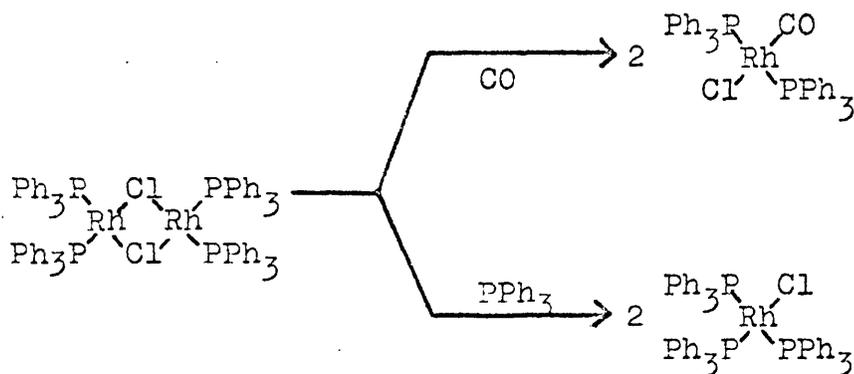
The reaction may be carried out in carbon tetrachloride. The ¹H n.m.r. spectrum of the reaction mixture, after removal of RhCl(COD)₂ by cooling, is identical to that of acetylacetonate in carbon tetrachloride and confirms the presence of free acetylacetonate.

Similarly Rh(acac)(PPh₃)₂ reacted with hydrogen chloride in diethyl ether to give the known ¹⁰⁸ complex $\mu\mu'$ -dichloro tetrakis(triphenylphosphine)dirhodium(I),

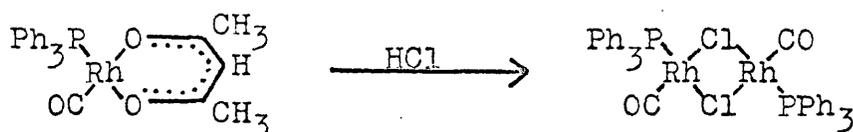


The presence of free acetylacetonate was shown by the ¹H n.m.r. spectrum of a carbon tetrachloride reaction mixture. The complex is rather reactive but its nature

was confirmed by reaction with the bridge splitting reagents carbon monoxide and triphenylphosphine. Thus with carbon monoxide the known ¹⁰⁸ complex trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ was formed and reaction with triphenylphosphine gave the known ¹⁰⁸ complex $\text{RhCl}(\text{PPh}_3)_3$. In both reactions quantitative yields were obtained.



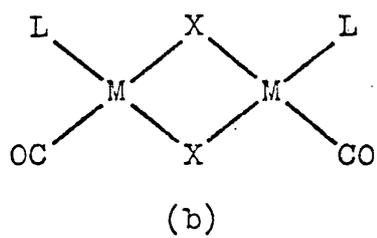
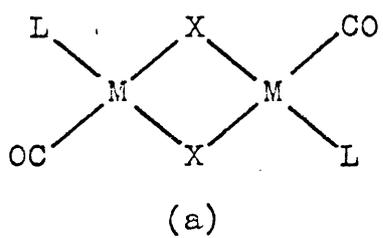
The reaction of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ with hydrogen chloride gave the new chloro bridged complex - dichloro bis(triphenylphosphine)bis(carbon monoxide) dirhodium(I), $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$.



Analytical, melting point and molecular weight data for the complex are given in Table 3.5. The presence of free acetylacetonate was shown by the ¹H n.m.r.

spectrum of a carbon tetrachloride reaction mixture. Molecular weight data in chloroform indicates that the complex is dimeric in solution. I.r. spectral data concerning halogen bridged dimers is shown in Table 3.6. It is well known⁸⁴ that a square planar halogen bridge should exhibit two i.r. active frequencies mainly associated with ν (M-X) stretching modes. This has been observed in $[\text{RhCl}(\text{COD})]_2$ ¹³⁴. However the far i.r. spectrum of $[\text{RhCl}(\text{PPh}_3)_2]_2$ is puzzling in that only one absorption is observed. This absorption is broad 50cm.^{-1} and may be an envelope of two or more absorptions.

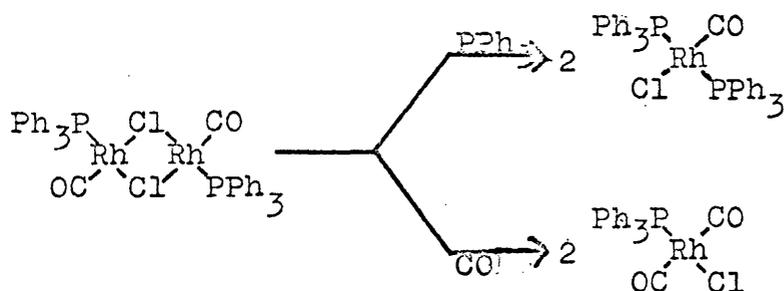
Two bands are observed for the complex $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$. The large differences between the two ν (Rh-Cl) frequencies in this complex as opposed to those observed for other rhodium-halogen bridged systems (See Table 3.6.) is probably a function of the different trans bond influences exerted by carbon monoxide and triphenylphosphine. The ν (CO) stretching mode occurs at 1977cm.^{-1} in the solid state and 1980cm.^{-1} in solution. This eliminates the possibility of a bridging carbonyl structure as such systems exhibit i.r. absorptions in the region $1898-1785\text{cm.}^{-1}$ ⁸⁴. It is well known⁸⁴ that complexes of the type trans - $\text{M}(\text{CO})_2\text{L}_4$ exhibit one i.r. active ν (CO) stretching frequency while complexes of the type cis - $\text{M}(\text{CO})_2\text{L}_4$ exhibit two i.r. active ν (CO)



Cis - trans isomerism in halogen bridged complexes.

Fig.3.4.

stretching frequencies. Similarly a complex of the type (a) shown in Fig. 3.4. will exhibit one i.r. active $\nu(\text{CO})$ stretching frequency while a complex of type (b) will show two such frequencies. Whilst the $\nu(\text{CO})$ absorption for $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$ in the solid state is broad, in chloroform solution a single sharp absorption is obtained. This may be taken as an indication that $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$ has the trans structure of Fig.3.4(a). The bridge splitting reagents carbon monoxide and triphenylphosphine reacted readily with $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$ giving the known ^{7,108} complexes trans - $\text{RhCl}(\text{CO})_2(\text{PPh}_3)$ and trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ quantitatively in accord with the proposed structure:



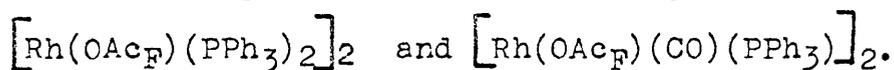
Reactions with Acetic Acid

Acetic acid did not react with any of the complexes under investigation although the complex $[\text{Rh}(\text{OAc})(\text{COD})]_2$ ¹²⁸ is known and may be prepared by the reaction of $[\text{RhCl}(\text{COD})]_2$ with a metal acetate in acetone.

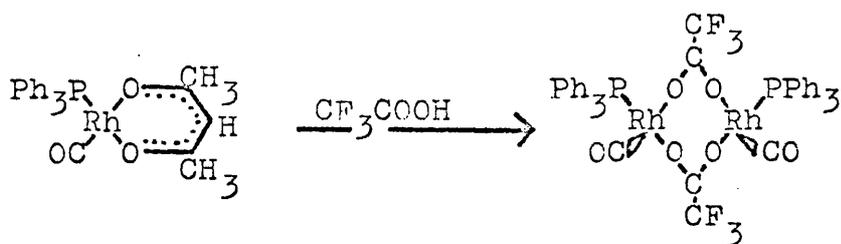
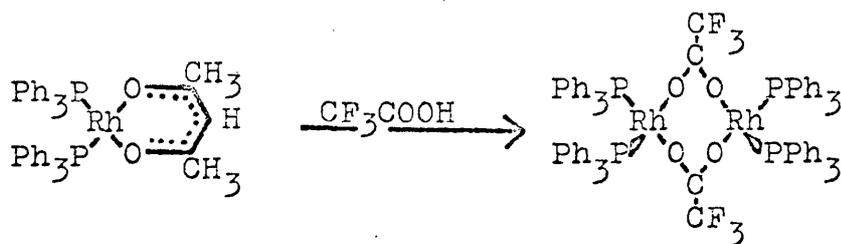
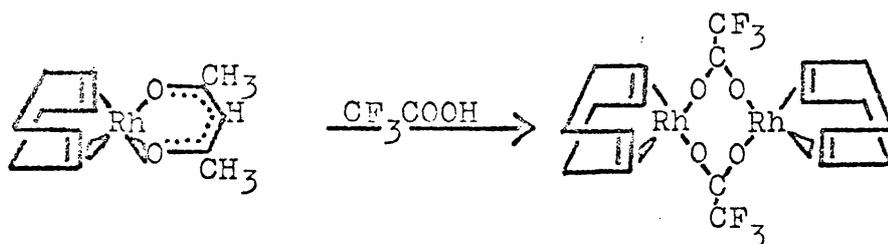
Reactions with Trifluoroacetic Acid

Trifluoroacetic acid reacted readily with all three complexes to give bis- $\mu\mu'$ -trifluoroacetato bis(cyclo-octa -1,5- diene)dirhodium(I), $[\text{Rh}(\text{OAc}_F)(\text{COD})]_2$; bis- $\mu\mu'$ -trifluoroacetato tetrakis(triphenylphosphine) dirhodium(I), $[\text{Rh}(\text{OAc}_F)(\text{PPh}_3)_2]_2$ bis- $\mu\mu'$ -trifluoroacetato bis(carbonyl)bis(triphenylphosphine)rhodium(I), $[\text{Rh}(\text{OAc}_F)(\text{CO})(\text{PPh}_3)]_2$. Analytical, melting point and molecular weight data are shown in Table 3.5.

From the molecular weight data it is apparent that the complexes are dimeric in solution and by analogy with the reaction of hydrogen chloride on the acetylacetonate complexes bridging trifluoroacetate structures are postulated for these complexes as shown in Fig. 3.5. I.r. spectral data is shown in Table 3.7. and does not indicate the presence of any metal hydride complexes. $\bar{\nu}(\text{OCO})$ could not be assigned unambiguously for any of the complexes and is almost certainly obscured by absorptions associated with coordinated phosphines for the complexes



The i.r. spectrum of the complex $[\text{Rh}(\text{OAc}_F)(\text{PPh}_3)_2]_2$ is consistent with the replacement of the acetylacetonate moiety by the trifluoroacetate moiety but the complex could not be obtained analytically pure. The i.r. spectrum of $[\text{Rh}(\text{OAc}_F)(\text{CO})(\text{PPh}_3)]_2$ shows two strong



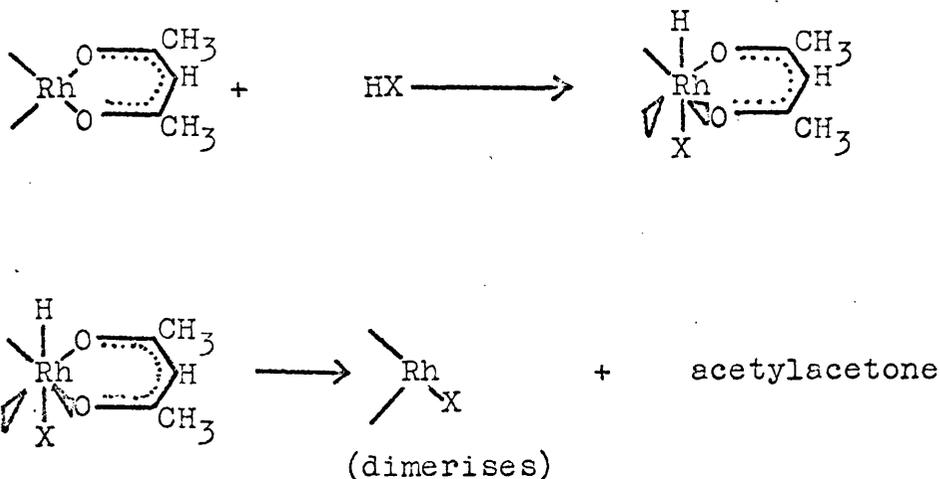
Reactions of rhodium acetylacetonate complexes with trifluoroacetic acid.

Fig.3.5.

absorptions in the $\nu(\text{CO})$ region in both solid state and solution spectra. This may be taken as a tentative indication that the two carbonyl groups are cis to one another as shown in Fig.3.5.

There are several possible mechanisms for the reaction of acids with metal-acetylacetonate complexes:

1. Oxidative addition of HX to Rh(I) to give a six coordinate Rh(III) complex which undergoes reductive elimination of acetylacetonate to give a Rh(I) species which dimerises:



2. Attack of H^+ at the acetylacetonate ring rather than the central metal atom.

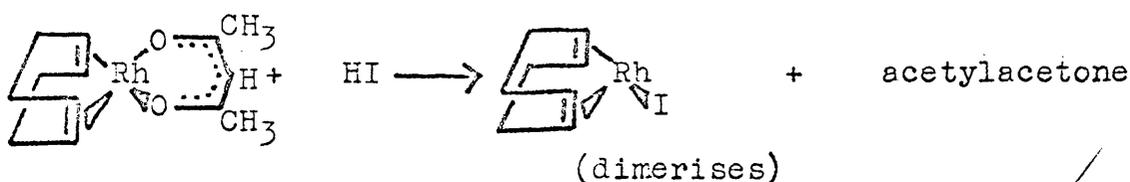
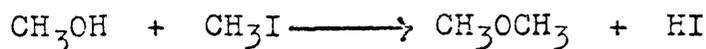
On the basis of ^1H n.m.r. spectral studies on a series of paramagnetic transition metal acetylacetonates Eaton ¹³⁵ has shown that both metal to ligand and ligand to metal charge transfer can occur via both bonding and antibonding ligand orbitals. Thus it is possible

to envisage proton attack at an orbital which has both metal and ligand character. The distinction between 1. and 2. then becomes a moot point.

It would seem that the reaction of square planar Rh(I) acetylacetonate complexes with acids to give bimolecular species is a general reaction although the lack of reactivity of acetic acid suggests that a strong acid is necessary to displace acetylacetonate.

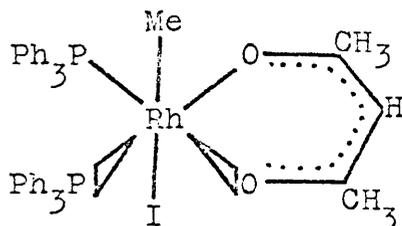
Reactions with Methyl Iodide

Rh(acac)(COD) does not react with methyl iodide in light petroleum or diethyl ether even under vigorous reflux conditions for several days. The ^1H n.m.r. spectrum of equimolar amounts of methyl iodide and Rh(acac)(COD) in carbon tetrachloride gives no evidence for the coordination of methyl iodide to rhodium and no reaction occurs in such mixtures at room temperature. On reflux a dark brown suspension is obtained from which no pure complexes could be isolated. Gentle reflux of a methanol solution of Rh(acac)(COD) with methyl iodide yields a dark brown precipitate. Recrystallisation of the benzene soluble portion yields brick red crystals of the known ¹²⁸ unstable complex $\mu\mu'$ -diiodo bis(cycloocta -1,5- diene)dirhodium(I), $[\text{RhI}(\text{COD})]_2$. Methanolysis of methyl iodide will take place under the conditions of the reaction and the resultant hydrogen iodide will react with Rh(acac)(COD) to give the observed product:



An ethereal suspension of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ reacted readily with methyl iodide on reflux to give 100% yield of the complex acetylacetonato(iodo)(methyl)-bis(triphenylphosphine)rhodium(III), $\text{Rh}(\text{acac})\text{I}(\text{Me})(\text{PPh}_3)_2$. Analytical, melting point and molecular weight data are shown in Table 3.5. The i.r. spectrum in both the solid state and solution (See Table 3.8.) indicates that the acetylacetonate moiety is O-bonded to rhodium. The ^1H n.m.r. spectrum of the complex at room temperature shows that the methyl groups of the acetylacetonate moiety are equivalent (See Table 3.9.) and there is no change in the ^1H n.m.r. spectrum on cooling to -50°C . From Table 3.9. it is seen that the position of methyl proton resonance for the methyl group bonded to $\text{Rh}(\text{III})$ is typical of such systems.

From the i.r. and ^1H n.m.r. spectra the stereochemistry of the complex is unambiguously defined and shown below:



This however does not indicate that trans oxidative addition has taken place. It has been shown ³⁰ that in the reaction of $\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2$ with alkyl halides although under certain conditions trans isomers are isolated as the final product the first stage of the addition reaction is almost certainly cis addition which is then followed by isomerisation.

No pure complexes could be isolated from the reaction of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ in diethyl ether with methyl iodide under reflux. However the i.r. and ^1H n.m.r. spectra of the mixtures obtained indicate the nature of the reaction:

I.r. Spectral Data (See Table 3.10)

The absorption at 2060cm^{-1} is typical of that obtained for a carbonyl bonded to $\text{Rh}(\text{III})$. The absorption at 1970cm^{-1} is assigned to $\nu(\text{C}\equiv\text{O})$ of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ and the absorption at 1700cm^{-1} is typical of an acetyl grouping bonded to $\text{Rh}(\text{III})$ as shown by Table 3.11.

¹H n.m.r. Spectral Data (See Table 3.10)

¹H n.m.r. data shown was obtained from a carbon tetrachloride reaction solution. Resonances at 4.55; 8.20 and 7.80 τ may be assigned to the starting materials $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ and methyl iodide. The regions associated with acetylacetonate, alkyl and acyl methyl proton resonances overlap to a large extent. This plus the formation of isomeric mixtures make assignment of the observed resonances impossible. However comparison of ¹H n.m.r. data shown in Tables 3.9., 3.10. and 3.11 coupled with i.r. spectral data does indicate that metal alkyl and metal acyl species are present.

Two similar reactions have been studied kinetically: 27,28

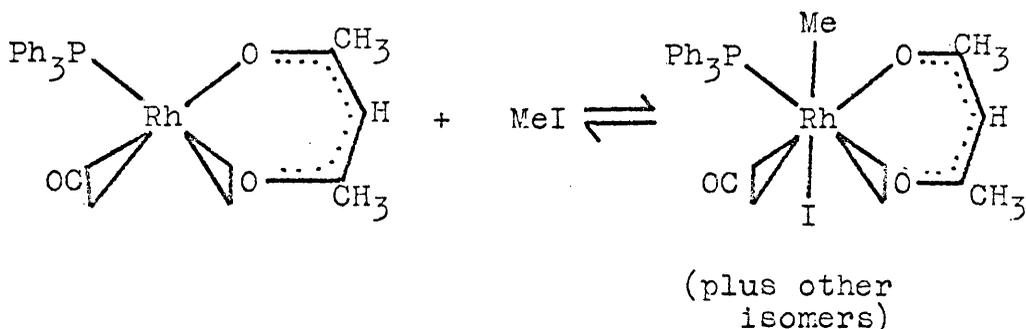
- a) trans - $\text{RhX}(\text{CO})\text{L}_2$ X=Cl, I; L= $\text{P}(\text{p-MeOC}_6\text{H}_4)_3$, PPh_3 , PEt_3 , $\text{P}(\text{p-FC}_6\text{H}_4)_3$, AsPh_3 with methyl iodide.
b) trans - $\text{RhCl}(\text{CO})_2(\text{PPh}_3)$ with methyl iodide.

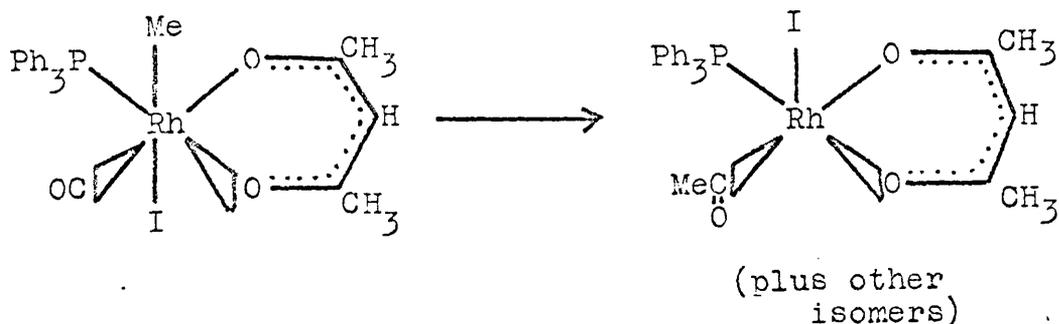
In both cases the first stage of the reaction is considered to be the oxidative addition of methyl iodide to give a six coordinate Rh(III) complex. For system

a) an equilibrium situation was observed and the presence of metal-alkyl species was shown by i.r. and ¹H n.m.r. spectral studies. The position of the equilibrium between trans - $\text{RhX}(\text{CO})\text{L}_2$ and the Rh(III)-methyl complex and also the rapidity with which this equilibrium was obtained was shown to be a function

of X and L. In the study of system b) kinetic data pointed to the formation of an intermediate which was, however, so short lived that its nature could not be established. A six coordinate Rh(III) species containing a metal-methyl bond was postulated. The next step in both systems was thought to be a nucleophile assisted methyl migration to give an acyl complex although neither study distinguished between methyl migration and carbonyl insertion. Direct nucleophilic attack of methyl iodide at the coordinated carbon monoxide of the starting Rh(I) complex as a means of forming the acyl complex may be ruled out for both these systems as this would involve a one step bimolecular path which is not observed. In system a) a complex ^1H n.m.r. spectrum is observed indicating the presence of several alkyl and acyl isomers.

Using systems a) and b) as a guide, a possible scheme for the reaction of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ with methyl iodide is as follows:

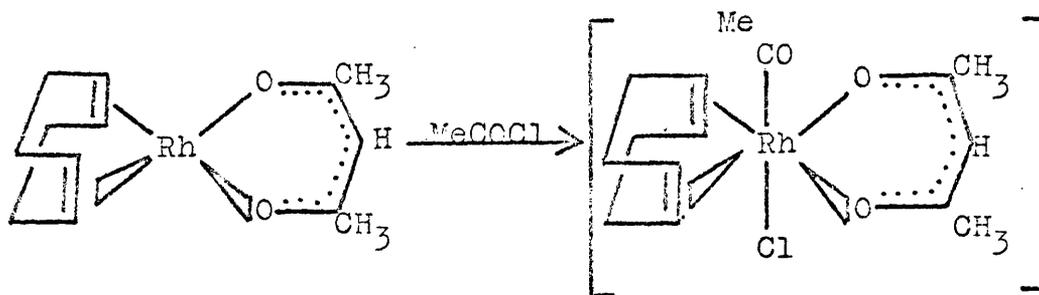


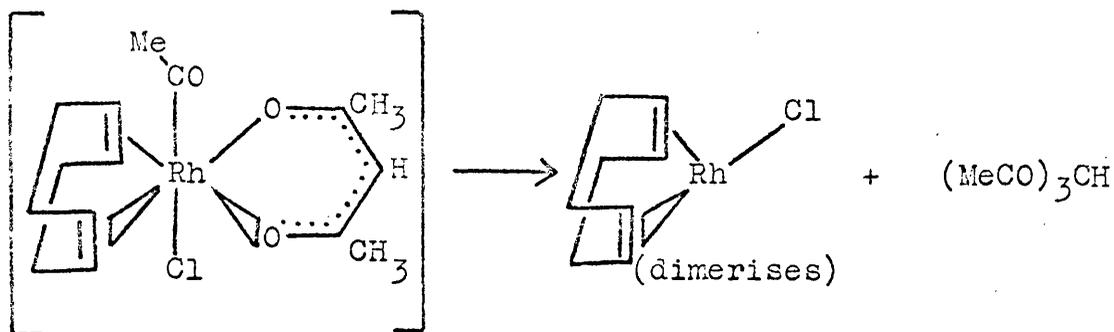


The possibility of two completely separate reactions giving rise to an alkyl and acyl complex in the absence of kinetic data cannot be discounted. As starting material was present in all samples obtained it could not be ascertained whether iodide had displaced acetylacetonate in either the alkyl or the acyl product.

Reactions with Acetyl Chloride

Rh(acac)(COD) reacts with acetyl chloride in diethyl ether to give an orange solution of $\mu\mu'$ -dichloro bis-(cycloocta -1,5- diene)dirhodium(I), $[\text{RhCl}(\text{COD})]_2$. To test for the formation of an Rh(III) acyl complex which undergoes reductive elimination of triacetyl methane to give $[\text{RhCl}(\text{COD})]_2$ via the reaction sequence shown below, the reaction was performed in carbon tetrachloride and the ¹H n.m.r. spectrum recorded.





(not isolated)

The carbon tetrachloride reaction solution was dark brown however and the only resonances observed were those due to starting material. As great care was taken in drying the solvents used and in redistilling the acetyl chloride under anhydrous conditions directly into the reaction mixture the presence of hydrogen chloride is unlikely and is not a probable explanation for the formation of $[\text{RhCl}(\text{COD})]_2$.

$\text{Rh}(\text{acac})(\text{PPh}_3)_2$ reacts with acetyl chloride in diethyl ether to give a pale yellow precipitate. Attempts to recrystallise this precipitate led to the formation of trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. I.r. spectral data for the pale yellow precipitate, shown in Table 3.12, indicates the presence of the complexes $\text{RhCl}_2(\text{Me})(\text{CO})(\text{PPh}_3)_2$ (See Table 3.9.), $\text{RhCl}_2(\text{COMe})(\text{PPh}_3)_2$ (See Table 3.11.) and trans - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. The formation of such complexes is consistent with the

initial production of $\text{RhCl}(\text{PPh}_3)_2$; which is known to react with acetyl chloride to give these complexes. The original production of the chloro species may be considered to take place via the oxidative addition of acetyl chloride followed by a reductive elimination as described for the reaction of $\text{Rh}(\text{acac})(\text{COD})$ with acetyl chloride.

$\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ reacted with acetyl chloride in diethyl ether to give the complex dichloro(acetyl)-(carbonyl)(triphenylphosphine)rhodium(III), $\text{RhCl}_2(\text{COCH}_3)(\text{CO})(\text{PPh}_3)$. Analytical and melting point data are given in Table 3.5. and i.r. spectral data are given in Table 3.12. The complex could not be recrystallised as dissolution in chloroform or acetone led to the formation of trans - $\text{RhCl}(\text{CO})_2(\text{PPh}_3)$. The complex is insoluble in benzene and may also be prepared by the reaction of acetyl chloride with $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$. The i.r. spectral data is very similar to that obtained for the complex $\text{RhCl}_2(\text{COMe})(\text{CO})(\text{PPh}_3)(0.5\text{CH}_2\text{Cl}_2)$ ¹⁷ (See Table 3.12.) This complex may be prepared by the reaction of acetyl chloride on trans - $\text{RhCl}(\text{CO})_2(\text{PPh}_3)$. It is thought that the expected product $\text{RhCl}_2(\text{COMe})(\text{CO})_2(\text{PPh}_3)$ is rendered unstable to the loss of carbon monoxide by the presence of strongly π -acidic ligands, i.e. carbon monoxide and the acetyl group, competing with one another for electron density on the central metal

atom through π - back donation. Thus it was deemed unlikely that the acetyl group is trans to carbon monoxide in $\text{RhCl}_2(\text{COMe})(\text{CO})(\text{PPh}_3)(0.5\text{CH}_2\text{Cl}_2)$ and the $\nu(\text{Rh}-\text{Cl})$ stretching frequency at 265cm^{-1} was assigned to $\nu(\text{Rh}-\text{Cl})$ trans acetyl. In the unsolvated analogue the bond at 268cm^{-1} may be assigned similarly. Both square based pyramid¹³⁷ and trigonal bipyramid¹³⁸ geometries are known for Rh(III) complexes and from the data available it is impossible to assign definitely either of these to the complex $\text{RhCl}_2(\text{COMe})(\text{CO})(\text{PPh}_3)$.

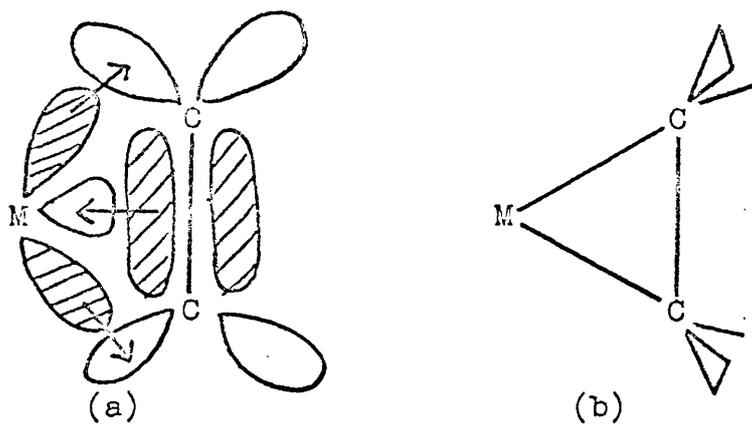
Reactions with Olefins

Reactions with Tetrachloroethylene

Tetrachloroethylene did not react with any of the complexes under investigation. This is not surprising as experiments with organic donor ligands have shown that it is a very poor π acceptor¹³⁹. Raddley⁴ has shown that strong π acceptor properties are essential for the formation of strong metal-olefin bonds in systems of the type $\text{IrX}(\text{CO})\text{L}_2$ olefin.

Reactions with Tetracyanoethylene

The bonding in metal-tetracyanoethylene complexes has been the subject of speculation^{4,5}. Two models have been put forward and are illustrated in Fig. 3.7., a) depicts the conventional Chatt - Duncanson model for metal-olefin interaction and b) depicts a three



Bonding models for tetracyanoethylene complexes.

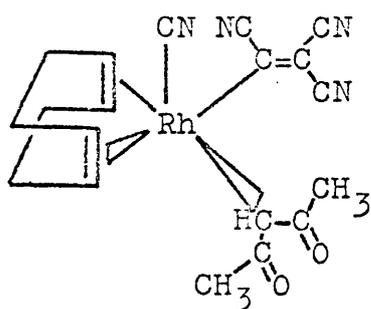
 = occupied orbital,
 = empty orbital.

Fig.3.7.

membered metallocyclopropane ring. Considering model a); in cases where both σ and π contributions to the metal olefin bond are significant there will be no apparent change in oxidation state of the metal. However tetracyanoethylene is one of the strongest π acids known and has σ donor properties which are practically negligible¹⁴⁰. Thus in a tetracyanoethylene complex considerable charge may be deposited in the olefin π^* orbital without any attendant σ donation from the olefin to the metal. Thus criteria of oxidation state e.g. $V(C\equiv O)$ cannot be used to test the applicability of models a) and b).

⁴ Paddley has argued that model a) is completely equivalent to the valence bond description b) and that a pure π bond and a metallocyclopropane ring are physically the same in terms of the atomic orbitals used. He considers that the molecular orbital approach of model a) may be preferable because of its flexibility in treating intermediate cases where both metal to olefin π bonding and olefin to metal σ bonding are important. This he has demonstrated by relating the M.O. bonding model to the stability of a series of iridium cyanoethylene complexes⁴.

Rh(acac)(COD) reacted with tetracyanoethylene in acetone to give an insoluble pale yellow complex which analyses as Rh(acac) $[C_2(CN)_4]$ (COD). Analytical and



Postulated structure for the complex
 $\text{Rh}(\text{CN})[\text{C}_2(\text{CN})_3](\text{acac})(\text{COD})$.

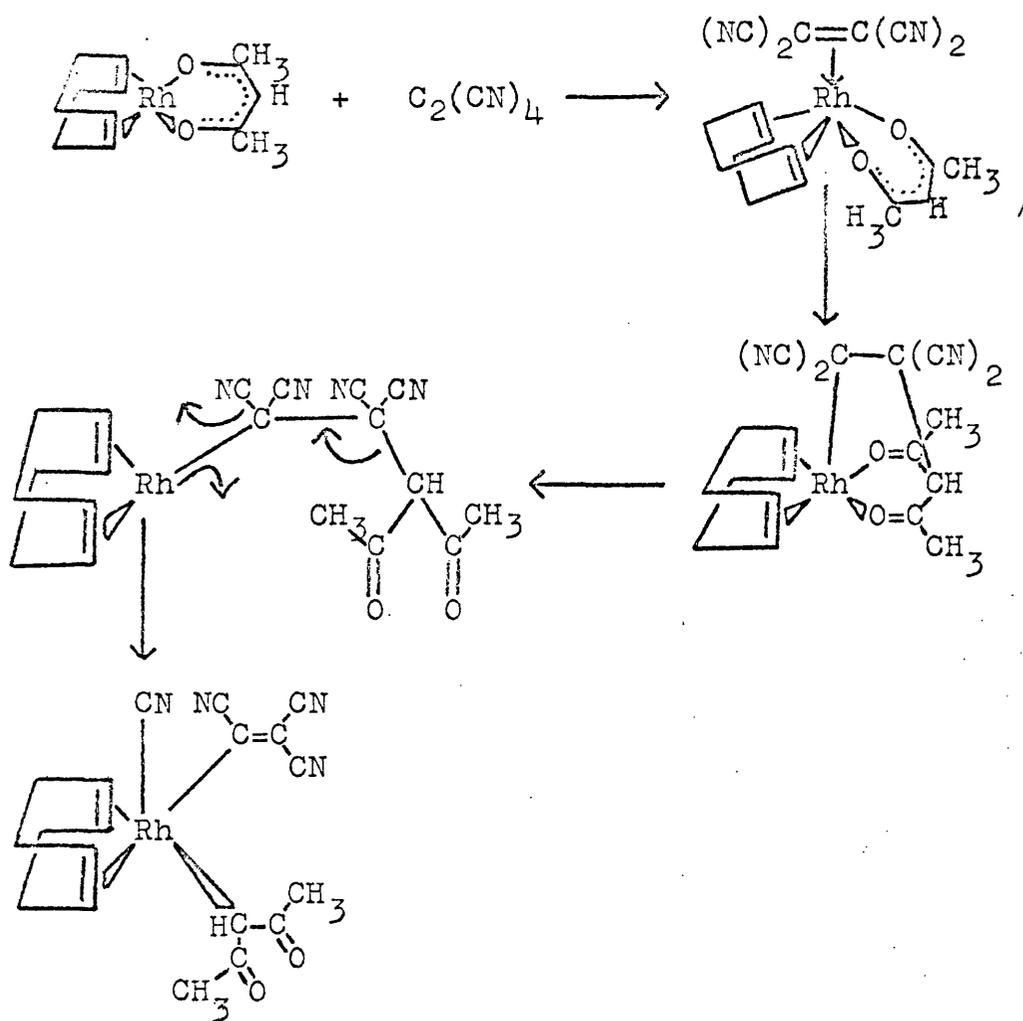
Fig.3.8.

melting point data are shown in Table 3.5. I.r. spectral data is given in Table 3.13. The strong absorption at 2148cm^{-1} is 100cm^{-1} lower than $\nu(\text{C}\equiv\text{N})$ in tetracyanoethylene and is in the range $2040\text{-}2170\text{cm}^{-1}$ which is typical of a cyanide ion bonded directly to a metal⁴⁴. The absorptions at 2239 and 2212cm^{-1} are similar to those of $\nu(\text{C}\equiv\text{N})$ for tetracyanoethylene; tetracyanoethylene exhibits two strong bands at 2262 and 2214cm^{-1} ¹⁴¹. The bands at 1739 and 1716cm^{-1} may be assigned to $\nu(\text{C}=\text{O})$ for a C-bonded acetylacetonate moiety. Values of $1600\text{-}1695\text{cm}^{-1}$ have been reported for $\nu(\text{C}=\text{O})$ in platinum complexes containing C-bonded acetylacetonates¹³¹.

Tetracyanoethylene is a most reactive dienophile, giving an adduct with butadiene below room temperature in almost quantitative yield¹⁴². It is tempting to postulate a structure resulting from 1,4-addition of tetracyanoethylene across the metal-acetylacetonate ring as has been observed in the reaction of hexafluorobut-2-yne with $\text{Rh}(\text{acac})(\text{COD})$. However such postulates do not account for the presence of a metal bonded cyanide ion. The structure shown in Fig.3.8. accounts for all the features observed in the i.r. spectrum. The absence of an absorption assignable to $\nu(\text{C}=\text{C})$ is puzzling but such absorptions are in some cases very weak e.g. trans - $\text{Pt}(\text{C}_2\text{Cl}_3)\text{Cl}(\text{PPh}_3)_2$ ⁷⁵. Coordination of cyanide via nitrogen may be eliminated as absorp-

tions due to $\nu(\text{C}\equiv\text{N})$ are observed at 2300cm^{-1} for such systems ¹⁴³. The monomeric nature of the complex is open to question in the absence of molecular weight data. The complex $\text{Rh}(\text{CN})[\text{C}_2(\text{CN})_3](\text{acac})(\text{COD})$ is a Rh(III) complex and it has been noted that Rh(III) olefin complexes are unstable, attempts to prepare them by oxidising Rh(I) olefin complexes being completely unsuccessful. The complex $\text{Rh}(\text{CN})[\text{C}_2(\text{CN})_3]$ ^{143a} $(\text{acac})(\text{COD})$ is in keeping with these observations as it decomposes readily in vacuum and slowly on standing in air.

The reaction of $\text{Rh}(\text{acac})(\text{COD})$ with tetracyanoethylene in light petroleum yielded a different product; an orange crystalline solid. On dissolution in ether, benzene, chloroform or acetone the insoluble $\text{Rh}(\text{CN})[\text{C}_2(\text{CN})_3](\text{acac})(\text{COD})$ was formed. The complex could not be obtained analytically pure. Like $\text{Rh}(\text{CN})[\text{C}_2(\text{CN})_3](\text{acac})(\text{COD})$ it was unstable under vacuum and decomposed slowly in air. I.r. spectral data is shown in Table 3.13. The absorptions at 1514 and 1567cm^{-1} may be assigned to an O-bonded acetylacetonate. The absorptions at 2222 and 2228cm^{-1} are typical for $\nu(\text{C}\equiv\text{N})$ in metal - tetracyanoethylene complexes ^{4,7}. The complex is then almost certainly $\text{Rh}(\text{acac})\text{C}_2(\text{CN})_4(\text{COD})$ although the possibility of a dimeric species involving either acetylacetonate or



Postulated mechanism for the formation of $Rh(CN)C_2(CN)_3(acac)(COD)$.

Fig.3.9.

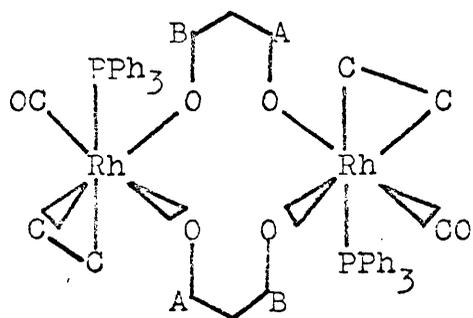
tetracyanoethylene bridges cannot be ruled out.

It seems probable that $\text{Rh}(\text{acac})[\text{C}_2(\text{CN})_4](\text{COD})$ is an intermediate in the formation of $\text{Rh}(\text{CN})[\text{C}_2(\text{CN})_3](\text{acac})(\text{COD})$. Considering the powerful dienophile nature of tetracyanoethylene the participation of coordinated tetracyanoethylene in a 1,4-addition across the rhodium-acetylacetonate ring is not unlikely. Further rearrangement to give a metal cyanide, a tricyanovinyl group and a C-bonded acetylacetonate moiety may then be envisaged. This reaction scheme is shown in Fig.3.9.

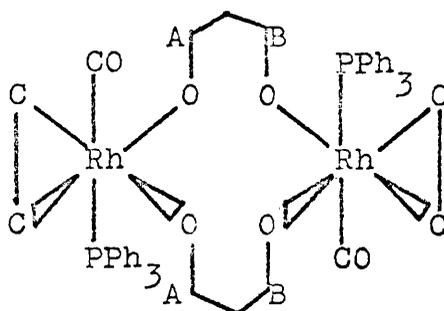
$\text{Rh}(\text{acac})(\text{PPh}_3)_2$ in diethyl ether reacted with tetracyanoethylene to give a brown solid. Treatment of this solid with acetone yielded a yellow insoluble complex which analysed as $\text{Rh}(\text{acac})[\text{C}_2(\text{CN})_4](\text{PPh}_3)$. Analytical and melting point data are given in Table 3.5.; i.r. spectral data in Table 3.14. The absorptions at 1565 and 1514cm^{-1} may be assigned to an O-bonded acetylacetonate while those at 2216 - 2248cm^{-1} are in the region typical for $\nu(\text{C}\equiv\text{N})$ in metal-tetracyanoethylene complexes^{4,7}. The presence of several absorptions assignable to $\nu(\text{C}\equiv\text{N})$ may be due to the presence of geometrical isomers or to solid state splitting effects. As the complex is extremely insoluble it was impossible to record solution spectra where the latter would be eliminated. It is interesting to note that a molecule of triphenylphosphine has been lost from the

complex. If the complex is monomeric and tetracyanoethylene is regarded as occupying two coordination sites the complex is formally five coordinate. Whether the structure is a square base pyramid or a trigonal bipyramid is open to conjecture. Both structures are known for Rh(III) complexes containing triphenylphosphine^{137,138}. However the possibility of a dimeric species containing acetylacetonate or tetracyanoethylene bridges cannot be discounted in the absence of molecular weight data.

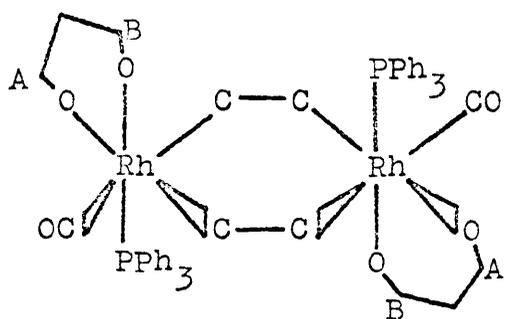
Rh(acac)(CO)(PPh₃) in benzene solution reacted readily with tetracyanoethylene to give a green solution from which was isolated a green crystalline solid. Recrystallisation from dichloromethane three times yielded a yellow crystalline complex which analysed as Rh(acac)[C₂(CN)₄](CO)(PPh₃). Analytical, melting point and molecular weight data are shown in Table 3.5., i.r. spectral data in Table 3.13. and ¹H n.m.r. spectral data in Table 3.14. From the i.r. spectrum it is seen that the acetylacetonate function is O-bonded. The absorption at 2235cm⁻¹ is typical for $\nu(\text{C}\equiv\text{N})$ for metal-tetracyanoethylene complexes⁴⁷ and the bands at 2075 and 2082 are typical for $\nu(\text{C}\equiv\text{O})$ in a Rh(III) complex. In solution only one absorption is observed for $\nu(\text{C}\equiv\text{O})$. The ¹H n.m.r. spectrum in the methyl group region is a doublet centred on 8.15 τ which



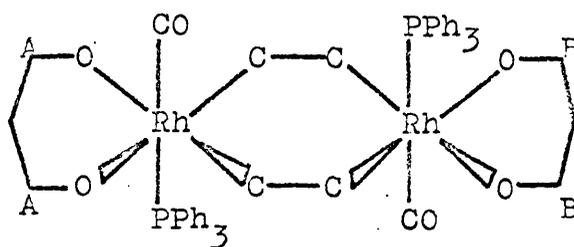
(a)



(b)



(c)



(d)

Equivalent methyl groups shown as A or B.

Possible structures for the complex
 $[\text{Rh}(\text{acac})[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)]_2$.

Fig. 3.10.

indicates that the methyl groups are nonequivalent. The molecular weight in chloroform has a value nearly twice that expected. Evidently the complex is a dimer. Bridging carbonyls may be eliminated as $\nu(\text{C}\equiv\text{O})$ for such systems occurs in the region $1898-1785\text{cm}^{-1}$ ⁸⁴. The solution i.r. spectrum indicates that the carbonyl groups are trans to one another. Bridging phosphine groups are considered to be unlikely and this leaves either bridging acetylacetonate groups or bridging tetracyanoethylene groups. Such structures as are consistent with available data are shown in Fig.3.10. (a-d). The methyl groups labelled A are not equivalent to those labelled B. The single $\nu(\text{C}\equiv\text{O})$ stretching frequency is catered for by trans carbonyl configurations.

The structures (a) and (b) do have a precedent in the complex $\text{Re}_2\text{Cl}_4(\text{acac})_4$ ¹⁴⁴, which is considered to contain bridging acetylacetonate groups, while complexes containing bridging $\text{C}_2(\text{CN})_4$ groups are at present unknown. Conclusive evidence must await a single crystal X ray study.

Reactions with Tetrafluoroethylene

$\text{Rh}(\text{acac})(\text{COD})$ in diethyl ether did not react at room temperature with tetrafluoroethylene but on heating to 70°C overnight a brown precipitate is formed. This substance decomposed rapidly in solution and absorbed water from the atmosphere very rapidly

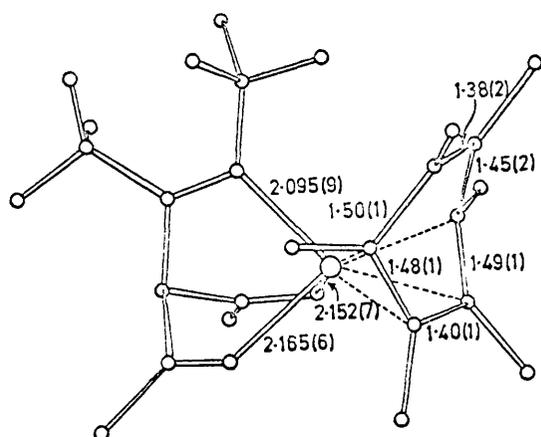
as shown by the i.r. spectrum. Meaningful analytical data could not be obtained. The i.r. spectrum shows a strong absorption at 2100cm^{-1} indicating that a carbonyl complex of some sort is present. The complex could not be further characterised. The formation of carbonyl complexes from reactions of rhodium complexes with tetrafluoroethylene has been reported¹⁴⁴.

$\text{Rh}(\text{acac})(\text{PPh}_3)_2$ in diethyl ether did not react with tetrafluoroethylene at room temperature, but on heating to 50°C overnight a clear yellow solution is obtained. From this solution may be isolated in good yield the known¹²⁵ complex $\text{Rh}(\text{acac})(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$. At higher temperatures e.g. 100°C the known¹²⁹ complex $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ was formed in good yield. A variety of fluoroolefins react with the complexes $\text{RhCl}(\text{PPh}_3)$ and $\text{Rh}_2\text{Cl}_2\text{L}_4$ at high temperatures to give carbonyl complexes $\text{RhCl}(\text{CO})\text{L}_2$ $\text{L}=\text{PPh}_3$, $\text{P}(\text{C}_6\text{F}_5)_3$, $\text{P}(\text{C}_6\text{F}_5)_2\text{Ph}$; $\text{P}(\text{C}_6\text{F}_5)\text{Ph}_2$ and the action of water on fluoroolefin complexes has been invoked to explain the carbonyl formation¹⁴⁴. On this basis the action of water on the complex $\text{Rh}(\text{acac})(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$ would seem a reasonable mechanism for the formation of the carbonyl complex $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$.

Reactions with Acetylenes

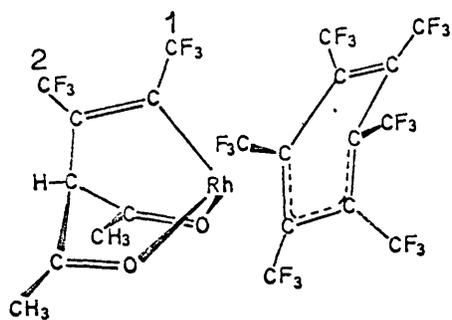
Reactions with Diphenyl Acetylene

The complexes under investigation did not react



The molecular geometry of $\text{Rh}(\text{C}_9\text{H}_7\text{F}_6\text{O}_2)[\text{C}_6(\text{CF}_3)_6]$; Bond lengths in Å with e.s.d. of last figure in parentheses. The fluorine atoms of $[\text{C}_6(\text{CF}_3)_6]$ have been omitted for clarity.

Fig.3.11.



Schematic representation of the complex
 $\text{Rh}(\text{C}_9\text{H}_7\text{F}_6\text{O}_2)[\text{C}_6(\text{CF}_3)_6]$.

Fig.3.12.

with diphenyl acetylene under refluxing solvent conditions.

Reactions with Hexafluorobut -2- yne

Rh(acac)(COD) reacted with hexafluorobut -2- yne in diethyl ether or benzene to give the complex $\text{Rh}(\text{C}_9\text{H}_7\text{F}_6\text{O}_2)[\text{C}_6(\text{CF}_3)_6]$. The reaction occurs readily at room temperature in benzene but is accompanied by the formation of much unidentified material dark red in colour. The complex is insoluble in benzene. An ethereal solution of Rh(acac)(COD) had to be heated to 60°C. before any appreciable reaction with hexafluorobut -2- yne took place, but much less side reaction occurred and a higher yield was obtained. The complex was easily precipitated from the ethereal solution by the addition of benzene or light petroleum. Analytical and melting point data are shown in Table 3.5; i.r. and ^{19}F n.m.r. spectral data are shown in Tables 3.15 and 3.16. respectively. An X ray structure determination ^{144a} has revealed the nature of the complex and this is shown in Fig.3.11. A schematic diagram of the complex is given in Fig.3.12.

The complex $\text{Rh}(\text{C}_5\text{H}_5)[\text{C}_6(\text{CF}_3)_6]$ exhibits an absorption at 1623cm^{-1} which was considered to be the $\nu(\text{C}=\text{C})$ stretching frequency of the uncoordinated double bond in the hexakis(trifluoromethyl)benzene moiety ¹⁴⁵. Hence the absorption at 1643cm^{-1} may be assigned

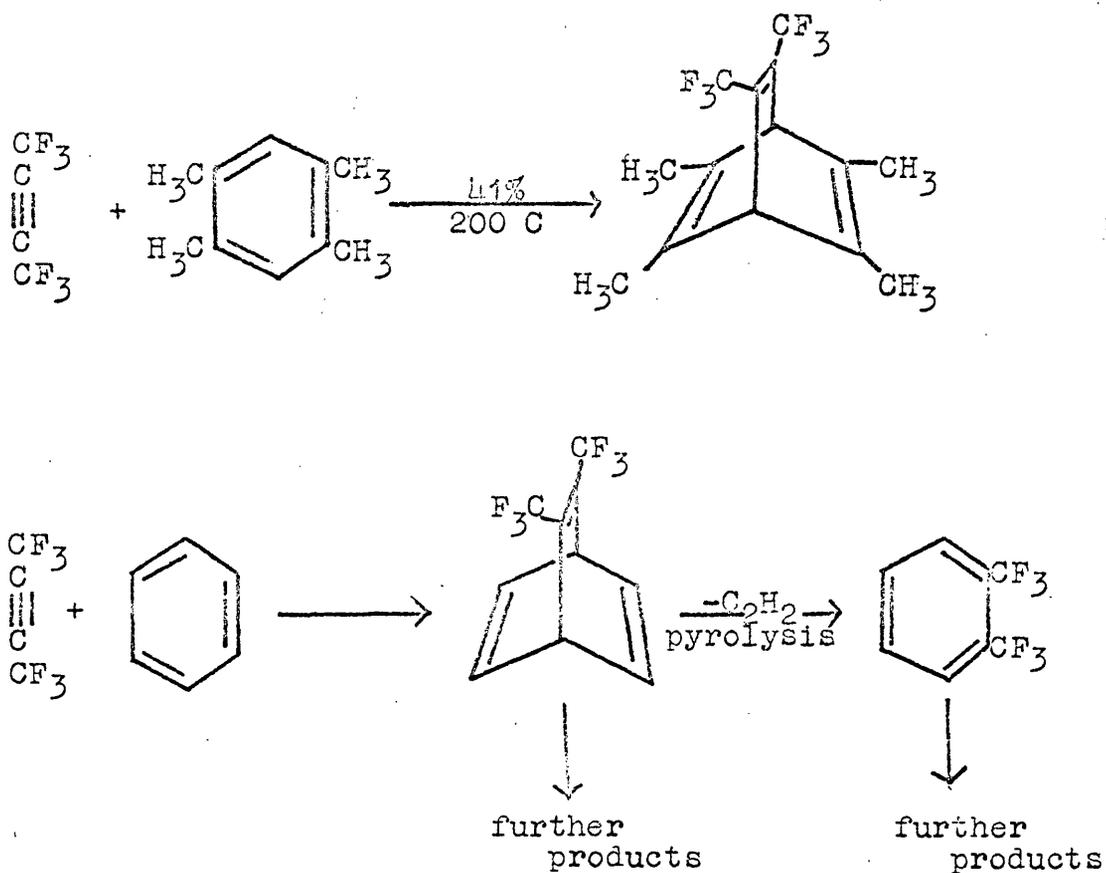
to such a vibration in the complex

$\text{Rh}(\text{C}_9\text{H}_7\text{F}_6\text{O}_2)[\text{C}_6(\text{CF}_3)_6]$. The dimeric complexes $[\text{Rh}(\text{acac})(\text{C}_2\text{F}_4)\text{L}]_2$ ($\text{L} = \text{CH}_3\text{CN}, \text{PhCN}, \text{HOCH}_2\text{CH}_2\text{CN}, n\text{-C}_5\text{H}_{11}\text{CN}, \frac{n\text{-C}_6\text{H}_{13}\text{CN}_1}{125}, \text{HCON}(\text{CH}_3)_2$) prepared by Parshall and having the structure shown in Fig.3.2. exhibit strong absorptions $\sim 1600\text{cm.}^{-1}$. These absorptions were assigned to the acetylacetonate function. The increase in frequency (compared with that of a normal acetylacetonate function) is due to the increased C-O bond order on formation of the Rh-C bonds. It seems reasonable to assign the bands at 1695 and 1662cm.^{-1} , similarly as 1,4 - addition of hexafluorobut-2-yne across the rhodium-acetylacetonate ring will lead to such an increase in C-O bond order. The remaining absorption at 1598cm.^{-1} may be assigned to $\nu(\text{C}=\text{C})$ for the bridging C=C bond. This is consistent with the assignment of absorptions in the region $1536\text{-}1600\text{cm.}^{-1}$ to $\nu(\text{C}=\text{C})$ for the complexes $\text{Co}_4(\text{CO})_{12}\text{C}_8\text{F}_{12}$ and $\text{Co}_2(\text{CO})_{146}(\text{C}_4\text{F}_6)\text{L}_2$ which contain C_4F_6 bridging groups.

The complex was sparingly soluble in deuteriochloroform and a ^1H n.m.r. spectrum could not be obtained. The complex decomposed rapidly in acetone and methanol to give dark brown solutions of unknown composition. The complex was sufficiently soluble in diethyl ether to permit the ^{19}F n.m.r. spectrum to be observed. (See Table 3.15). The resonance at -1.7 p.p.m. is a

well defined quartet. It is assigned to CF_3 -2 (See Fig.3.12.) $J_{1-2} = 8.2\text{c.p.s.}$ and is in fair agreement with those values reported for other cis isomers $\sim 12\text{c.p.s.}$ ⁶⁵ The resonance at -6.3p.p.m. is assigned to two CF_3 groups of the hexakis(trifluoromethyl)benzene moiety plus CF_3 -1. This is in accord with the resonance for a CF_3 group geminal to a metal appearing at a lower field than a CF_3 group trans to a metal as observed for the complex $\text{Pt}[\text{CF}_3\text{C} = \text{C}(\text{H})\text{CF}_3]\text{Cl}(\text{PEt}_3)_2$.⁶⁵ The two remaining resonances at -5.25 and -2.42p.p.m. are assigned to the hexakis(trifluoromethyl)benzene moiety. It is interesting to note that resonances associated with this moiety are all upfield to those observed for the exactly similar moiety in the complex $\text{Rh}(\text{C}_5\text{H}_5)[\text{C}_6(\text{CF}_3)_6]$.¹⁴⁵

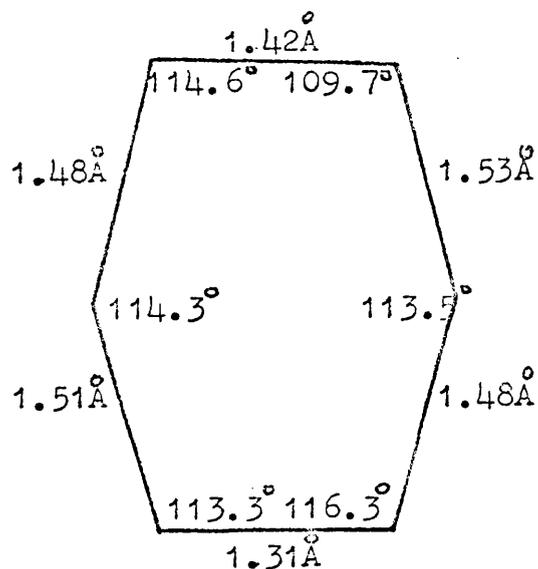
A number of transition metal complexes cause polymerisation of hexafluorobut -2- yne under mild conditions either to hexakis(trifluoromethyl)benzene or a white infusible polymer.¹⁴⁷ The complex $\text{Rh}(\text{C}_5\text{H}_5)(\text{CO})_2$ reacts with the alkyne to give cyclopentadienyl-hexakis(trifluoromethyl)benzene rhodium(I).¹⁴⁵ Crystallographic studies have demonstrated that there is localised bonding between the substituted benzene and the rhodium.¹⁴⁸ Thus the formation of such a system in the reaction of $\text{Rh}(\text{acac})(\text{COD})$ with hexafluorobut -2- yne is not surprising. The 1,4 - addition of C_4F_6



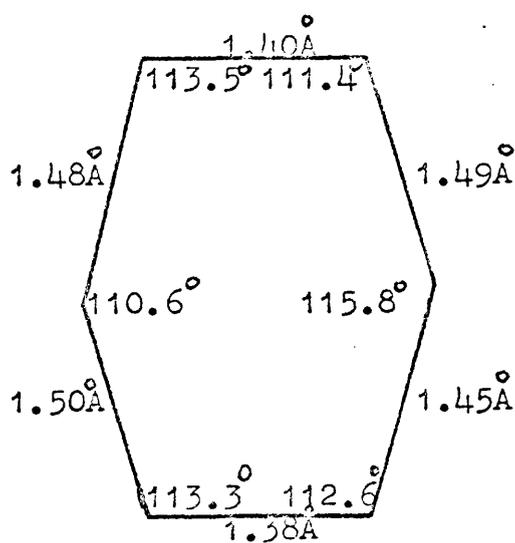
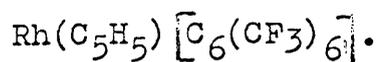
Dienophile properties of hexafluorobut-2-yne.

Fig.3.13.

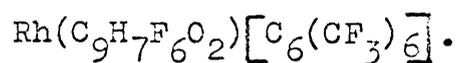
-181-



angles between planes = 47.9°
C-CF₃ bond lengths vary from
1.48(2)-1.55(3) Å.

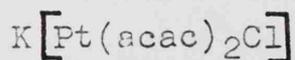


angles between planes = 42.5°
C-CF₃ bond lengths vary from
1.49(1)-1.53(1) Å.



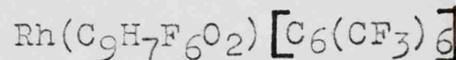
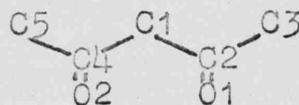
Bond lengths and bond angles in hexakis(trifluoro-
methyl)benzene ligands.

Fig.3.14.



C1-C2	=	1.53	(3)	Å
C2-C3	=	1.53	(3)	Å
C2-O1	=	1.21	(2)	Å
C1-C4	=	1.54	(3)	Å
C4-C5	=	1.52	(3)	Å
C4-O2	=	1.19	(3)	Å

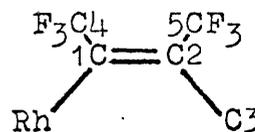
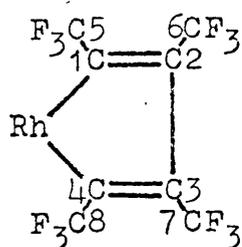
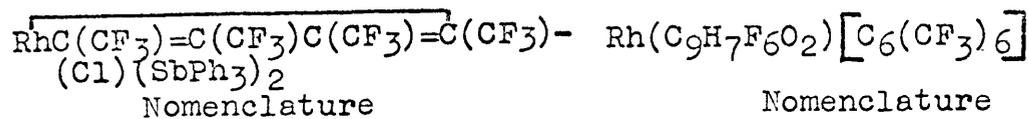
Nomenclature



C1-C2	=	1.51	(1)	Å
C2-C3	=	1.50	(1)	Å
C2-O1	=	1.23	(1)	Å
C1-C4	=	1.52	(1)	Å
C4-C5	=	1.48	(1)	Å
C4-O2	=	1.23	(1)	Å

Bond lengths in C-bonded acetylacetonate moieties.

Fig.3.15.



Rh-C1	=	2.00(1)	Å
Rh-C4	=	1.96(1)	Å
C1-C2	=	1.33(2)	Å
C4-C3	=	1.37(1)	Å
C2-C3	=	1.39(1)	Å
C1-C5	=	1.49(1)	Å
C2-C6	=	1.61(2)	Å
C3-C7	=	1.58(2)	Å
C4-C8	=	1.48(1)	Å

Rh-C1	=	2.09(1)	Å
C1-C2	=	1.35(1)	Å
C2-C3	=	1.54(1)	Å
C4-C1	=	1.47(1)	Å
C5-C2	=	1.52(1)	Å

Bond lengths in Rh-C₄F₆ moieties.

Fig.3.16.

across the rhodium-acetylene ring is however novel. Hexafluorobut -2- yne is a very reactive dienophile, as is illustrated by its reaction with durene¹⁴⁹ at 200°C and even benzene¹⁵⁰ at 250°C; in which normal Diels-Alder addition takes place. These reactions are summarised in Fig. 3.13.

From Fig.3.14 it is seen that the geometry of the hexakis(trifluoromethyl)benzene ring in $\text{Rh}(\text{C}_9\text{H}_7\text{F}_6\text{O}_2)[\text{C}_6(\text{CF}_3)_6]$ is essentially very similar to that of the same moiety in $\text{Rh}(\text{C}_5\text{H}_5)[\text{C}_6(\text{CF}_3)_6]$ ¹⁴⁸. From Fig.3.15. it is seen that the bond lengths in the C-bonded acetylacetonate moiety are similar to those observed for the C-bonded acetylacetonate in the complex $\text{K Pt}(\text{acac})_2\text{Cl}$ ¹⁵¹. The Rh-O distances in the $\text{RhC}_9\text{H}_7\text{F}_6\text{O}_2$ system are 2.152(7)Å and 2.165(6)Å. Rh-C single bonds are ~2Å in length, and thus it seems reasonable to postulate coordination of the oxygens to rhodium in the $\text{Rh}(\text{C}_9\text{H}_7\text{F}_6\text{O}_2)$ system. The dimensions of the Rh-C₄F₆-C bridge in the complex are similar to the analogous dimensions observed in the complex $\overline{\text{RhC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)}(\text{Cl})(\text{SbPh}_3)_2$ (See Fig.3.16.) with the exception that the C2-C3 bond length in the latter complex is only 1.388(14)Å indicating delocalisation of electrons around the metallocycle ring, whereas C2-C3 in $\text{Rh}(\text{C}_9\text{H}_7\text{F}_6\text{O}_2)[\text{C}_6(\text{CF}_3)_6]$ is 1.54(1)Å; a normal value for a C-C single bond.

$\text{Rh}(\text{acac})(\text{PPh}_3)_2$ in diethyl ether reacted with

hexafluorobut -2- yne at room temperature to give an orange solution. One complex may be isolated from this solution but no analytical data could be obtained owing to its tendency to revert to an unstable oil. However i.r., ^1H n.m.r. and ^{19}F n.m.r. spectral data indicate the probable nature of the complex. These data are given in Tables 3.15. and 3.16.

From the i.r. spectrum it is apparent that the acetylacetonate function is still acting as an O-bonded chelate; and the ^1H n.m.r. spectrum shows that the methyl groups are not equivalent. The i.r. absorption at 1664cm.^{-1} may be assigned to a lowered $\nu(\text{C}\equiv\text{C})$. The complexes $\text{RhCl}(\text{R}'\text{C}\equiv\text{CR})(\text{CO})(\text{PPh}_3)_2$ ($\text{R}'=\text{R}=\text{CO}_2\text{H}$, $\text{R}'=\text{H}$, $\text{R}=\text{CO}_2\text{H}$) exhibit i.r. absorptions at 1600 and 1640cm.^{-1} and these have been assigned to such vibrations¹⁵². The ^{19}F n.m.r. spectrum exhibits two resonances of equal intensity -10.22 and 7.92p.p.m. This indicates that the trifluoromethyl groups are not equivalent. The complex $\text{RhCl}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{SbPh}_3)_3$ in which the trifluoromethyl groups are not equivalent exhibits a similar ^{19}F n.m.r. spectrum, resonance occurring at -12.7 and -9.8p.p.m. ¹¹. Thus the structure shown in Fig. 3.17. may be assigned to the complex. A metallocycle complex involving rhodium and two C_4F_6 groups is not considered a plausible structure for this complex as $\nu(\text{C}=\text{C})$ for such structures occurs below 1600cm.^{-1} ¹¹. The ^{19}F n.m.r. spectra of such

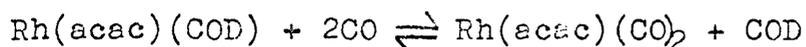
systems exhibit resonances more widely separated e.g. $\text{RhCl}(\text{C}_8\text{F}_{12})(\text{MPh}_3)_2$ $\text{M}=\text{As}$, resonance occurs at -10.2 and -5.2 p.p.m.; $\text{M}=\text{Sb}$, resonance occurs at -10.9 and -5.1 p.p.m.; relative to benzotrifluoride. Also such a system would be asymmetric to the extent that each trifluoromethyl group would be non-equivalent and a much more complex ^{19}F n.m.r. spectrum would be observed.

$\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ in diethyl ether reacted readily with hexafluorobut-2-yne to give an orange solution. Only an intractible oil could be obtained from the solution.

Miscellaneous Reactions

Reactions with Carbon Monoxide

A solution of $\text{Rh}(\text{acac})(\text{COD})$ in light petroleum reacted readily with carbon monoxide to give a quantitative yield of the known complex acetylacetonatodicarbonyl rhodium(I), $\text{Rhacac}(\text{CO})_2$. A similar reaction has been observed for the complex $\text{Ir}(\text{acac})(\text{COD})$.⁶² It has been reported that cycloocta-1,5-diene displaces carbon monoxide from the complexes $\text{M}(\text{acac})(\text{CO})_2$ ($\text{M}=\text{Rh}, \text{Ir}$). Thus it would seem that an equilibrium situation prevails:



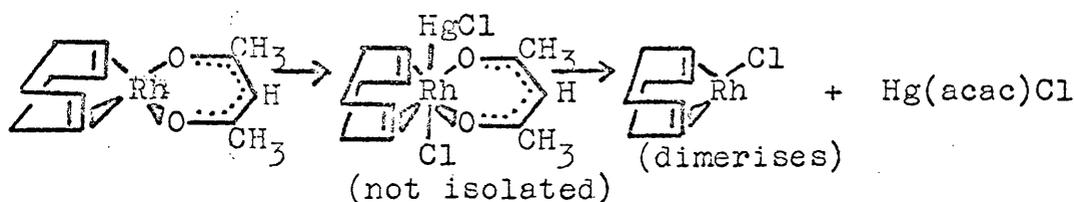
A stirred suspension of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ in diethyl ether reacted readily with carbon monoxide to give the known complex acetylacetonato(carbonyl)(triphenyl-

phosphine)rhodium(I), $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ quantitatively. This reaction is analogous to the reaction of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ with tetracyanoethylene assuming that the complex $\text{Rh}(\text{acac})[\text{C}_2(\text{CN})_4](\text{PPh}_3)$ is monomer; triphenylphosphine a good σ donor but poor π acceptor being replaced in both cases by good π acceptors.

Reactions with Mercuric Chloride

A dichloromethane solution of $\text{Rh}(\text{acac})(\text{COD})$ reacted instantly with an acetone solution of excess mercuric chloride to give the known complex

$\mu\mu'$ -dichlorobis(cycloocta -1,5- diene)dirhodiumbis-(mercuric chloride), $\text{Rh}_2\text{Cl}_2(\text{COD})_2(\text{HgCl}_2)_2$. Attempts to prepare the adduct $\text{Rh}(\text{acac})(\text{COD})(\text{HgCl}_2)$ by using stoichiometric quantities of $\text{Rh}(\text{acac})(\text{COD})$ and mercuric chloride failed, low yields of the chloro bridged adduct being obtained. Such a bridged system presumably forced by the initial oxidative addition mercuric chloride to $\text{Rh}(\text{acac})(\text{COD})$ to give the complex $\text{Rh}(\text{acac})\text{Cl}(\text{HgCl})(\text{COD})$ which then undergoes reductive elimination of $\text{Hg}(\text{acac})\text{Cl}$ to give $\text{RhCl}(\text{COD})$ which dimerises and reacts further with mercuric chloride:



The oxidative addition of mercuric chloride to the complex trans - IrCl(CO)(PPh₃)₂ has been reported¹¹² to give an Ir(III) complex, IrCl₂(HgCl)(CO)(PPh₃)₂ analogous to the intermediate postulated above. However trans - RhCl(CO)(PPh₃)₂¹¹² did not react with mercuric chloride.

A suspension of Rh(acac)(PPh₃)₂ reacted with an acetone solution of mercuric chloride to give an orange powder which analyses as Rh(acac)(HgCl)₂(PPh₃)₂. Analytical and melting point data are shown in Table 3.5. The complex is not very soluble and can only be recrystallised with difficulty and considerable loss of complex. I.r. spectral data indicates the presence of an O-bonded acetylacetonate but no meaningful structural information can be derived from the far i.r. spectrum, bands occurring at 339,327,280,263, 246 and 228 cm.⁻¹.

TABLE 3.1.

Infrared absorptions associated with Metal-Acetylacetonates (cm.^{-1})

<u>Complex</u>	<u>Ref.</u>	<u>Mixture of $\overline{\nu}(\text{VC}=\text{O})$ & $\overline{\nu}(\text{C}=\text{C})$ modes</u>	<u>O - bonded</u>	<u>C - bonded</u>	
				<u>Mainly $\overline{\nu}(\text{C}=\text{O})$</u>	
$\text{K}[\text{Pt}(\text{acac})_2\text{Cl}]$	131	1570 ^a (s)	1565(s, sh)	1546(s) 1522 ^a (s)	1653(m)
$\text{K}[\text{Pt}(\text{acac})_3]$	131	1570(s)	1556(s)	1515 ^a (s)	1679(s) 1658(s)
$\text{Pt}(\text{acac})\text{Cl}(\text{PPh}_3)$	127	1571(s)	1560(s)	1516(s)	1642(s) 1624 ^a (s)
$\text{Rh}(\text{acac})(\text{CO})_2$	129	1553(s)	1513(s)	-	-
$\text{Rh}(\text{acac})(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$	125	1595(s)	1517(s)	-	-
$[\text{Rh}(\text{acac})(\text{C}_2\text{F}_4)(\text{CH}_3\text{CN})]_2$	125	-	-	-	1657(s)

s = strong, m = medium, sh = sharp

a, shown by deuteration studies to have some δ (C-H) character.

TABLE 3.2.

Infrared Data for Rh(I) - Acetylacetonate Complexes (cm.⁻¹)

<u>Complex</u>	<u>Ref.</u>	<u>Solution</u>	<u>Solid</u>
Rh(acac)(COD)	132	1570(s) 1512(s) ^a	1576(s) 1518(s)
Rh(acac)(CO)(PPh ₃)	129	1580(s) 1520(s) ^a	1590(s) 1570(s) 1518(s)
Rh(acac)(PPh ₃) ₂	-	1580(s) 1510(w) ^b	1578(s) 1560(s) 1507(s)

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Solid state spectra were recorded from Nujol mulls using KBr windows.

s = strong, w = weak

a. chloroform solution b. benzene solution

TABLE 3.3.

¹ H n.m.r. spectral data for metal acetylacetonate complexes

Complex Type (b)	Ref.	$\delta(\text{CH}_3)(\tau)$	$\delta(\text{C}^3\text{-H})(\tau)$
Pt(acac)Cl(PPh ₃)	127	7.99 8.54	4.63
Pt(acac)Cl(AsPh ₃)	127	7.99 8.50	4.58
Pt(acac)Cl(SbPh ₃)	127	7.96 8.35	4.52
Pt(acac)Cl(CO)	127	7.89 7.91	4.30
Type (d) Rh(acac)(C ₂ F ₄)(Ph ₂ PCH ₂ CH ₂ PPh ₂)	125	8.33 8.60	5.27
Rh(acac)(C ₂ F ₄)((CH ₃) ₂ SO) ₂	125	7.95 8.14	4.53
Rh(acac)(C ₂ F ₄)(C ₅ H ₅ N)	125	8.0 8.2	4.78
Type (e) Rh(acac)(CO) ₂	129	7.89	4.48
Ir(acac)(CO) ₂	129	8.18	4.33
Type (c) Rh(acac)(C ₂ F ₄)[P(C ₄ H ₉) ₃] ₂	125	8.22	4.93
Rh(acac)(C ₂ F ₄)(PPh ₃) ₂	125	8.32	4.62

TABLE 3.4.

¹H n.m.r. spectral data for Rh(I) Acetylacetonate complexes (τ)

Complex	Ref.	Room Temperature $\delta(\text{CH}_3)$	Room Temperature $\delta(\text{C3-H})$	-50°C $\delta(\text{CH}_3)$	-50°C $\delta(\text{C3-H})$
Rh(acac)(COD)	132	8.08(s) [6]	4.65(s) [1]	No change	No change
Rh(acac)(PPh ₃) ₂	-	Complex	4.42(s) 5.30(s)	No change	No change
Rh(acac)(CO)(PPh ₃)	132a	8.00(s) [3] 8.55(s) [3]	4.61(s) [1]	No change	No change
Rh(acac)(CO)(PPh ₃)+PPh ₃	-	8.10(s) [6]	4.50(s) [1]	7.83(s) [3] 8.30(s) [3]	4.50(s) [1]

¹H n.m.r. spectra recorded from deuteriochloroform solution.

s = singlet, relative intensities shown in [].

TABLE 3.5.

Analytical, melting point and molecular weight data

Complex	Analytical Data			Molecular Weight Found Required	Melting Point (°C)
	Found (%)	Required (%)			
	C	H	Other		
Rh(acac)(PPh ₃) ₂	67.77	5.23	8.15(P) 14.20(Rh)	571	135
[RhCl(CO)(PPh ₃) ₂]	67.84	5.14	8.54(P) 14.17(Rh)	727	200
[Rh(OAc _F)(COD)] ₂	53.18	3.66	8.14(Cl)	880	170
[Rh(OAc _F)(CO)(PPh ₃) ₂]	53.18	3.50	8.28(Cl)	858	170
[Rh(OAc _F)(CO)(PPh ₃) ₂]	37.04	3.70	17.59(F)	648	170
[Rh(OAc _F)(CO)(PPh ₃) ₂]	49.52	3.12	11.23(F)	952	170
Rh(CH ₃)I(acac)(PPh ₃) ₂	49.76	2.96	11.26(F)	1013	165
Rh(CH ₃)I(acac)(PPh ₃) ₂	57.93	4.61	16.28(I) 7.06(P)	854	200
Rh(CH ₃)Cl ₂ (CO)(PPh ₃) ₂	58.08	4.64	14.61(I) 7.06(P)	869	200
Rh(CH ₃)Cl ₂ (CO)(PPh ₃) ₂	50.21	3.62	13.82(Cl)	-	-
Rh(CH ₃)Cl ₂ (CO)(PPh ₃) ₂	49.67	3.55	14.00(Cl)	-	-

Contd...

TABLE 3.5. Contd....

Complex	Analytical Data			Molecular Weight Found Required	Melting Point (°C)
	Found (%)				
	C	H	Other		
Rh(CN) $[\text{C}_2(\text{CN})_3](\text{acac})(\text{COD})$	57.21	4.97	12.90(N)	-	200
	57.29	4.76	14.07(N)	-	
Rh(acac) $[\text{C}_2(\text{CN})_4](\text{PPh}_3)$	58.45	3.83	9.69(N)	-	>300
	58.77	3.72	9.46(N)	-	
$[\text{Rh}(\text{acac})[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)]_2$	57.98	3.66	9.19(N)	1142	180
	58.07	3.55	9.03(N)	1240	
Rh(C ₉ H ₇ F ₆ O ₂) $[\text{C}_6(\text{CF}_3)_6]$	29.58	0.87	46.88(F)	-	260
	29.65	0.82	53.65(F)	-	
Rh(acac)(HgCl ₂) ₂ (PPh ₃) ₂	36.85	2.74	10.85(Cl)	-	200
	38.80	2.94	33.10(Hg)	-	
			11.17(Cl)	-	
			31.95(Hg)	-	

TABLE 3.6.

Infrared spectral data concerning Rh(I)-Halogen bridged dimers (cm.^{-1})

Complex	Ref.	$\nu(\text{Rh-X})$ Solid State	$\nu(\text{C=O})$ Solid State	Solution
$[\text{RhCl}(\text{COD})]_2$	134	277.9 260.2	-	-
$[\text{RhCl}(\text{PPh}_3)_2]_2$	-	344(s,b)	-	-
$[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$	-	294(s) 251(m)	1977(s)	1980(s)
$[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$	134	275.7 262.1	-	-
$[\text{RhCl}(\text{SnCl}_3)_2]^{4-}$	134	288.4 271.6	-	-
$[\text{RhBr}(\text{COD})]_2$	134	194.8 184.4	-	-
$[\text{RhBr}(\text{SnBr}_3)_2]^{4-}$	134	197.5 175.8	-	-

Spectra were recorded from Nujol mulls or chloroform solution using KBr windows.

s = strong, b = broad, m = medium

TABLE 3.7.

Infrared spectral data concerning Rh(I) Trifluoroacetate complexes (cm.⁻¹)

Complex	Vas(COO)		V(C≡O)	
	Solid	Solution	Solid	Solution
[Rh(OAc _F)(COD)] ₂	1665(s)	1670(s)	-	-
[Rh(OAc _F)(PPh ₃) ₂] ₂	1685(s)	1680(s)	-	-
[Rh(OAc _F)(CO)(PPh ₃) ₂] ₂	1665(s)	1670(s)	1995(s) 1977(s)	1990(s) 1965(s)

I.r. spectra were recorded using KBr windows from Nujol mulls or chloroform solution.

s = strong.

TABLE 3.8.

Infrared spectral data for the complex Rh(acac)I(Me(PPh₃)₂)₂ (cm.⁻¹)

[ν (C=O)+ ν (C=C)]

Solid State 1581(s) 1572(m) 1512(s)

Solution 1580(s) 1515(m)

Spectra were recorded from Nujol mulls or chloroform solution using KBr windows.

s = strong, m = medium.

TABLE 3.9.

¹H n.m.r. spectral data for Rh(III)-Methyl complexes (τ)

Complex	Ref.	Rh-CH ₃ δ(CH ₃)	Rh-Acac δ(CH ₃)
Rh(acac)I(Me)(PPh ₃) ₂	-	9.13(s) [3]	8.52(s) [6] δ(C3H) 5.74(s) [1]
RhCl ₂ (Me)(CO)(PPh ₃) ₂	14	9.15	-
RhCl ₂ (Me)(CO)(PMe ₂ Ph) ₂	136	9.28	-
RhBr ₂ (Me)(CO)(PMe ₂ Ph) ₂	136	9.18	-
[Rh(C ₅ H ₅)(Me)(CO)(PMe ₂ Ph)] ₂ [BPh ₄]	24	9.18	-
RhClI(Me)(CO)(PPh ₃) ₂	27	9.15	-

The spectrum of Rh(acac)I(Me)(PPh₃)₂ was recorded from deuteriochloroform solution.

s = singlet. Relative intensities shown in [].

TABLE 3.10

Infrared and ^1H n.m.r. spectral data from $\text{MeI}+\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ reaction mixtures

I.r. data (cm.^{-1})		^1H n.m.r. data (τ)	
$\nu(\text{C}\equiv\text{O})$	$\nu(\text{C}=\text{O})$	$\delta(\text{CH}_3)$	$\delta(\text{C}^3\text{H})$
2060(s)	1700(s)	6.98 7.70 7.80	4.55 5.05
1970(s)		7.85 7.98 8.20	
		8.30 8.60 8.90	

I.r. spectra were recorded from Nujol mulls using KBr windows.

^1H n.m.r. spectra were recorded from deuteriochloroform solution.

TABLE 3.11.

Infrared and ^1H n.m.r. spectral data concerning Acyl complexes

Complex	Ref.	I.r. Spectral data (cm.^{-1}) $\nu(\text{C=O})$	$\nu(\text{C}\equiv\text{O})$	^1H n.m.r. Spectral data $\delta(\text{CH}_3)$	τ
$\text{RhCl}_2(\text{COMe})(\text{PPh}_3)_2$	14	1708 1713	-	7.42 6.74	
$\text{RhCl}_2(\text{COMe})(\text{CO})(\text{PMe}_2\text{Ph})_2$	136	1665	2090 2067	8.43	
$\text{RhBr}_2(\text{COMe})(\text{CO})(\text{PMe}_2\text{Ph})_2$	136	1650	2090 2065	8.31	
$[\text{Rh}(\text{C}_5\text{H}_5)(\text{COMe})(\text{CO})(\text{PMe}_2\text{Ph})] + [\text{PPh}_4]^+$	24	1715	2089 2066	7.58	
$[\text{Rh}(\text{C}_5\text{H}_5)(\text{COMe})(\text{CO})(\text{PMe}_2\text{Ph})] + \text{Br}^-$	24	1710 1689	2079 2061	7.48	
$\text{Rh}(\text{C}_5\text{H}_5)(\text{COMe})\text{Cl}(\text{PMe}_2\text{Ph})$	24	1668 1644	-	7.18	
$\text{Rh}(\text{C}_5\text{H}_5)(\text{COMe})\text{Br}(\text{PMe}_2\text{Ph})$	24	1665 1643	-	7.08	

TABLE 3.12.

Infrared spectral data for reactions with Acetyl Chloride (cm.^{-1})

<u>Complex</u>	<u>Ref.</u>	<u>$\nu(\text{C=O})$</u>	<u>$\nu(\text{C=O})$</u>	<u>$\nu(\text{Rh-Cl})$</u>	<u>Other</u>
<u>Product from</u> $\text{Rh}(\text{acac})(\text{PPh}_3)_2 + \text{CH}_3\text{COCl}$	--	2062(s) 1969(s)	1708(s) 1713(sh)	-	-
$\text{RhCl}_2(\text{CMe})(\text{CO})(\text{PPh}_3)_2$	--	2096(s)	1712(s)	344(m) 268(s)	315(w) 289(w)
$\text{RhCl}_2(\text{CMe})(\text{CO})(\text{PPh}_3)_2(0.5\text{CH}_2\text{Cl}_2)$	17	2086(s)	1706(s)	344(m) 264(s)	318(w) 258(m) 240(w)

-201-

I.r. spectral data were recorded from Fujol mulls using KPr (5000-400 cm.^{-1}) and polythene (400-200 cm.^{-1}) windows.

s = strong, sh = sharp, m = medium, w = weak

TABLE 3.13.

Infrared spectral data concerning Tetracyanoethylene complexes (cm.^{-1})

Complex	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}\equiv\text{O})$	Acac absorp- tions
$\text{Rh}(\text{CN})[\text{C}_2(\text{CN})_3](\text{acac})(\text{COD})$	2239(sh) 2212(s) 2148(s)	-	1739(s) 1716(s)
$\text{Rh}(\text{acac})[\text{C}_2(\text{CN})_4](\text{COD})$	2228(s) 2222(s)	-	1567(s) 1514(s)
$\text{Rh}(\text{acac})[\text{C}_2(\text{CN})_4](\text{PPh}_3)$	2248(s) 2225(sh) 2222(sh)(s) 2216(sh)(s)	-	1565(s) 1514(s)
$[\text{Rh}(\text{acac})[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)]_2$	2235(m) (2235(sh)solution)	2075(s)(sh) 2082(s) (2080(sh)(s)solution)	1568(s) 1560(s) 1510(s)

-202-

Infrared spectra were recorded from Nujol mulls or chloroform solution using KBr windows.

sh = sharp, s = strong

TABLE 3.14.

¹H n.m.r. spectral data concerning $[\text{Rh}(\text{acac})[\text{C}_2(\text{CN})_2](\text{CO})(\text{PPh}_3)]_2$ (τ)

$\delta(\text{CH}_3)$	$\delta(\text{C}_3\text{H})$	$\delta(\text{C}_6\text{H}_5)$
8.25(s)[3]	4.95(s)[1]	~2.5 complex [15]

¹H n.m.r. spectrum was recorded from deuteriochloroform solution.
Relative intensities shown in []. s = singlet

TABLE 3.15.

I.r. spectral data concerning products from reactions with hexafluorobut -2- yne (cm.⁻¹)

Complex	$\nu(\text{C}=\text{C})$	lowered $\nu(\text{C}\equiv\text{C})$	$\nu(\text{C}=\text{O})$	$[\nu(\text{C}=\text{O}) + \nu(\text{C}=\text{O})]$
$\text{Rh}(\text{C}_9\text{H}_7\text{F}_6\text{O}_2)[\text{C}(\text{CF}_3)_6]$	1598(m) 1643(m)	--	1695(s) 1667(w)	--
$\text{Rh}(\text{acac})(\text{C}_4\text{F}_6)(\text{PPh}_3)_2$	--	1664(m)	--	1585(s) 1510(s)

TABLE 3.16.

¹⁹F n.m.r. data concerning products from reactions with hexafluorobut -2- yne (p.p.m. relative to benzotrifluoride.)

Complex	Chemical Shift (ppm)	Assignment
Rh(C ₉ H ₇ F ₆ O ₂)[C ₆ (CF ₃) ₆]	-6.31(3)	broad and poorly resolved
	-5.25(2)	Complex splitting.
	-2.42(2)	Complex splitting
	-1.70(1)	Quartet J(CF ₃ -CF ₃) = 8c.p.s.
Rh(acac)(C ₄ F ₆)(PPh ₃) ₂	-10.22	broad singlet
	-7.92	broad singlet

¹H n.m.r. data concerning products from reactions with hexafluorobut -2- yne

Complex	Chemical Shift (ppm)	Assignment
Rh(acac)(C ₄ F ₆)(PPh ₃) ₂	8.00(3)	singlet
	8.75(3)	singlet
	4.75(1)	singlet
	~2.5(30)	complex

¹⁹F n.m.r. spectral data were recorded from diethyl ether solution.

¹H n.m.r. spectral data were recorded from deuteriochloroform solution. Relative intensities shown in brackets ().

EXPERIMENTAL

Analytical, melting point and molecular weight data are shown in Table 3.5. and in this section. Melting points are uncorrected and were recorded on a Reichert hot-stage apparatus. ^1H n.m.r. spectra were recorded on a Varian Associates Spectrometer at 60MC/S. ^{19}F n.m.r. spectra were recorded on a Varian Associates DA60 Spectrometer at 56.4 MC/S. Results are shown in Tables 3.4, 3.9, 3.10, 3.14, & 3.16. I.r. spectra were recorded from Nujol mulls or chloroform solution (unless otherwise stated) on a Perkin-Elmer 225 Spectrophotometer, using KBr(5000-400 cm.^{-1}) and polythene (400-200 cm.^{-1}) windows. Results are shown in Tables 3.2, 3.7, 3.8, 3.10, 3.12,

AnalaR benzene and AnalaR diethyl ether were dried over sodium wire before use. Other solvents used were of reagent grade unless otherwise stated. Light petroleum b.p. 40-60°C was used throughout. All reaction solvents were saturated with nitrogen before use and all reactions were carried out in an atmosphere of nitrogen.

Triphenylphosphine was supplied by Albright and Wilson Ltd., and recrystallised from ethanol before use. Methyl-iodide was supplied by B.D.H. Ltd. and redistilled under nitrogen and stored at 0°C before use. Acetylchloride was supplied by B.D.H. Ltd. and redistilled under nitrogen in anhydrous conditions directly into reaction mixtures. Tetrachloroethylene was supplied by B.D.H. Ltd. and

redistilled under nitrogen and stored over molecular sieves before use. Tetrafluoroethylene was prepared by thermal decomposition of polytetrafluoroethylene (supplied by I.C.I. Ltd.) under vacuum in a silica tube. Tetracyanoethylene, cycloocta 1,5 - diene diphenylacetylene, trifluoroacetic acid and acetic acid were supplied by Koch Light Chemicals Ltd. and used without further purification. Hexafluorobut -2-yne was supplied by Cambrian Chemicals Ltd. Rhodium salts were obtained on loan from Johnson Matthey Ltd.

Preparation of Starting Materials:

The complex $\text{Rh}(\text{acac})(\text{COD})$ was prepared by the literature method ¹²⁸.

Preparation of acetylacetonato bis(triphenylphosphine) rhodium(I):

To a solution $\text{Rh}(\text{acac})(\text{COD})$ (0.50g.) in diethyl ether (20ml.) was added triphenylphosphine (0.85g.). The yellow solution turned dark red and on gentle reflux for 10 minutes bright orange crystals of the complex acetylacetonato bis(triphenylphosphine)rhodium(I) were deposited. The crystals were filtered off, washed with diethyl ether and air dried. (Found: C, 67.77; H, 5.23; P, 8.15; Rh, 14.20; $\text{C}_{41}\text{H}_{37}\text{O}_2\text{P}_2\text{Rh}$ requires C, 67.84; H, 5.14; P, 8.54; Rh, 14.17%) Yield 100% (1.17g.) m.p. 135°C decomp. The complex decomposes rapidly in undegassed solvents and no satisfactory procedure for recrystallisation, even under nitrogen could be devised.

Providing starting materials are pure, the product obtained is analytically pure.

Preparation of acetylacetonato(carbonyl)(triphenylphosphine)rhodium(I)

Carbon monoxide was bubbled through a stirred suspension of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ (0.50g.) in diethyl ether (30ml.) for 10 minutes. A suspension of yellow crystals is obtained. Evaporation of this suspension to half volume under reduced pressure and addition of light petroleum (10ml.) ensures complete precipitation of the complex. The yellow crystalline precipitate was filtered off, washed with light petroleum, air dried and identified as acetylacetonato carbonyl(triphenylphosphine)rhodium(I) from the m.p. and i.r. spectrum which were both identical to those of an authentic sample.. Yield 100% (0.34g.) m.p. 175°C decomp.

REACTIONS OF ACETYLACETONATO CYCLOOCTA -1,5 - DIENE RHODIUM(I)

1. Reaction of $\text{Rh}(\text{acac})(\text{COD})$ with hydrogen chloride:

Dry hydrogen chloride was bubbled through a solution of $\text{Rh}(\text{acac})(\text{COD})$ (0.20g.) in diethyl ether (10ml.) for 1 minute. The yellow solution became orange and on cooling to -78°C an orange solid was deposited. This was filtered off, washed with light petroleum, air dried and identified as bis(cycloocta 1,5 - diene) $-\mu\mu'$ - dichloro-dirhodium(I) from the m.p. and i.r. spectrum which

were both identical to those of an authentic sample.

Yield 94.3% (0.15g.) m.p. 256°C decomp.

2. Reaction of Rh(acac)(COD) with acetic acid:

To a solution of Rh(acac)(COD) (0.20g.) in acetone (20ml.) was added glacial acetic acid (0.1ml.). The mixture was refluxed overnight. No colour change occurred and on evaporation to dryness under reduced pressure the starting material was recovered quantitatively.

3. Reaction of Rh(acac)(COD) with trifluoroacetic acid:

Preparation of bis(cycloocta 1,5 - diene) - μ 'bis (trifluoroacetato)dirhodium(I)

To a solution of Rh(acac)(COD) (0.20g.) in acetone (20ml.) was added trifluoroacetic acid (0.1ml.) The reaction mixture was refluxed overnight and became orange in colour. The orange solution was evaporated to dryness to give an orange oil which was taken up in ethyl acetate (10ml.). Addition of light petroleum (10ml.) and storage at 0°C for two days gave orange crystals of the complex. These were filtered off, washed with light petroleum and air dried. (Found: C, 37.18; H, 3.76; F, 17.56; M(CHCl₃), 619; C₁₀H₁₂F₃O₂Rh requires C, 37.04; H, 3.70; F, 17.59%; M, 324) Yield 50% (0.10g.) m.p. 170°C decomp.

4. Reaction of Rh(acac)(COD) with methyl iodide:

i) To a solution of Rh(acac)(COD) (0.20g.) in either diethyl ether or light petroleum (30ml.) was added methyl iodide (1ml.). The mixture was refluxed overnight.

There was no colour change and on evaporation to dryness under reduced pressure starting material was recovered quantitatively.

ii) To a solution of Rh(acac)(COD) (0.20g.) in methanol (30ml.) was added methyl iodide (1ml.) The mixture was maintained at 40°C for 2 hours. A red-brown solution was formed from which was deposited a black precipitate and brown crystals. The solution was filtered and the brown crystals recrystallised from benzene to give brick red crystals of the complex bis(cycloocta 1,5 - diene) - $\mu\mu'$ -diodo dirhodium(I) identified from the m.p. and i.r. spectrum which were both identical to those of an authentic sample. Yield 46% (0.1g.) m.p. decomposes 180-200°C.

iii) To a solution of Rh(acac)(COD) (0.20g.) in carbon tetrachloride (30ml.) was added methyl iodide (1ml.). No reaction occurred at room temperature and on gentle reflux a dark brown solution was formed from which no pure complexes could be isolated.

5. Reaction of Rh(acac)(COD) with acetyl chloride:

A few drops of acetyl chloride were distilled into a flask containing a solution of Rh(acac)(COD) (0.20g.) in diethyl ether (30ml.). Gentle reflux overnight gave rise to an orange solution which on evaporation to half volume under reduced pressure and the addition of light petroleum (20ml.) deposited an orange crystalline solid. This was identified as bis(cycloocta 1,5 - diene) - $\mu\mu'$ -dichloro dirhodium(I) from the m.p. and i.r. spectrum

which were identical to those of an authentic sample.

Yield 71% (0.17g.) m.p. 256°C decomp.

6. Reaction of Rh(acac)(COD) with diphenyl acetylene:

To a solution of Rh(acac)(COD) (0.20g.) in diethyl ether (30ml.) was added diphenyl acetylene (0.46g.). The mixture was refluxed overnight. No colour change occurred and on evaporation to dryness a mixture of diphenyl acetylene and Rh(acac)(COD) was obtained.

7. Reaction of Rh(acac)(COD) with hexafluorobut - 2- yne:

Preparation of Rh(C₉H₇F₆O₂) [C₆(CF₃)₆]

i) Hexafluoro -2- yne (1ml.) was condensed onto a solution of Rh(acac)(COD) (0.50g.) in benzene (15ml.) contained in a Carius tube. The mixture was warmed to room temperature and within 10 minutes the reaction mixture darkened to give a red solution plus yellow crystals. The mixture was kept at room temperature overnight. The crystals were filtered off, washed with benzene and recrystallised for analysis from a dichloromethane - light petroleum mixture. (Found: C, 29.58; H, 0.87; F, 46.88; C₂₁H₇F₂₄O₂Rh requires C, 29.65; H, 0.82; F, 53.65%). Yield 48% (0.66g.) m.p. 260°C decomp.

ii) Hexafluorobut -2- yne (1ml.) was condensed onto a solution of Rh(acac)(COD) (0.50g.) in diethyl ether (20ml.) contained in a Carius tube. The mixture was maintained at 65°C overnight. Evaporation of the solution to half volume under reduced pressure followed by addition of light petroleum (20ml.) gave yellow crystals

of the complex. Yield 62% (0.85g.)

8. Reaction of Rh(acac)(COD) with tetrachloroethylene:

To a solution of Rh(acac)(COD) (0.20g.) in diethyl ether (30ml.) was added tetrachloroethylene (1ml.). The mixture was refluxed overnight. No colour change was observed, and on evaporation to dryness under reduced pressure starting material was recovered quantitatively.

9. Reaction of Rh(acac)(COD) with tetracyanoethylene:

i) Preparation of acetylacetonato(tetracyanoethylene) (cycloocta 1,5 - diene)rhodium(III):

To a solution of Rh(acac)(COD) (0.20g.) in light petroleum (15ml.) was added tetracyanoethylene (0.082g.). The mixture was shaken vigorously for 30 minutes. The resultant orange crystalline precipitate was filtered off, washed with light petroleum and air dried. Consistent analytical data could not be obtained. Yield 35% (0.10g.) m.p. decomposes at 110°C.

ii) Preparation of acetylacetonato(tricyanovinyl) cyano(cycloocta 1,5 - diene)rhodium(III):

To a solution of Rh(acac)(COD) (0.20g.) in acetone (15ml.) was added tetracyanoethylene (0.082g.). The solution darkened and on addition of light petroleum (1ml.) a precipitate of fine cream coloured crystals was formed. This was filtered off and washed with acetone. (Found: C, 57.21; H, 4.97; N, 12.90; $C_{19}H_{17}N_4O_2Rh$ requires

C, 57.29;H, 4.76;N, 14.07% Yield 71% (0.20g.) m.p. 140°C darkens, 200°C decomp.

10. Reaction of Rh(acac)(COD) with tetrafluoroethylene:

Tetrafluoroethylene (2ml.) was condensed onto a solution of Rh(acac)(COD) (0.50g.) in diethyl ether (20ml.) contained in a Carius tube. The mixture was maintained at 100°C for 3 hours and then vigorously shaken. The resultant brown precipitate was then filtered off, washed with light petroleum and dried under vacuum at 56°C. Consistent analytical data could not be obtained; the brown powder was hygroscopic and decomposed in solution. Yield 0.25g.

11. Reaction of Rh(acac)(COD) with carbon monoxide:

Carbon monoxide was bubbled through a solution of Rh(acac)(COD) (0.20g.) in light petroleum (20ml.) for 5 minutes; a slight darkening of the solution was observed. Evaporation to a small volume under reduced pressure and cooling to 0°C led to the deposition of crystals of the known complex acetylacetonato dicarbonyl rhodium(I); identified by the m.p. and i.r. spectrum which were both identical to those of an authentic sample. Yield 95% (0.16g.) m.p. 155°C decomp.

12. Reaction of Rh(acac)(COD) with mercuric chloride:

A solution of Rh(acac)(COD) (0.40g.) in chloroform (20ml.) was added dropwise to a stirred solution of mercuric chloride (5.00g.) in acetone (20ml.). A red crystalline precipitate was formed. This was filtered

off, washed with a 1:1 mixture of acetone and chloroform, and identified as bis(cycloocta -1:5- diene)- $\mu\mu'$ dichlorodirrhodium(I)bis(mercuric chloride). from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 67% (0.45g.) m.p. 105°C decomp.

REACTIONS OF ACETYLACETONATO BIS(TRIPHENYLPHOSPHINE) RHODIUM(I):

1. Reaction of Rh(acac)(PPh₃)₂ with hydrogen chloride:

Dry hydrogen chloride was bubbled through a stirred suspension of Rh(acac)(PPh₃)₂ (0.50g.) in diethyl ether (30ml.) for 30 minutes. The resultant pink precipitate was filtered off, washed with diethyl ether, air dried and identified as tetrakis(triphenylphosphine)- $\mu\mu'$ -dichloro dirrhodium(I) from the i.r. spectrum and the reactions in chloroform with the bridge splitting reagents carbon monoxide and triphenylphosphine (see below). Yield 85% (0.39g.) m.p. decomposes ~200°C.

2. Reaction of [RhCl(PPh₃)₂]₂ with triphenylphosphine:

To a solution of [RhCl(PPh₃)₂]₂ (0.20g.) in chloroform (20ml.) was added triphenylphosphine (0.08g.). The mixture was refluxed for 2 hours. The resultant deep red crystalline solid was filtered off, washed with petroleum, air dried and identified as chloro tris(triphenylphosphine)rhodium(I) from the m.p. and

i.r. spectrum which were identical to those of an authentic sample. Yield 90% (0.25g.) m.p.

3. Reaction of $[\text{RhCl}(\text{PPh}_3)_2]_2$ with carbon monoxide:

Carbon monoxide was bubbled through a solution of $[\text{RhCl}(\text{PPh}_3)_2]_2$ (0.20g.) in chloroform (20ml.) for 5 minutes. The solution became yellow immediately. Evaporation to half volume under reduced pressure followed by addition of light petroleum (20ml.) led to the deposition of yellow crystals. These were filtered off, washed with light petroleum, air dried and identified as trans - chloro carbonyl bis(triphenylphosphine)rhodium (I) from the m.p. and i.r. spectrum which were both identical to those of an authentic sample. Yield 90% (0.19g.) m.p. 195-197°C decomp.

4. Reaction of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ with acetic acid:

To a suspension of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ (0.20g.) in diethyl ether (30ml.) was added glacial acetic acid (0.1ml.). The mixture was refluxed overnight. No colour change was observed and on filtration starting material was recovered quantitatively.

5. Reaction of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ with trifluoroacetic acid:

Preparation of tetrakis(triphenylphosphine)-bis(trifluoroacetato)dirhodium(I):

To a suspension of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ (0.50g.) in diethyl ether (30ml.) was added trifluoroacetic acid (0.1ml.). The mixture was refluxed overnight. The resulting suspension was filtered, the filtrate being

retained, and the orange crystalline solid identified as starting material from the m.p. and i.r. spectrum. Yield 60% (0.30g.). The brown coloured filtrate was evaporated to half volume under reduced pressure, light petroleum (20ml.) was added and mixture shaken vigorously to coagulate the resultant light brown precipitate. This was filtered off, washed with light petroleum and air dried. The complex may be reprecipitated from diethyl ether solution with light petroleum but could not be obtained analytically pure. Yield 19% (0.10g.) m m.p. 155-170°C decomp.

6. Reaction of Rh(acac)(PPh₃)₂ with methyl iodide:

Preparation of acetylacetonato(methyl)(iodo)bis(tri-phenylphosphine)rhodium(III):

To a suspension of Rh(acac)(PPh₃)₂ (0.50g.) in diethyl ether (30ml.) was added methyl iodide (1ml.). The mixture was refluxed for 3 hours. A brick red crystalline precipitate was formed. This was filtered off, washed with diethyl ether, air dried and recrystallised for analysis from a dichloromethane - diethyl ether mixture. (Found: C, 57.93;H, 4.61;I, 16.28; P, 7.06;Rh, 11.68;M(CHCl₃), 854;C₄₄H₄₀IO₂P₂Rh requires: C, 58.08;H, 4.64;I, 14.61;P, 7.06;Rh, 11.84%) Yield 100% (0.60g.) m.p. 165°C decomp.

7. Reaction of Rh(acac)(PPh₃)₂ with acetyl chloride:

A few drops of acetyl chloride were distilled into a flask containing a suspension of Rh(acac)(PPh₃)₂

(0.50g.) in diethyl ether (30ml.). Gentle reflux for 3 hours gave a pale cream precipitate. This was filtered off, washed with diethyl ether, air dried and shown to be a mixture of the known complexes dichloro(acetyl)¹⁴ bis(triphenylphosphine)rhodium(III) and dichloro(methyl)(carbonyl)bis(triphenylphosphine)rhodium(III) from the i.r. spectrum. Attempts to obtain pure complexes from the mixture were unsuccessful. Yield 0.60g.

8. Reaction of Rh(acac)(PPh₃)₂ with diphenyl acetylene:

To a solution of Rh(acac)(PPh₃)₂ (0.20g.) in diethyl ether (30ml.) was added diphenyl acetylene (0.20g.). The mixture was refluxed overnight. No colour change occurred and filtration of the reaction mixture led to quantitative recovery of starting material identified by m.p. and i.r. spectrum.

9. Reaction of Rh(acac)(PPh₃)₂ with hexafluorobut -2- yne:

Preparation of acetylacetonato(hexafluorobut -2- yne)bis(triphenylphosphine)rhodium(III):

Hexafluorobut -2- yne (1ml.) was condensed onto a suspension of Rh(acac)(PPh₃)₂ (0.50g.) in diethyl ether (15ml.) contained in a Carius tube. The mixture was warmed to room temperature and shaken vigorously overnight to give an orange solution. Evaporation to half volume under reduced pressure, addition of light petroleum gave rise to a pale yellow precipitate. This was filtered off, washed with light petroleum and air

dried. The complex could not be obtained analytically pure and exhibited a tendency to revert to an oil.

Yield 48 % (0.30g.)

10. Reaction of Rh(acac)(PPh₃)₂ with tetrachloroethylene:

To a suspension of Rh(acac)(PPh₃)₂ (0.30g.) was added tetrachloroethylene (1ml.). The mixture was refluxed overnight. No colour change was observed in filtration of the resulting suspension led to total recovery of starting material identified by the m.p. and i.r. spectrum.

11. Reaction of Rh(acac)(PPh₃)₂ with tetracyanoethylene:

Preparation of acetylacetonato(tetracyanoethylene)(triphenylphosphine)rhodium(III):

To a suspension of Rh(acac)(PPh₃)₂ (0.80g.) in diethyl ether (30ml.) was added tetracyanoethylene (0.50g.). The mixture was refluxed gently for 2 hours to give a brown crystalline precipitate. This was filtered off, washed with diethyl ether, air dried and shaken with acetone (20ml.) to give a yellow crystalline powder and a brown solution. The yellow powder was filtered off, washed with acetone and air dried. (Found: C, 58.45; H, 3.83; N, 9.69; C₂₉H₂₂N₄O₂P₂Rh requires C, 58.77; H, 3.72; N, 9.46%) Yield 15% (0.10g.) m.p. 300°C. No pure complexes could be obtained from the brown filtrate.

12. Reaction of Rh(acac)(PPh₃)₂ with tetrafluoroethylene:

i) Tetrafluoroethylene (2ml.) was condensed onto a suspension of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ (0.50g.) in diethyl ether (20ml.) contained in a Carius tube. The mixture was kept at 56°C overnight. The resulting yellow solution was evaporated to half volume under reduced pressure and cooled to -78°C whereupon a pale yellow precipitate was formed. This was filtered off, washed with diethyl ether at -78°C and identified as acetylacetonato (tetrafluoroethylene)bis(triphenylphosphine)rhodium(III) from the m.p. and i.r. spectrum which were both identical to those of an authentic sample. Yield 88% (0.50g.) m.p. $148-149^\circ\text{C}$ decomp.

ii) Tetrafluoroethylene (2ml.) was condensed onto a suspension of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ (0.50g.) in diethyl ether (20ml.) contained in a Carius tube and the mixture was maintained at 100°C overnight. The resulting yellow solution was evaporated to half volume under reduced pressure and on addition of light petroleum (15ml.) yellow crystals were deposited. These were filtered off, washed with light petroleum, air dried and identified as acetylacetonato carbonyl triphenylphosphine rhodium(I) from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 80% (0.27g.) m.p. 175°C decomp.

13. Reaction of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ with mercuric chloride:
Preparation of acetylacetonato bis(triphenylphosphine)
rhodium(I)bis(mercuric chloride):

To a suspension of $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ (0.50g.) in diethyl ether (30ml.) was added a solution of mercuric chloride (0.375g.) in acetone (2ml.). The mixture was refluxed gently for 2 hours and the resultant orange precipitate filtered off, washed with diethyl ether and air dried. (Found: C, 36.85; H, 2.74; Cl, 10.85; Hg, 33.1; Rh, 8.30; $\text{C}_{41}\text{H}_{37}\text{Cl}_4\text{Hg}_2\text{O}_2\text{P}_2\text{Rh}$ requires C, 38.80; H, 2.94; Cl, 11.17; Hg, 3.95, Rh, 8.11%) Yield 84% (0.73g.) m.p. 200°C decomp.

REACTIONS OF ACETYLACETONATO(CARBONYL)(TRIPHENYLPHOSPHINE)RHODIUM(I)

1. Reaction of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ with hydrogen chloride:

Preparation of di- $\mu\mu'$ -chloro dicarbonyl bis(triphenylphosphine)dirhodium(I):

Dry hydrogen chloride was bubbled through a stirred solution of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ (0.50g.) in diethyl ether (30ml.) for 5 minutes. The resulting crystalline orange precipitate was filtered off, washed with diethyl ether, and air dried. (Found: C, 53.18; H, 3.66; Cl, 8.14; $\text{M}(\text{CHCl}_3)$, 880; $\text{C}_{19}\text{H}_{15}\text{ClO}_2\text{PRh}_2$ requires C, 53.18; H, 3.50; Cl, 8.28%, M, 858) Yield 92% (0.40g.) m.p. darkens 190°C , 200°C decomp.

2. Reaction of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ with acetic acid:

To a solution of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ (0.20g.) in

diethyl ether (25ml.) was added glacial acetic acid (0.1ml.). The mixture was refluxed overnight. No colour change was observed. Evaporation to half volume under reduced pressure followed by the addition of light petroleum (15ml.) led to the deposition of yellow crystals. These were filtered off, washed with light petroleum, air dried and identified as starting material from the m.p. and i.r. spectrum. The recovery of starting material was quantitative.

3. Reaction of Rh(acac)(CO)(PPh₃) with trifluoroacetic acid:

Preparation of bis- $\mu\mu'$ -trifluoroacetato dicarbonyl bis(triphenylphosphine)dirhodium(I):

To a solution of Rh(acac)(CO)(PPh₃) (0.45g.) in diethyl ether (30ml.) was added trifluoroacetic acid (0.1ml.). The mixture was refluxed overnight and the resulting red solution was evaporated to half volume under reduced pressure. Addition of light petroleum (15ml.) and storage at 0°C led to the deposition of a red crystalline solid. This was filtered off, washed with light petroleum and air dried. (Found: C, 49.52; H, 3.12; F, 11.23; M(CHCl₃), 952; C₂₁H₁₅F₃O₃PRh₂ requires C, 49.76; H, 2.96; F, 11.26%; M, 1013) Yield 86% (0.40g.) m.p. 170°C decomp.

4. Reaction of Rh(acac)(CO)(PPh₃) with methyl iodide:

To a solution of Rh(acac)(CO)(PPh₃)₂ (0.40g.) in

diethyl ether (30ml.) was added methyl iodide (1.0ml.). The mixture was refluxed overnight and became dark brown in colour. Addition of light petroleum (15ml.) to the reaction mixture precipitates a brown solid which is seen from the i.r. and ^1H n.m.r. spectra to contain Rh(III) alkyl and acyl complexes. However no pure complexes could be isolated from the reaction mixture.

5. Reaction of Rh(acac)(CO)(PPh₃) with acetyl chloride:
Preparation of acetyl dichloro(carbonyl)(triphenylphosphine)rhodium(III):

A few drops of acetyl chloride were distilled into a flask containing a solution of Rh(acac)(CO)(PPh₃) (0.50g.) in diethyl ether (30ml.). Gentle reflux for 3 hours gave a cream coloured precipitate which was filtered off, washed with diethyl ether and air dried. (Found: C, 50.21; H, 3.62; Cl, 13.82; C₂₁H₁₈Cl₂O₂PRh requires C, 49.67; H, 3.55; Cl, 14.00%) Yield 80% (0.41g.) m.p. 150°C darkens, 200°C decomp.

6. Reaction of Rh(acac)(CO)(PPh₃) with diphenyl acetylene:

To a solution of Rh(acac)(CO)(PPh₃) (0.20g.) in diethyl ether (30ml.) was added diphenyl acetylene (0.20g.). The mixture was refluxed overnight. No colour change was observed. Evaporation to half volume under reduced pressure followed by addition of light petroleum (20ml.) led to the deposition of yellow crystals which were filtered off, washed with light

petroleum, air dried and identified as starting material from the m.p. and i.r. spectrum. The recovery of starting material was quantitative.

7. Reaction of Rh(acac)(CO)(PPh₃) with hexafluorobut -2- yne:

Hexafluorobut -2- yne (2ml.) was condensed onto a solution of Rh(acac)(CO)(PPh₃) (0.50g.) in diethyl ether (20ml.) contained in a Carius tube. The mixture was shaken vigorously overnight at room temperature to give a bright orange solution. Evaporation to dryness under reduced pressure yielded an intractible oil.

8. Reaction of Rh(acac)(CO)(PPh₃) with tetrachloroethylene:

To a solution of Rh(acac)(CO)(PPh₃) in diethyl ether (30ml.) was added tetrachloroethylene (1ml.). The mixture was refluxed overnight. No colour change was observed. Evaporation to half volume under reduced pressure followed by the addition of light petroleum (20ml.) led to the deposition of yellow crystals which were filtered off, washed with light petroleum, air dried and identified as starting material from the m.p. and i.r. spectrum. The recovery of starting material was quantitative.

9. Reaction of Rh(acac)(CO)(PPh₃) with tetracyanoethylene:

Preparation of acetylacetonato(tetracyanoethylene)
(carbonyl)(triphenylphosphine)rhodium(III) -dimer:

To a solution of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ (0.40g.) in benzene (30ml.) was added tetracyanoethylene (0.11g.). The mixture was left at room temperature overnight. Evaporation to half volume under reduced pressure followed by the addition of light petroleum (15ml.) led to the deposition of a green crystalline solid which was filtered off, washed with light petroleum, air dried and recrystallised thrice from dichloromethane - light petroleum mixtures to give a yellow crystalline solid. (Found: C, 57.98;H, 3.66;N, 9.19;M(CHCl_3), 1142; $\text{C}_{30}\text{H}_{22}\text{N}_4\text{O}_3\text{PRh}_2$ requires C, 58.07;H, 3.55;N, 9.03%, M 1240) Yield 79% m.p.140°C darkens, 180°C decomp.

REACTIONS OF DI- $\mu\mu'$ -CHLORO DICARBONYL BIS(TRIPHENYL-
PHOSPHINE)DIRHODIUM(I):

1. Reaction of $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$ with acetyl chloride:

Preparation of acetyl dichloro(carbonyl)(triphenyl-
phosphine)rhodium(III):

A few drops of acetyl chloride were distilled into a flask containing a suspension of $[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$ (0.40g.) in diethyl ether (30ml.). The mixture was refluxed gently for 2 hours. The resultant cream precipitate was filtered off, washed with diethyl ether and air dried. (Found: C, 49.42;H, 3.50;Cl, 13.26;

$C_{21}H_{18}Cl_2O_2PRh$ requires C, 49.67; H, 3.55; Cl, 14.00

Yield 80% (0.38g.) m.p. $150^{\circ}C$ darkens, $200^{\circ}C$ decomp.

2. Reaction of $[RhCl(CO)(PPh_3)]_2$ with triphenylphosphine:

To a solution of $[RhCl(CO)(PPh_3)]_2$ (0.30g.) in chloroform (25ml.) was added triphenylphosphine (0.20g.). The mixture was stirred at room temperature for 1 minute. The resulting yellow solution was evaporated to half volume under reduced pressure and ethanol (15ml.) was added. The resultant yellow crystalline precipitate was filtered off, washed with ethanol, air dried and identified as trans - chlorocarbonyl bis(triphenylphosphine)rhodium(I) from the m.p. and i.r. spectrum which were identical to those of an authentic sample. Yield 100% (0.41g.) m.p. $195-197^{\circ}C$ decomp.

3. Reaction of $[RhCl(CO)(PPh_3)]_2$ with carbon monoxide:

Carbon monoxide was bubbled through a solution of $[RhCl(CO)(PPh_3)]_2$ (0.30g.) in benzene (25ml.) for 5 minutes. The resulting orange solution was evaporated to half volume under reduced pressure and light petroleum (15ml.) added. The resultant orange crystalline precipitate was filtered off, washed with light petroleum, air dried and identified as trans - chloro dicarbonyl(triphenylphosphine)rhodium(I) from the i.r. spectrum which was identical to that of an authentic sample. Yield 100% (0.32g.).

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