THE REACTIVITY OF SOME
\( \pi \)-BONDED KETONE AND
OLEFIN COMPLEXES OF
PLATINUM

A thesis presented for the
Degree of Doctor of Philosophy
in the
Faculty of Science
by
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STATEMENT

The experimental work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester, between October 1970 and September 1973, under the supervision of Dr. R.D.W. Kemmitt. The work has not been, and is not concurrently being presented for any other degree.

M.M. Hunt

ACKNOWLEDGEMENTS

I wish to acknowledge with particular thanks the help and guidance of Dr. R.D.W. Kemmitt without whose enthusiasm and encouragement this project could not have been achieved.

To Dr. J. Burgess I am very grateful for invaluable discussion and guidance during the kinetics project.

I am also grateful to Mrs. Sheila Davis for patiently running many n.m.r. spectra, and Mrs. Barbara Hamner for typing the manuscript.
To Sylvia, Sonia and Kate

who were very patient.
SUMMARY

The introduction to the first chapter contains a review of the complexes formed during the reactions of hexafluoroacetone and related electrophilic molecules with low-valent metal complexes of the Group VIII transition metals. The reactivity of the complexes is described. The remainder of the chapter is concerned with the preparation of some π-bonded ketone complexes of platinum of general formula $L_2Pt(ketone)$ ($L = triphenylphosphine, triphenylarsine$). The reactions of the ketone complexes with oxygen and a series of electrophilic unsaturated molecules demonstrates that the complexes are more reactive towards ring expansion than the corresponding hexafluoroacetone platinum complex. Reactions of the ketones with peroxobis(triphenylphosphine)platinum are described.

Also included in this chapter are the reactions of isatin and benzoyl cyanide with zero-valent platinum complexes.

The introduction to the second chapter contains a brief review of olefin to vinyl isomerisation reactions of platinum olefin complexes and a description of results obtained during kinetic studies of such reactions. The second part of the chapter contains results obtained from a kinetic study of the vinyl isomerisation of the olefin complex bromotrifluoroethylenebis(triphenylarsine)-platinum to bromo(trifluorovinyl)bis(triphenylarsine)platinum(II).
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CHAPTER ONE
1.1. Introduction

Complexes of the Group VIII transition metals containing \( \pi \)-bonded ketone and related molecules and their reactivity.

Since the discovery that hexafluoroacetone can co-ordinate to zero-valent platinum via its \( \pi \)-\( \pi \) orbitals\(^1\) a number of analogous molecules, e.g. hexafluoroacetone, \((\text{CF}_3)_2\text{CO}\); 1,3-dichlorotetrafluoroacetone, \((\text{CF}_2\text{Cl})_2\text{CO}\); trifluoroacetylcyanoide, \(\text{CF}_3\text{COCN}\); hexafluoroisopropylideneamine, \((\text{CF}_3)_2\text{CNH}\); N-methylhexafluoroisopropylideneamine, \((\text{CF}_3)_2\text{CNMe}\); and trifluoroacetonitrile, \(\text{CF}_3\text{CN}\) have all been shown to co-ordinate in a similar way to low-valent complexes of the Group VIII metals.

The presence of highly electron withdrawing groups in these molecules reduces the electron density at the unsaturated centre and hence enhances their reactivity towards the excess electron density present in a low-valent metal complex. In this way the molecules are analogous to fluoro-olefins and acetylenes.

The reactions of this type of molecule generally involve the formation of three membered ring systems analogous to the metallacyclopropane ring systems formed by fluoro-olefins and as such the interaction of, say, hexafluoroacetone with tetrakis(triphenylphosphine)platinum(0) to give \((\text{PPh}_3)_2\text{PtC}(\text{CF}_3)_2\text{O}\) may be regarded as an oxidative-elimination type reaction.

A general reaction of the three membered ring systems is ring expansion to five membered rings in the presence of
an electron deficient unsaturated system, i.e.

\[
\begin{align*}
\text{M} & \quad \text{C} \quad \text{O} \\
\text{O} & \quad \text{C} \quad \text{M} \\
\text{C} & \quad \text{O} \\
\text{M} & \quad \text{C} \quad \text{O} \\
\end{align*}
\]

The ability of this type of reaction to proceed appears to be very dependent on the electron density on the metallacyclopropane type system and hence on the ligands bonded to the metal and the molecule forming the metallacyclopropane type system.

In this account reactions of metal complexes of each triad with the type of organic systems described and the reactivity of complexes formed will be reviewed.

**Iron, Ruthenium, Osmium.**

Specific zero-valent complexes of all three metals have been shown to undergo oxidative-elimination type reactions with hexafluoroacetone to give three membered ring systems.

Tricarbonyltetramethylcyclobutadieneiron, in hexane on irradiation with u.v. light, in the presence of hexafluoroacetone, has been shown to give a mixture of three isomers\(^2\), (Ia), (Ib), (Ic).

![Structural diagrams](image-url)
This mixture of isomers reacts with trimethylphosphite to produce (II) in which hexafluoroacetone has added across the iron-cyclobutadiene bond.\(^3\)

\[
\text{(II) } (L = \text{P(OMe)}_3)
\]

trans-(CO)\(_3\)L\(_2\)Ru (L=EtC(CH\(_2\)O)\(_3\)P or PhPMe\(_2\)) undergoes a thermal reaction with hexafluoroacetone to give a three membered ring system, RuC(CF\(_3\))\(_2\)O(CO)\(_2\)L\(_2\), the ligands L being in the trans configuration when L=PhPMe\(_2\)\(^4\) and in the cis configuration when L=EtC(CH\(_2\)O)\(_3\)P\(^5\). It is of interest to note that hexafluoroacetone does not react with trans-(CO)\(_3\)(PPh\(_3\))\(_2\)Ru. Similarly trans-(CO)\(_3\)(PhPMe\(_2\))\(_2\)Os reacts with hexafluoroacetone\(^6\) to give the three membered ring system OsC(CF\(_3\))\(_2\)O(CO)\(_2\)(PhPMe\(_2\)) in which the phosphine ligands are in a cis configuration.

Hexafluoroacetone reacts with tricarbonylcyclo-octatetraeneruthenium to give a 1:1 adduct\(^7\), but from the n.m.r. data this has been formulated as (III), a 1,2-addition product of hexafluoroacetone with the cyclo-octatetraene ring system.
Cobalt, Rhodium, Iridium

No cobalt complexes containing hexafluoroacetone metallacyclopropane type ring systems have been reported but d⁸ complexes of rhodium and iridium undergo oxidative-addition and oxidative-elimination reactions with hexafluoroacetone and analogous molecules to give three and five membered rings.

trans-Chloro(carbonyl)bis(triphenylphosphine)iridium(I) and trans-chloro(carbonyl)bis(methyldiphenylphosphine)iridium(I) both react with hexafluoroacetone to give six co-ordinate 1:1 adducts¹. Both complexes show a singlet resonance in the ¹⁹F n.m.r. spectrum and for the complex with methyldiphenylphosphine the P-Me resonances in the ¹H n.m.r. occur as triplets indicating that the complexes contain phosphines in the trans configuration as shown in (IV).

(IV) (L = PPh₃ or MePPh₂)

The reactions of trifluoroacetylcyanide with trans-chloro(carbonyl)bis(triphenylphosphine)iridium(I) and trans-chloro(carbonyl)bis(methyldiphenylphosphine)iridium(I)⁸ were undertaken to determine whether co-ordination occurred via the >C=O, as in hexafluoroacetone complexes, or via the electrophilic -C≡N (as in Pt(CF₃C≡N)(PPh₃)₂ - see next section) or possibly with cleavage of the C-CN bond,
in a manner analogous to acyl halides,\textsuperscript{9} to give
Ir(CO)Cl(COCF\textsubscript{3})(CN)(PPh\textsubscript{3})\textsubscript{2}. It was found that co-ordination
curred via $\overset{\text{>}}{\text{C}=\text{O}}$ to give 1:1 adducts, in each case,
showing singlet resonance in the $^{19}$F n.m.r. and for the
complex with methyldiphenylphosphine overlapping triplets
in the $^{1}$H n.m.r. for P-Me indicating that the phosphines
are in a \textit{trans} configuration as shown in (V).

\textbf{(V) (L = PPh\textsubscript{3} or MePPh\textsubscript{2})}

\textit{trans}-Chloro(carbonyl)bis(methyldiphenylphosphine)rhodium(I)
also forms a 1:1 adduct with trifluoroacetylcyancide,\textsuperscript{8} but the
complex formed shows a doublet in the $^{19}$F n.m.r. due to
\textit{trans} $^{31}$P coupling and P-Me resonances in the $^{1}$H n.m.r.
occur as doublets indicating that the phosphines are in a
\textit{cis} configuration as shown in (VI).

\textbf{(VI) (L = MePPh\textsubscript{2})}

It is interesting to note the difference in
configuration of the iridium and rhodium complexes ((V) and (VI))
which gives some indication of the sensitivity of the stereochemical path of the reaction.

Acetylacetonatobis(methyldiphenylphosphine)rhodium(I) forms a 1:1 adduct with hexafluoroacetone\textsuperscript{10} for which the \textsuperscript{19}F and \textsuperscript{1}H n.m.r. spectra indicate a trans configuration for the phosphines, (VII).

![Diagram](image)

(VII) \((L = \text{MePPh}_2)\)

This complex does not react further with hexafluoroacetone but reacts with tetrafluoroethylene at room temperature to give a 1:1 adduct which is formulated as the ring expanded product (VIII), from n.m.r. data.

![Diagram](image)

(VIII) \((L = \text{MePPh}_2)\)

In contrast the reaction of acetylacetonatobis(triphenylphosphine)rhodium(I) with hexafluoroacetone gives an oxidative-elimination product\textsuperscript{10} in which two molecules of hexafluoroacetone form a five membered ring (IX). The \textsuperscript{19}F n.m.r. spectrum of this complex shows two multiplet resonances.
Hexafluoroisopropylideneamine undergoes oxidative-elimination reactions with both acetylacetonatobis(methyl-diphenylphosphine)rhodium(I) and acetylacetonatobis(triphenylphosphine)rhodium(I)\textsuperscript{10} to give complexes which show singlet resonances in the \textsuperscript{19}F n.m.r. spectra and on this evidence are given structure (X).

There was no evidence of five membered ring formation in these two reactions.

A 1:1 adduct between hydrido(carbonyl)bis(triphenylphosphine)iridium(I) and hexafluorothioacetone\textsuperscript{11} can be made by the reaction of the iridium complex with 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietan (XIa) in benzene at room temperature. In the \textsuperscript{1}H n.m.r. the hydride appears as a triplet due to coupling to two equivalent \textsuperscript{31}P.
nuclei. On this evidence, the complex was assigned a structure with the phosphines in a cis configuration, (XIIb).

\[
\begin{align*}
\text{(XIa)} & \quad \text{(XIb)} (L = \text{PPh}_3)
\end{align*}
\]

Nickel, Palladium, Platinum

This triad of metals is the most fruitful in this area of chemistry and zero-valent complexes of nickel, palladium and platinum form complexes with hexafluoroacetone and related molecules to give both three and five membered ring systems. Whether three or five membered rings are formed appears to depend on the ligands attached to the metal, the metal and the type of system reacting to form the ring. The most important of these considerations is probably the nature of the ligands attached to the metal, which will of course influence the electron density at the metal.

Bis(cyclo-octadiene)nickel\textsuperscript{12} reacts with hexafluoroacetone and 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietan\textsuperscript{13} below 0\textdegree, to give orange crystalline products showing singlet resonances in the \textsuperscript{19}F n.m.r. and which have been assigned structure (XII).
The hexafluorothioacetone complex appears to be the more stable, melting at 165.5°, whilst the hexafluoroacetone complex decomposes above 82°. It is interesting to note that the formation of hexafluorothioacetone from 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietan does not occur below 600° as the reaction is concerted and thermally forbidden. The reaction with bis(cyclo-octaa-1,5-diene)nickel probably involves initially the co-ordination of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietan onto nickel which results in an alteration in orbital symmetry of the molecule such that further reaction becomes possible.

On treatment of \((1,5-C_8H_{12})\text{NiC(CF}_3\text{)}_2\text{X}\), (XII) (X=O or S) with MePPh₂, PPh₃, (PhO)₃P, EtC(CH₂)₃P, \([\text{Ph}_2\text{PCH}_2\text{]}_2\) and dipyridyl, displacement of cyclo-octaa-1,5-diene occurs to give stable crystalline complexes which from n.m.r. data are given structure (XIII).

Generally it appears that the hexafluorothioacetone complexes are more stable than the hexafluoroacetone
complexes.

The reaction of (XII) with carbon monoxide does not yield \((\text{OC})_2\text{NiC(CF}_3\text{)}_2^0\) but yields tetracarbonylnickel, cyclo-octa-1,5-diene and hexafluoroacetone.\(^{14}\)

\[ \text{L}_2\text{NiC(CF}_3\text{)}_2^0, \text{(XIII)} \quad (\text{X}=\text{O};\text{L}=\text{MePPh}_2^{13} \text{ or P(Et)}_3^{14}) \]

can also be prepared by the action of hexafluoroacetone on tetrakis(methyldiphenylphosphine)nickel and tetrakis(triethylphosphine)nickel or (\(\text{X}=\text{O};\text{L}=\text{PPh}_3\)) by the displacement of ethylene from bis(triphenylphosphine)(\(\pi\)-ethylene)nickel.\(^{15}\)

The crystal structure of (XIII)\(^{16}\) (\(\text{X}=\text{O};\text{L}=\text{PPh}_3\)) confirms the structure assigned and shows the nickel, carbon, oxygen plane to be tilted some 6.9° to the nickel, phosphorus, phosphorus plane and that the carbon-oxygen bond length is 0.09Å longer than in free hexafluoroacetone.

The complexes (XII) and (XIII) appear not to undergo ring expansion reactions in the presence of excess hexafluoroacetone.\(^{13,14,15}\)

Hexafluoroisopropylideneamine and N-methylhexafluoroisopropylideneamine displace ethylene from bis(triphenylphosphine)(\(\pi\)-ethylene)nickel\(^{17}\) to give orange crystalline complexes analogous to the hexafluoroacetone complexes and were assigned structure (XIV) on the basis of \(^{19}\text{F}\) n.m.r. data.

\[ \text{(XIV)} \quad (\text{X} = \text{NH or NMe}; \text{L} = \text{PPh}_3) \]
N-methylhexafluorbisopropylideneamine reacts with an ether solution of bis(cyclo-octa-1,5-diene)nickel to give a complex showing a singlet resonance in the $^{19}$F n.m.r. spectrum even at low temperatures and was given structure (XIV) ($X=\text{NMe}; L_2=1,5-C_8H_{12}$). In this compound and other compounds having structure (XIV), the presence of the methyl group on the nitrogen ($sp^3$ hybridised) would be expected to cause inequivalence of the gem-CF$_3$ groups and their apparent equivalence probably occurs as a result of rapid inversion at the nitrogen atom, even at low temperatures. On treating ($1,5-C_8H_{12}$)NiC(CF$_3$)$_2$NMe, (XIV) ($X=\text{NMe}; L_2=1,5-C_8H_{12}$) with triphenylphosphine, methyldiphenylphosphine, 1,2-bis(dimethylphosphino)ethane and bipyridyl, cyclo-octa-1,5-diene is displaced to give complexes having the structure $L_2NiC(CF_3)_2NMe$, (XIV) ($X=\text{NMe}; L=\text{PPh}_3$, MePPh$_2$) or, $L_2=[\text{Me}_2\text{PCH}_2]_2$, bipyridyl).

Addition of an excess of these ligands did not displace (CF$_3$)$_2$CNMe but the reaction with the good π-acceptor ligand trimethylphosphite displaced cyclo-octa-1,5-diene and (CF$_3$)$_2$CNMe to yield tetrakis(trimethylphosphite) nickel. This reaction and the reaction of carbon monoxide with (XII), ($X=\text{O}$) to yield cyclo-octa-1,5-diene hexafluoroacetone and tetracarbonylnickel indicates that in these ligand exchange reactions the stability of the hexafluoroacetone or N-methylhexafluoroisopropylideneamine complex formed is dependent on the balance of the σ-donor and π-acceptor properties of the co-ordinating ligands.
Attempts to ring-expand (PPh₃)₂NiC(CF₃)₂NH, (XIV) (X=NH; L=PPh₃) with hexafluoroacetone, led only to the ligand displacement reaction to give (PPh₃)₂NiC(CF₃)₂O, (XIII) (X=O; L=PPh₃).

In contrast to the reactions of hexafluoroacetone and hexafluoroisopropylideneamine with NiL₄ (L=Et₃P, MePPh₂ or L₂=1,5-C₈H₁₂) and bis(triphenylphosphine)(π-ethylene)nickel to give three membered ring systems, hexafluoroacetone and hexafluoroisopropylideneamine react with tetrakis(t-butyl-isocyanide)nickel¹⁸ to give complexes containing five membered rings.¹⁹ These complexes show two multiplet resonances in the $^{19}$F n.m.r. and are considered, therefore, to have structure (XV).

(XV) (X = O or NH; L = Bu¹NC)

This gives some indication of the importance of the nature of the ligand in determining whether three or five membered ring systems are formed. It was postulated that these five membered ring systems were formed via reactive three membered ring intermediates and it was found to be possible to synthesise the postulated three membered ring intermediates via the displacement of cyclo-octa-1,5-diene.
from $\text{(1,5-C}_8\text{H}_{12})\text{NiC(CF}_3\text{)}_2\text{O}$ and $\text{(1,5-C}_8\text{H}_{12})\text{NiC(CF}_3\text{)}\text{NH}$ with $\text{Bu}^+\text{NC}$ to give (XVa) ($X=\text{O}$) and (XVb) ($X=\text{NH}$).

Both (XVa) and (XVb) reacted rapidly with hexafluoroacetone and hexafluoroisopropylideneamine respectively to give the five membered ring systems (XV) ($X=\text{O}$) and (XV) ($X=\text{NH}$).

$(\text{Bu}^+\text{NC})_2\text{NiC(CF}_3\text{)}_2\text{O}$, (XVa) also reacts with hexafluoroisopropylideneamine to give one product which shows two signals in the $^{19}\text{F n.m.r.}$ and hence can be assigned structure (XVIa) or (XVIb).

A crystal structure study shows that the complex has structure (XVIb) in which the mean plane of the five membered ring is in the nickel, $\text{Bu}^+\text{NC},\text{Bu}^+\text{NC}$ plane and also that ring expansion occurred via the breaking of a nickel-carbon rather than a nickel-oxygen bond.
(Bu^NC)_2Ni(CF_3)_2NH, (XVb) reacts with hexafluoroacetone\textsuperscript{19} to give two products, one being (XVIb), (Bu^NC)_2Ni(CF_3)_2NHC(F_3)_2O and the other, which shows two multiplets in the \textsuperscript{19}F n.m.r. is most likely (XVIa).

Both (XVa), (Bu^NC)_2Ni(CF_3)_2O and (XVb), (Bu^NC)_2Ni(CF_3)_2NH when treated with tetrafluoroethylene give the displacement product (Bu^NC)_2NiCF_2CF_2CF_2. This reaction most likely occurs via the three membered tetrafluoroethylene ring complex which is then ring expanded with another molecule of tetrafluoroethylene.

In contrast to the reaction of hexafluoroacetone with tetrakis(t-butylisocyanide)nickel to give a five membered ring, hexafluoroacetone reacts with tetrakis(phenylisocyanide)nickel to give a three membered ring system,\textsuperscript{20} (PhNC)_2Ni(CF_3)_2O which can also be prepared by the displacement of cyclo-octa-1,5-diene from (1,5-C_8H_{12})Ni(CF_3)_2O with phenylisocyanide. The inability of hexafluoroacetone to give a five membered ring system is considered to be due to the withdrawal of electron density by phenylisocyanide from the nickel by a \pi bonding mechanism so that the nucleophilicity of the metal is reduced, hence making the approach of a second molecule of hexafluoroacetone to nickel unlikely.

Although (PhNC)_2Ni(CF_3)_2O does not react further with hexafluoroacetone it reacts with hexafluoroisopropylideneamine to give a five membered ring product, which shows two signals in the \textsuperscript{19}F n.m.r. and hence can be given structure (XVIIa) or (XVIIb).
The confirmed structure (XVIb) \((\text{Bu}^\text{tNC})_2\text{NiC(CF}_3)_2\text{O}\) indicates that (XVIIa) is the correct structure in which ring expansion has occurred via the cleavage of a carbon-nickel bond as in (XVIb).

Hexafluoroacetone reacts with tetrakis(phenyl-dimethylarsine)nickel and bis[o-bis(dimethylarsino)benzene]-nickel to give mixtures of products, \(^{21}\) from which crystalline products could not be isolated, but \(o-C_6H_4(\text{AsMe}_2)_2\text{NiC(CF}_3)_2\text{O}\), (XIII) \((X=O;L_2=o-C_6H_4(\text{AsMe}_2)_2)\) can be prepared by displacing cyclo-octa-1,5-diene from \((1,5-C_8H_{12})\text{NiC(CF}_3)_2\text{O}\) with o-bis(dimethylarsino)benzene. \(o-C_6H_4(\text{AsMe}_2)_2\text{NiC(CF}_3)_2\text{O}\) reacts further with hexafluoroacetone on heating at 60° to give a yellow product showing two multiplet signals in the \(^{19}\text{F n.m.r.}\), which accords with the structure \(o-C_6H_4(\text{AsMe}_2)_2\text{NiC(CF}_3)_2\text{OC(CF}_3)_2\text{O}\). \(o-C_6H_4(\text{AsMe}_2)_2\text{NiC(CF}_3)_2\text{O}\) also reacts with hexafluoroisopropylidenamine to give one ring expanded product, whose \(^{19}\text{F n.m.r.}\) shows two signals and can hence be assigned structure (XVIIIa) or (XVIIIb).
The structure (XVIIIb) is the most likely by analogy to the confirmed structure (XVIb) \((\text{Bu}^\text{tNC})_2\text{Ni(CF}_3\text{)}_2\text{NHC(CF}_3\text{)}_2\text{O}\).

A reaction related to the above ring expansion reactions occurs when peroxobis(t-butylisocyanide)nickel\(^{22}\) in ether is treated with one mole-equivalent of hexafluoroacetone at \(-50^\circ\) to give a 1:1 adduct\(^{23}\) which shows a single resonance in the \(^{19}\text{F}\) n.m.r. The complex is assigned the peroxo-structure (XIX) by analogy to the reaction of acetone with peroxobis(triphenylphosphine)platinum(II) to give a confirmed peroxo-structure\(^{24}\).

![Diagram of (XIX) (L = Bu\text{tNC})]

Treatment of peroxobis(t-butylisocyanide)nickel or (XIX) with excess of hexafluoroacetone yields a complex which shows two \(\text{C(CF}_3\text{)}_2\) environments in the \(^{19}\text{F}\) n.m.r. and a band in the infrared spectrum at 1670 \(\text{cm}^{-1}\). From this data the complex is assigned structure (XX) in which a second molecule of hexafluoroacetone is loosely co-ordinated to nickel via the oxygen. The band at 1670 \(\text{cm}^{-1}\) in the infrared spectrum is regarded as the absorption of the co-ordinated hexafluoroacetone carbonyl group.
Complex (XX) reversibly loses one molecule of hexafluoroacetone to give (XIX).

In diethyl ether (XIX) is unstable and a peroxy-oxygen atom is lost to give a complex showing one signal in the $^{19}F$ n.m.r. and which is assigned the four membered ring structure $(Bu^+NC)_2NiOC(CF_3)_2O$.

Tetrakis(triphenylphosphine)palladium$^{25}$, tetrakis(triphenylphosphite)palladium$^{26}$ and tetrakis(methyldiphenylphosphine)palladium$^{26}$ react with hexafluoroacetone to give three membered ring complexes (XXI).

For $L = PPh_3$ and MePPh$_2$ the $^{19}F$ n.m.r. spectrum shows double doublets due to cis and trans $^{31}P$ coupling, but for $L = P(OPh)_3$ a triplet resonance is observed, which is probably due to dissociation of phosphite ligands, causing an averaging of $J(P-F)_{cis}$ and $J(P-F)_{trans}$. Molecular weight
studies show dissociation in (XXI) (L=\(P(\text{OPh})_3\)).

1,2-Bis(diphenylphosphino)ethane displaces triphenylphosphite from (XXI), (L=\(P(\text{OPh})_3\)) to give 
\[
\left[\text{Ph}_2\text{PCH}_2\right]_2\text{Pd}\left(\text{CF}_3\right)_2\text{O}^{26} \text{, (XXI)} \text{ (X=O; } L=\left[\text{Ph}_2\text{PCH}_2\right]_2\right)
\]
but in contrast methyldiphenylphosphine displaces hexafluoroacetone to give \(\text{Pd}\left[\text{P(\text{OPh})}_3\right]_2\left[\text{MePPh}_2\right]_2\).

Tetrakis(triphenylphosphine)palladium reacts with hexafluoroisopropylideneamine to give a three membered ring complex, \(\text{(PPh}_3)_2\text{Pd}\left(\text{CF}_3\right)_2\text{NH}\), (XXI) (X=NH; L=\(\text{PPh}_3\)). The \(^{19}\text{F n.m.r.}\) shows one signal, a doublet of doublets due to \text{cis} and \text{trans} \text{\(^3P\) coupling and the inequivalence of the gem -CF}_3 groups due to the presence of the N-H (\text{Nsp}^3\text{hybridised}) is not seen probably due to rapid inversion at the nitrogen atom.

In contrast to the above reactions bis(t-butylisocyanide)palladium, \(2^7\) tetrakis(trimethylphosphite)palladium, \(2^6\) tetrakis(dimethylphenylphosphonite)palladium and \(2^6\) tetrakis(dimethylbenzylarsine)palladium react with hexafluoroacetone to give five membered ring complexes that show two multiplet resonances in the \(^{19}\text{F n.m.r.}\) and are assigned structure (XXII).

\[
(\text{XXII}) \quad (X=\text{O}; \ L=\text{Bu}^+\text{NC, P(OMe)}_3, \text{PPh(OMe)}_2, \text{Me}_2\text{As(CH}_2\text{Ph)}_2)
\]
Hexafluoroisopropylideneamine reacts with bis(t-butylisocyanide)palladium and tetrakis(dimethylphenylarsine)palladium to give five membered ring systems, $^{27} L_2PdC(CF_3)_2NHC(CF_3)_2NH$, (XXII) ($X=NH; L=Bu^tNC, Me_2AsPh$). Each shows two multiplet resonances in the $^{19}F$ n.m.r. N-methylhexafluoroisopropylideneamine gives only an unstable complex with bis(t-butylisocyanide)palladium. The complexes $L_2PdC(CF_3)_2X$, (XXI) ($X=O; L=P(OPh)_3, PPh_3$ and $X=NH; L=PPh_3$) could not be ring expanded with hexafluoroacetone and hexafluoroisopropylideneamine respectively, suggesting that the ligands $P(OPh)_3$ and $PPh_3$ have a deactivating effect to ring expansion reactions. Direct formation of five membered ring systems $L_2PdC(CF_3)_2X(CF_3)_2X$, (XXII) ($X=O; L=Bu^tNC, P(OMe)_3, PPh(OMe)_2, Me_2As(CH_2Ph)$ and $X=NH; L=Bu^tNC, Me_2AsPh$) suggest, assuming that five membered ring formation goes through a reactive three membered ring intermediate, that the ligands $Bu^tNC, P(OMe)_3, PPh(OMe)_2, Me_2As(CH_2Ph)$ and $Me_2PPh$ have an activating $^{26}$ effect to ring expansion reactions.

The complexes $(MePPh_2)_2PdC(CF_3)_2O$, (XXI) ($X=O; L=MePPh_2$) and $[Ph_2PCH_2]_2PdC(CF_3)_2O$, (XXI) ($X=O; L=[Ph_2PCH_2]_2$) on prolonged heating at $60^\circ$ with hexafluoroacetone give ring expanded products $^{26}$ showing two resonances in the $^{19}F$ n.m.r. spectrum and are assigned structures $L_2PdC(CF_3)_2OC(CF_3)_2O$, (XXII) ($L=MePPh_2$ or $L_2=[Ph_2PCH_2]_2$). Hexafluoroisopropylideneamine also ring expands the complex $[Ph_2PCH_2]_2PdC(CF_3)_2O$ and from $^{19}F$ n.m.r. spin decoupling data and by analogy to the nickel complex of proven structure, $(Bu^tNC)_2NiC(CF_3)_2NHC(CF_3)_2O$, (XVIb).
the product is assigned structure (XXIII) in which hexafluoroisopropylideneamine has inserted into the palladium-carbon bond.

 Attempts made to ring expand (PPh₃)₂PdC(CF₃)₂NH with hexafluoroacetone led only to the ligand exchange reaction and the formation of (PPh₃)₂PdC(CF₃)₂O.

 The trimethylphosphite ligands in the complex \([P(\text{OMe})_3]_2\text{PdC(CF}_2\text{)}_2\text{OC(CF}_3\text{)}_2\text{O}\), (XXII) (X=O; L=P(OMe)_3) can be displaced²⁶ by 1,2-bis(triphenylphosphino)ethane to give (XXII) (X=O; L=[Ph₂PCH₂]₂) but methyldiphenylphosphine only displaces one trimethylphosphite to give (XXIV).

 In contrast, in the reaction with triethylphosphine, two molecules of triethylphosphine co-ordinate with the displacement of only one trimethylphosphite ligand. The
product is given a trigonal-bipyramidal structure (XXV), with the electronegative oxygen in an apical position.

\[
\begin{array}{c}
\text{F}_3\text{C} & \text{CF}_3 \\
\text{O} & \text{C} \\
\text{Pd} & \text{C} \\
\text{L} & \text{CF}_3 \\
\text{L'} & \text{CF}_3
\end{array}
\]

(XXV) \((\text{L}=\text{PET}_3; \text{L}'=\text{P}(\text{OMe})_3)\)

The reaction of \textit{trans}-\text{PdMe}_2(\text{PET}_3)_2 with dodecafluoropinacol\(^{26}\) gives (XXVI) with the liberation of methane. The \(^{19}\text{F}\) n.m.r. spectrum shows a single resonance in contrast to the five membered ring systems (XXII) \((\text{X}=\text{O})\) which show two resonances. An X-ray study has confirmed the assigned structure.

\[
\begin{array}{c}
\text{L} & \text{O} & \text{O} \\
\text{Pd} & \text{C} & \text{C} \\
\text{L} & \text{CF}_3^2 & \text{CF}_3^2
\end{array}
\]

(XXVI) \((\text{L}=\text{PET}_3)\)

From the results for palladium it is possible to draw up a series for the activating power of ligands towards the ring expansion reaction \(\text{L}_2\text{PdC(CF}_3)\text{OC(CF}_3)\text{O}.\) The series assumes that where five membered rings are formed initially, they are formed
via reactive three membered ring intermediates.

Activating power: $P(\text{OPh})_3 = P\text{Ph}_3 < \text{MePPPh}_2 = \left[\text{Ph}_2\text{PCH}_2\right]_2$

$< P(\text{OME})_3 = P\text{Ph}(\text{OME})_2 = \text{Me}_2\text{P}(\text{CH}_2\text{Ph}) = \text{Bu}^t\text{NCH}$. 

Tetrakis(triphenylphosphine)platinum, tetrakis(methyldiphenylphosphine)platinum and tetrakis(triphenylphosphite)platinum react with hexafluoroacetone to give three membered ring systems, which show in the $^{19}\text{F}$ n.m.r. spectrum a triplet of double doublets due to cis and trans $^{31}\text{P}$ coupling and $^{195}\text{Pt}$ coupling (XXVII).

1,3-Dichlorotetrafluoroacetone reacts with tetrakis(triphenylphosphine)platinum to give a three membered ring complex, $(\text{PPh}_3)_2\text{PtC(CF}_2\text{Cl})_2\text{O}$, analogous to the hexafluoroacetone complex. 2,2,4,4-Tetrakis(trifluoromethyl)-1,3-dithietan reacts with tris(triphenylphosphine)platinum in refluxing ether to give white crystals of $(\text{PPh}_3)_2\text{PtC(CF}_3)_2\text{S}$, the hexafluorothioacetone three membered ring complex which shows a $^{19}\text{F}$ n.m.r. spectrum comparable to that of $(\text{PPh}_3)_2\text{PtC(CF}_3)_2\text{O}$ except that no cis $^{31}\text{P}$- $^{19}\text{F}$ coupling is observed.

The complex $\left[\text{Ph}_2\text{PCH}_2\right]_2\text{PtC(CF}_3)_2\text{O}$, (XXVII) $(\text{L}_2=\left[\text{Ph}_2\text{PCH}_2\right]_2)$ can be prepared by the displacement of triphenylphosphine from (XXVII) $(\text{L}=\text{PPh}_3)$ with 1,2-bis(diphenylphosphino)ethane.
Iodine reacts with \((\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{O}\), (XXVII) 
\((\text{L} = \text{PPh}_3)\) to liberate hexafluoroacetone with the 
formation of \((\text{PPh}_3)_2\text{PtI}_2\).\(^{25}\)

Analogous hexafluoroisopropylideneamine and 
N-methylhexafluoroisopropylideneamine three membered 
ring complexes can be prepared by the displacement of 
trans-stilbene from trans-stilbenebis(triphenylphosphine)- 
platinum.\(^{30}\) As in the analogous nickel and palladium 
complexes there is no inequivalence of the gem-CF\(_3\) groups 
due to the present of N-H or N-Me (Nsp\(^3\)hybridised) and as 
before this is probably due to rapid inversion at the 
nitrogen atom in solution. The complexes are assigned 
structure (XXVIII) on the basis of \(^{19}\text{F}\) n.m.r. data.

\[
\begin{array}{c}
\text{L} \\
\text{Pt} \\
\text{X} \\
\text{C} \\
\text{CF}_3 \\
\end{array}
\]

(XXVIII) \((X = \text{NH or NMe}; \text{L} = \text{PPh}_3)\)

The three membered ring complex \(\left[\text{Ph}_2\text{PCH}_2\right]_2\text{PtC(CF}_3\text{)}_2\text{NH}\),
(XXVIII) \((X = \text{NH}; \text{L}_2 = \left[\text{Ph}_2\text{PCH}_2\right]_2)\) can be prepared by the 
displacement of triphenylphosphine from (XXVIII)
\((X = \text{NH}; \text{L} = \text{PPh}_3)\) with 1,2-bis(diphenylphosphino)ethane.\(^{28}\)
Hexafluoroisopropylideneamine does not react with 
tetrakis(triphenylphosphite)platinum and tetrakis(trimethyl-
phosphite)platinum.

The complex \((\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{NH}\) reacts with 
trifluoroacetic acid\(^{30}\) in methylene chloride at room
temperature to give a platinum(IV) complex which is assigned structure (XXIXa).

\[
\text{(XXIXa) } (X=\text{NH}; Z=Y=\text{OCO}CF_3; L=\text{PPh}_3) \\
\text{(XXIXb) } (X=\text{NMe}; Z=\text{H}, Y=\text{OCO}CF_3; L=\text{PPh}_3)
\]

Complex \((\text{PPh}_3)_2\text{PtC(CF}_3)_2\text{NMe}\) undergoes an analogous reaction to give a platinum(IV) complex but in this case the hydrido-platinum(IV) complex (XXIXb) \((X=\text{NMe}; Z=\text{H}, Y=\text{OCO}CF_3; L=\text{PPh}_3)\). It is suggested that these two reactions go via the oxidative-addition of trifluoroacetic acid to give the hydrido-platinum(IV) species which, in the case of (XXIXa), reacts with more trifluoroacetic acid to give the bis(trifluoroacetate)platinum(IV) complex.

A comparison of these reactions with the reaction of \((\text{PPh}_3)_2\text{PtC}_2\text{F}_4\) with trifluoroacetic acid to give \((\text{PPh}_3)_2\text{Pt(OCO}CF_3)(\text{CF}_2\text{CF}_2\text{H})^{31}\) suggests that it is possible that this reaction goes via a platinum(IV) intermediate analogous to (XXIXb).

Hexafluoroacetone reacts with tetrakis(tri-methylphosphite)platinum to give a five membered ring
system\textsuperscript{28} which shows two signals in the $^{19}$P n.m.r. and is assigned structure (XXX).

\[
\begin{align*}
\text{(XXX)} \quad (L=P(\text{OMe})_3)
\end{align*}
\]

Assuming that this reaction goes \textit{via} a reactive three membered ring intermediate it can be seen, as in nickel and palladium systems, how important a role the ligand plays in three to five membered ring expansions. As trimethylphosphite is a more basic ligand than, for example, triphenylphosphite there will be increased electron density on platinum in the three membered ring system, which will be available for back donation into the $\pi^*$ orbitals of the second hexafluoroacetone molecule. Five membered ring formation will hence be more readily accomplished.

The thermal reaction of (1,5-C$_6$H$_{12}$)PtPr$_2^{\text{iso}}$ with hexafluoroisopropylideneamine yields a bis-hexafluoroisopropylideneamido-complex of platinum(II), (XXXI). This complex may be formed \textit{via} the protolysis of the platinum-carbon $\sigma$-bond by acidic (CF$_3$)$_2$CNH or by oxidative-addition of two (CF$_3$)$_2$CNH molecules with loss of propane.
(XXXI) \( (L_2=1,5\text{-C}_8\text{H}_{12}) \)

\((\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{O}\) and \([\text{P(0Ph)}_3]_2\text{PtC(CF}_3\text{)}_2\text{O}\) are not ring expanded even after prolonged heating \((60^\circ, 3\text{ days})\) with hexafluoroacetonate,\(^{28}\) but \([\text{Ph}_2\text{PCH}_2]_2\text{PtC(CF}_3\text{)}_2\text{O}\) and \((\text{MePPh}_2)_2\text{PtC(CF}_3\text{)}_2\text{O}\) react slowly with hexafluoroacetonate to give ring expanded products showing two signals in the \(^{19}\text{F}\) n.m.r. and are hence assigned structure (XXX) \((L_2=\text{[Ph}_2\text{PCH}_2]_2\text{ and } L=\text{MePPh}_2)\).

Hexafluoroisopropylideneamine reacts with \((\text{MePPh}_2)_2\text{PtC(CF}_3\text{)}_2\text{O}\) and \((\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{O}\) to give good yields of ring expanded products,\(^{28}\) which can be assigned structure (XXXIIa) or (XXXIIb).

Complex \((\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{NH}\) cannot be ring expanded with excess hexafluoroisopropylideneamine, but \([\text{Ph}_2\text{PCH}_2]_2\text{PtC(CF}_3\text{)}_2\text{NH}\) reacts rapidly\(^{28}\) to give a ring
expanded product showing two signals in the $^{19}\text{F\ n.m.r.}$ and is hence assigned structure $\left[\text{Ph}_2\text{PCH}_2\right]_2\text{PtC(CF}_3\text{)}_2\text{NHC(CF}_3\text{)}_2\text{NH}$. $(\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{NH}$ reacts slowly with hexafluoroacetone to give a ring expanded product$^{30}$ identical to that obtained from the reaction of $(\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{O}$ with hexafluoroisopropylideneamine and can have structure (XXXIIa) or (XXXIIb).

The reaction of hexafluoroacetone with $(\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{NMe}$ yields the ligand displacement product $(\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{O}$.

Trifluoroacetonitrile displaces trans-stilbene from trans-stilbenebis(triphenylphosphine)platinum to give a complex showing a doublet (trans$^{31}\text{P-}^{19}\text{F coupling}$) with $^{195}\text{Pt}$ satellites in the $^{19}\text{F\ n.m.r.}$ spectrum and an absorption at 1734 cm$^{-1}$ in the infrared spectrum.$^{32}$ The complex is assigned a three membered ring structure from this data, the band at 1734 cm$^{-1}$ in the infrared spectrum being due to the $\pi$ co-ordinated $\text{-C=N, v(C=\text{N})}$ absorption, (XXXIII).

\[
\text{(XXXIII) (L = PPh}_3\text{)}
\]

From the reaction of trifluoroacetonitrile with tetrakis(triphenylphosphine)platinum a product can be isolated having a molecular formula $(\text{PPh}_3)_2\text{Pt(CF}_3\text{CN})_2\text{N}$. An X-ray crystallographic study of this complex$^{32}$ showed it to have
structure (XXXIV), in which the fragment N-H probably arises from the hydrolytic degradation of CF$_3$CN by traces of moisture in the reaction system. The plane of the six membered ring is approximately co-planar with the phosphorus, platinum, phosphorus plane.

![Structure XXXIV](image)

Trifluoroacetonitrile is displaced from (XXXIII) by diphenylacetylene$^{33}$ to give diphenylacetylenebis(triphenylphosphine)platinum, but displaces 1,1-difluoroethylene from 1,1-difluoroethylenebis(triphenylphosphine)platinum to give (XXXIII). With hexafluoroacetone (PPh$_3$)$_2$PtN-CCF$_3$ reacts to give the known complex (PPh$_3$)$_2$PtC(CF$_3$)$_2$O$^{25}$ by a straightforward displacement reaction and also a ring expanded complex, which is assigned structure (XXXV) on the basis of $^{19}$F n.m.r. and infrared data.

![Structure XXXV](image)

(XXXV) (L = PPh$_3$)
Recrystallisation of (XXXIII) from acetone in the presence of oxygen results in the displacement of trifluoroacetonitrile and the formation of the known five membered ring complex \((\text{PPh}_3)_2\text{PtOC(CH}_3\text{)}_2\text{OO}\). This reaction probably occurs via the displacement of trifluoroacetonitrile by oxygen to give peroxobis(triphenylphosphine)platinum, which reacts with acetone to give the five membered ring complex.\(^{24}\)

In contrast to the reactions of \((\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{NH, (XXVIII)} (X=\text{NH; } L=\text{PPh}_3)\) and \((\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{NMe, (XXVIII)} (X=\text{NMe; } L=\text{PPh}_3)\) with trifluoroacetic acid to give (XXIXa) and (XXIXb) respectively, \((\text{PPh}_3)_2\text{PtN=CCF}_3\) reacts to give trans-hydrido-trifluoroacetobis(triphenylphosphine)platinum and the ring opened product, trans-(\(\text{PPh}_3\))_2\text{Pt(OCOCF}_3\text{)(CF}_3\text{C=NH)}, (XXXVI) the stereochemistry being inferred from the \(^{19}\text{F} n.m.r.\) spectrum which shows no \(^{31}\text{P}\text{-}^{19}\text{F}\) coupling indicating a trans configuration for the phosphines.

\[
\begin{align*}
\text{(XXXVI)} \quad (L=\text{PPh}_3; \quad X=-\text{OCOCF}_3)
\end{align*}
\]

Attempts to obtain complexes analogous to \((\text{PPh}_3)_2\text{PtN=CCF}_3\) using trichloroacetonitrile, chloromethylcyanide and pentafluorobenzonitrile have not been successful.\(^{33}\)
Treatment of peroxobis(triphenylphosphine)platinum with some aldehydes and ketones leads to reactions analogous to the ring expansion reactions of three membered ring complexes containing hexafluoroacetone and similar molecules.

Peroxobis(triphenylphosphine)platinum reacts with a wide range of aldehydes and ketones to give 1:1 adducts having five membered rings involving a peroxo group,\(^ {34,35,36,37,38,}\) (XXXVII).

![Chemical Structure](XXXVII) \( (L = \text{PPh}_3) \)

Some examples include: \( R=R'=\text{CH}_3 \); \( R=\text{CH}_3; R'=\text{H} \); \( R=\text{CH}_2\text{CH}_3, R'=\text{H} \); \( R=\text{ClCH}_2, R'=\text{CH}_3 \); \( R=R'=\text{CF}_3 \); \( R=\text{CH}_3, R'=\text{CF}_3 \); \( R=\text{CH}_3, R'=\text{COCH}_3 \); \( R=\text{C}_6\text{H}_5, R'=\text{COC}_6\text{H}_5 \).

An X-ray crystallographic study for the 1:1 adduct between peroxobis(triphenylphosphine)platinum and acetone\(^ {36} \) confirmed the assigned structure and showed that the phosphorus, platinum, phosphorus plane is almost co-planar with the plane of the five membered ring (XXXVII) \( (R=R'=\text{CH}_3; L=\text{PPh}_3) \).

When hydrogen or nitrogen is bubbled through a solution of the 1:1 adduct \( (\text{PPh}_3)_2\text{PtOC(CH}_3\text{)}_0\text{O} \) an oxygen atom is lost from the peroxo group and a complex containing a four membered ring is formed,\(^ {35} \) (XXXVIII).
This reaction is analogous to the reaction of the peroxycarbonate complex \((\text{PPh}_3)_2\text{PtOC(}0\text{)OO}\) \(^{37}\) (formed in the reaction of carbon dioxide with peroxobis(triphenylphosphine) platinum) with triphenylphosphine to yield the carbonate complex, \((\text{PPh}_3)_2\text{PtOC(}0\text{)O}\), which contains a four membered ring, and triphenylphosphine oxide. The 1:1 adduct between hexafluoroacetone and peroxobis(triphenylphosphine) platinum, \((\text{PPh}_3)_2\text{PtOC(CF}_3\text{)}_2\text{OO}\), undergoes a similar reaction with triphenylphosphine to give the four membered ring complex \((\text{PPh}_3)_2\text{PtOC(CF}_3\text{)}_2\text{O}\), (XXXVIII) \((R=R'=\text{CF}_3; \text{L=PPPh}_3)\) and triphenylphosphine oxide.

Complexes containing the peroxy group show weak bands in the infrared at around 780 cm\(^{-1}\) \(^{34,35}\) which have been assigned to \(v(O-O)\). The three complexes above, which contain four membered rings do not show these bands.

The seven membered ring complex \(^{34}\), (XXXIX), can be prepared by the reaction of excess hexafluoroacetone on peroxobis(triphenylphosphine)platinum(II) but not via the ring expansion of \((\text{PPh}_3)_2\text{PtOC(CF}_3\text{)}_2\text{OO}\) in the presence of hexafluoroacetone.

The complex shows two signals in the \(^{19}\text{F}\) n.m.r. spectrum.
When recrystallised from methylene chloride (XXXIX) loses one molecule of hexafluoroacetone and reverts to the five membered ring system.

It is interesting to note that trifluoroacetone will displace acetone from \((\text{PPh}_3)_2\text{PtOC(CH}_3\text{)_2 OO}\) to give the trifluoroacetone five membered ring complex, \((\text{PPh}_3)_2\text{PtO(CF}_3\text{)C(CH}_3\text{)_2 OO}\). Similarly hexafluoroacetone will displace trifluoroacetone to give the hexafluoroacetone five membered ring complex, \((\text{PPh}_3)_2\text{PtOC(CF}_3\text{)_2 OO}\).

With unsymmetrical \(\alpha\)-diketones (e.g. 2,3-pentanedione, \(\text{C}_2\text{H}_5\text{COCOCH}_3\); 1-phenyl-1,2-propanedione, \(\text{C}_6\text{H}_5\text{COCOCH}_3\); \(p\)-methoxy-1-phenyl-1,2-propanedione, \(\text{CH}_3\text{OC}_6\text{H}_4\text{COCOCH}_3\)) mixtures of 1:1 adducts with peroxobis(triphenylphosphine) platinum are formed as the two carbonyl groups are not equivalent. Figure 1.1.

\[
\text{R}_1\text{COR}_2 + (\text{PPh}_3)_2\text{PtOO} \rightarrow
\]

![Figure 1.1](image) \((L = \text{PPh}_3)\)

Adducts with \(\alpha\)-diketones (e.g. (XXXVII), \(R = \text{CH}_3\), \(R' = \text{COCH}_3\); \(R = \text{C}_6\text{H}_5\), \(R' = \text{COCH}_3\))
R' = COC₆H₅ etc.) undergo a slow rearrangement, even in the solid state, to give the dicarboxylate complex, the rearrangement being catalysed by light. Figure 1.2.

![Figure 1.2. (L = PPh₃)](image)

This rearrangement, when the α-diketone is glyoxal (CHO-CHO), occurs rapidly and it is not possible to isolate the peroxo five membered ring complex.

**A mechanism for ring expansion reactions.**

It has been suggested that three to five membered ring expansion reactions go via six co-ordinate octahedral intermediates in which the incoming molecule is co-ordinated to the metal e.g. Figure 1.3.

![Figure 1.3. (L = MePPh₂)](image)
The intermediate once formed can revert back to the three membered ring system, or if the electronic conditions are right (as in the example shown above) rearrange to the ring expanded product.

This type of intermediate is also postulated for displacement reactions when the six co-ordinate intermediate rearranges back to the alternative three membered ring rather than to the five membered ring expanded product.

The displacement of hexafluoroacetone from \((\text{Bu}^\text{t}\text{NC})_2\text{NiC(CF}_3)_2\text{O}\) to give \((\text{Bu}^\text{t}\text{NC})_2\text{NiCF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\) via, it is assumed, \((\text{Bu}^\text{t}\text{NC})_2\text{NiCF}_2\text{CF}_2\) is an example of a displacement reaction in which the displacing ligand itself undergoes a ring expansion reaction. Figure 1.4.

\[ \text{Figure 1.4. } (L = \text{Bu}^\text{t}\text{NC}) \]
This type of mechanism is also applicable to the reaction of aldehydes and ketones with peroxobis(triphenylphosphine)platinum and the reaction of peroxobis(t-butylisocyanide)nickel with hexafluoroacetone.

The general reactivity towards three to five membered ring expansion.

This is a general reaction of three membered ring complexes formed by hexafluoroacetone type systems as is apparent from the data available.

It appears for the nickel triad, that the order of reactivity towards three to five membered ring expansion reactions, involving hexafluoroacetone and similar systems, is Ni<Pd<Pt which appears to be the opposite trend to the analogous ring expansion reactions of tetrafluoroethylene systems. This is quite well illustrated by examples:

\[
\text{Ni(MePPh}_2\text{)}^2_{4}+2\text{CF}_2=\text{CF}_2 \rightarrow (\text{MePPh}_2\text{)}^2_{2}\text{NiCF}_2\text{CF}_2\text{CF}_2\text{CF}_2
\]

\[
\text{Pt(MePPh}_2\text{)}^2_{4}+\text{CF}_2=\text{CF}_2 \rightarrow (\text{MePPh}_2\text{)}^2_{2}\text{PtCF}_2\text{CF}_2
\]

but

\[
(\text{PPh}_3\text{)}^2_{2}\text{NiC(CF}_3\text{)}^2_{2}\text{NH}+(\text{CF}_3\text{)}^2_{2}\text{CO} \rightarrow (\text{PPh}_3\text{)}^2_{2}\text{NiC(CF}_3\text{)}^2_{2}\text{O}+(\text{CF}_3\text{)}^2_{2}\text{CNH}
\]

\[
(\text{PPh}_3\text{)}^2_{2}\text{PtC(CF}_3\text{)}^2_{2}\text{NH}+(\text{CF}_3\text{)}^2_{2}\text{CO} \rightarrow (\text{PPh}_3\text{)}^2_{2}\text{PtC(CF}_3\text{)}^2_{2}\text{ONH(CF}_3\text{)}^2_{2}\text{C}
\]

Where five membered rings are formed initially it is assumed that this occurs via reactive three membered ring intermediates.

The ability of a three membered ring system to ring expand appears to be very dependent on the ligands present on the metal, implying that the electron density on the metal is an important consideration.
Electron density on the metal increases with the \(\sigma\)-donor properties of the ligands and trends show that as \(\sigma\)-donor properties of the ligands increase three membered ring systems become more reactive towards ring expansion. This can be seen in terms of increasing nucleophilicity of the metal, making the approach of a second electrophilic hexafluoroacetone molecule (or similar system) easier, hence making the probability of a ring expansion reaction higher. A ligand which has good \(\pi\)-acceptor properties will, of course, tend to decrease electron density on the metal hence making a ring expansion reaction less probable.

This ligand effect is almost certainly not entirely an electronic effect and steric considerations must play some part.

\[
\begin{align*}
\text{Pt} & \left[ (\text{OMe})_3 \right]_4^+ (\text{CF}_3)_2\text{CO} \rightarrow \left[ (\text{OMe})_3 \right]_2\text{PtC(} \text{CF}_3)_2\text{OC(} \text{CF}_3)_2^0 \\
\text{Pt} & \left[ (\text{OPh})_3 \right]_4^+ (\text{CF}_3)_2\text{CO} \rightarrow \left[ (\text{OPh})_3 \right]_2\text{PtC(} \text{CF}_3)_2\text{OC(} \text{CF}_3)_2^0
\end{align*}
\]

In the above examples trimethylphosphite is a better \(\sigma\)-donor ligand than triphenylphosphite and the observed reactivity towards five membered ring formation, assuming that for trimethylphosphite as ligand the reaction goes via a reactive three membered ring intermediate, can be thought of as being due to the increased electron density on platinum in the trimethylphosphite case. However, trimethylphosphite is a far less bulky ligand than triphenylphosphite making the formation of an intermediate to the ring expansion sterically more favourable. It is likely, therefore, that five membered ring formation occurs
with trimethylphosphite as ligands, due to a combination of electronic and steric effects.

For palladium the series for the activating effect of ligands towards the ring expansion reaction,

\[
\text{L}_2\text{PdC(CF}_3\text{)}_2\text{OC(CF}_3\text{)}_2\text{O} \rightarrow \text{L}_2\text{PdC(CF}_3\text{)}_2\text{OC(CF}_3\text{)}_2\text{O},
\]

which must be considered to be due to both steric and electronic effects, is as follows:

\[
P(\text{OPh})_3 = \text{PPh}_3 = \text{MePPh}_2 = \text{Ph}_2\text{PCH}_2\text{J} < \text{P(OMe)}_3 = \text{PPh(OMe)}_2 = \text{Me}_2\text{P(CH}_2\text{Ph)} = \text{Bu}^+\text{NC}.
\]

This series is generally applicable to the analogous reaction for nickel and platinum.

**Bonding in the three membered ring systems.**

The complex \((\text{PPh}_3)_2\text{PtC(CF}_3\text{)}_2\text{O}\) will be used to illustrate the bonding occurring in this type of three membered ring system.

The \(^{19}\text{F}\) n.m.r. spectrum indicates that the molecule is planar, there being cis and trans \(^{31}\text{P}\) coupling to the C(CF\(_3\))\(_2\) group. \((J(\text{Ptrans-F})11.3\text{Hz}., J(\text{Pcis-F})1.3\text{Hz})\). The system is rigid, there being no fluxional effects.

The bonding in the molecule can be considered to be analogous to that postulated for zero-valent platinum olefin complexes. This bonding scheme was first suggested by Dewar\(^{41}\) for silver(I) olefin complexes and used by Chatt and Duncanson\(^{42}\) for platinum(II) complexes, but can be modified to discuss complexes of zero-valent platinum.
The platinum-olefin bond has two components. It is proposed that the 2p\π molecular orbital on the olefin feeds charge into a vacant \textit{sp}² hybrid orbital on platinum. Simultaneously charge is fed onto the olefin \textit{via} overlap of filled non-bonding \textit{d} orbitals on platinum and empty 2p\π* orbitals on the olefin.

Some rehybridisation occurs at the olefin carbons since the nodal plane of the filled 2p\π orbital of the olefin is not a plane of symmetry of the molecule and there will be some mixing of the \textit{σ}2s and 2p\π orbitals of the olefin.⁴³,⁴⁴. As a result, the \textit{s} and \textit{p} character at the olefin carbons will approach that found in cyclopropane. Proton n.m.r. studies of \textit{¹H} coupling constants in complexes of the type Pt(acac)X(olefin)⁴⁵ suggest that the hybridisation at the olefinic carbons approaches that for a saturated system.

This rehybridisation at the olefin carbons suggests that there is some contribution from a structure in which bonding to platinum occurs \textit{via} two platinum-carbon \textit{σ}-bonds. Support for this comes from \textit{¹³C} n.m.r. studies of zero-valent platinum ethylene and acetylene complexes.

This type of scheme can be applied to the bond between hexafluoroacetone and platinum. Electron density from the \textit{C}=0 \textit{π}-\textit{π} orbital is fed onto platinum \textit{via} overlap with a vacant \textit{sp}² hybrid orbital on platinum and back donation of electron density from a filled platinum \textit{d} orbital into the \textit{C}=0 \textit{π}-antibonding orbitals will occur. As for olefins, rehybridisation will undoubtedly occur at
the >C=O carbon and oxygen resulting in some contribution from a structure in which there is a platinum-carbon and a platinum-oxygen σ-bond. The rehybridisation of the >C=O orbitals probably results in hybridisation at carbon and oxygen approaching that found in an epoxide type system.

The bonding is illustrated by the scheme shown in Figure 1.5.

![Figure 1.5](image)

Figure 1.5.
1.2. Results and Discussion

The preparation and reactivity of some \( \pi \)-bonded ketone complexes of platinum.

The poly-ketones triketoindane, diphenyltriketone, diphenyltetraketone and alloxan contain an electron deficient carbonyl group which is susceptible to nucleophilic attack by water to give a gem-diol hydrate, Figure 1.6a.

\[
\begin{align*}
\text{triketoindane} & \xrightarrow{H_2O, 140^\circ} \text{ninhydrin} \\
\text{PhCOCOCOPh} & \xrightarrow{H_2O, \text{distil}} \text{PhCOC(OH)\textsubscript{2}COPh} \\
\text{diphenyltriketone} & \xrightarrow{H_2O, \text{distil}} \text{diphenyltriketone hydrate} \\
\text{diphenyltetraketone} & \xrightarrow{H_2O, \text{distil}} \text{diphenyltetraketone hydrate} \\
\text{alloxan} & \xrightarrow{H_2O, 150^\circ} \text{alloxan hydrate}
\end{align*}
\]

Figure 1.6a.
This suggested that these organic molecules may \( \pi \)-bond via the \( \pi_m-\pi_m \) orbitals of the electrophilic carbonyl to zero-valent platinum complexes to give complexes containing three membered metallacyclopropane type ring systems analogous to the \( \pi \)-bonded hexafluoroacetone complex \((\text{PPh}_3)_2\text{PtC}(\text{CF}_3)_2\text{O}\).

(i) Preparation

The four electrophilic ketones each gave crystalline complexes with the zero-valent platinum complexes tetrakis(triphenylphosphine)platinum(0), trans-stilbenebis-(triphenylphosphine)platinum(0) and diphenylacetylenebis-(triphenylphosphine)platinum(0) at room temperature and surprisingly the ketone hydrates gave exactly the same complexes under the same conditions.

This last observation suggests that zero-valent platinum is a powerful enough nucleophile to displace water from the hydrates. It is worth noting that the reaction with the ketone hydrates was about four times slower than with the ketones, indicating that the activation energy for the formation of the complexes from the hydrates was higher than that from the ketones as would be expected. A possible mechanism for the displacement of water is shown in Figure 1.6b.

Elemental analysis and molecular weight data indicated that the complexes formed can be represented by the general formula ketonebis(triphenylphosphine)platinum(0).
The formation of the complexes via the ketone hydrates as well as the ketones seems to be good evidence for the presence of systems π-bonded via the electrophilic carbonyl. It is unlikely that co-ordination of the ketones would occur by any of the less electrophilic carbonyl groups present in the molecules and the fact that isatin does not react with tetrakis(triphenylphosphine)-platinum(0) or trans-stilbenesbis(triphenylphosphine)platinum(0) at room temperature adds weight to this argument.

The presence of four membered ring systems analogous to that in (PPh₃)₂PtOC(CF₃)₂O formed in the triphenylphosphine reduction of (PPh₃)₂PtOC(CF₃)₂OO can be ruled out by the analytical data and the reactivity of the complexes towards ring expansion and displacement reactions, which will be discussed in later sections. Structures containing fragments of the ketones formed during oxidative-addition of the ketones, via carbon-carbon bond cleavage,
to zero-valent platinum can also be ruled out on this basis.

The complexes, on the above arguments, are assigned a structure in which the ketones are \( \pi \)-bonded by the central electrophilic carbonyl group's \( \pi \)-\( \pi \) orbitals to give the three membered ring systems shown in Figure 1.7.

\[
\text{triketoindanebis(triphenylphosphine)platinum(0)}
\]

\[
\text{diphenyltriketonebis(triphenylphosphine)platinum(0)}
\]

\[
\text{diphenyltetraketonebis(triphenylphosphine)platinum(0)}
\]

\[
\text{alloxanbis(triphenylphosphine)platinum(0)}
\]

Figure 1.7.
\((L=\text{PPh}_3)\)
These complexes all show strong carbonyl absorptions in the infrared except that with diphenyltriketone. The diphenyltriketone complex shows medium-strong absorptions at 1501 and 1492 cm$^{-1}$ in a region approximately 180 cm$^{-1}$ lower than the carbonyl absorption in free diphenyltriketone hydrate (1680 cm$^{-1}$). This suggests that the two carbonyl groups adjacent to the central π-bonded carbonyl are associated with platinum in some way which weakens their $\geq C=O$ bonds giving a lowering of their energy of absorption.

Possible mechanism for lowering in energy of $\geq C=O$ absorptions in diphenyltriketone complex.

This association is probably a weak one and similar in nature to that for the loosely bonded hexafluoroacetone in structure (XX) shown in Section 1.1. in which the carbonyl absorption appears at about 140 cm$^{-1}$ lower than in free hexafluoroacetone and which loses the molecule
of hexafluoroacetone very readily.

A similar situation probably occurs in the diphenyltetraketone complex which shows only one strong absorption in the carbonyl region at 1670 cm\(^{-1}\).

The triphenylarsine analogue of the triketoindane complex could be prepared by the reaction of triketoindane or ninhydrin with tetrakis(triphenylarsine)platinum(O).

The complexes appeared to be indefinitely stable when stored under nitrogen but in the atmosphere the dark red diphenyltriketone complex faded rapidly (after several days) to give a pale pink solid and the other complexes discoloured although not as rapidly. The triphenylarsine analogue of the triketoindane complex, which is bright yellow, discoloured rapidly to a pale brown complex after one day of exposure to the atmosphere.

Attempts to perform ligand exchange reactions on the triphenylarsine analogue of the triketoindane complex using methyldiphenylphosphine and 1,2-bis(diphenylphosphino)-ethane gave only intractable red oils or red gums, probably because of the reactivity of triketoindane towards the phosphines. In the reaction of triketoindane with tetrakis(triphenylphosphine)platinum(O) small amounts of an orange crystalline solid could occasionally be isolated (benzene insoluble), which was shown to be an adduct between triketoindane and triphenylphosphine.

Similar difficulties were experienced during attempts to prepare the 1,2-bis(diphenylphosphine)ethane and
methyldiphenylphosphine analogues of the triketoindane complex via the reactions of triketoindane with bis[1,2-bis(diphenylphosphino)ethane]platinum(O) and tetrakis(methyldiphenylphosphine)platinum(O).

Triketoindane and diphenyltriketone did not react with trans-chloro(carbonyl)bis(triphenylphosphine)iridium(I) and chlorotris(triphenylphosphine)rhodium(I) to give π-bonded ketone complexes analogous to the hexafluoroacetone complexes of rhodium and iridium.

Table I gives the colour and carbonyl absorptions in the infrared spectrum for the ketone complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>$\nu(\text{C=O})_{\text{cm}^{-1}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triketoindane</td>
<td>Yellow</td>
<td>1709m, 1678s</td>
</tr>
<tr>
<td>(PPh$_3$ complex)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diphenyltriketone</td>
<td>Dark Red</td>
<td>(1501m, 1492m)</td>
</tr>
<tr>
<td>Diphenyltetraketone</td>
<td>Orange</td>
<td>1706s</td>
</tr>
<tr>
<td>Alloxan</td>
<td>Buff</td>
<td>1716s, 1694m, 1682m, sh, 1648s, ν(N-H) 3160m, 3047m</td>
</tr>
<tr>
<td>Triketoindane</td>
<td>Yellow</td>
<td>1712m, 1684s</td>
</tr>
<tr>
<td>(AsPh$_3$ complex)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table I.
(ii) **Displacement Reactions**

The triketoindane complex reacted with hydrogen chloride and 3,4,5,6-tetrachloro-1,2-benzoquinone to give respectively, cis-dichlorobis(triphenylphosphine)platinum(II) and 3,4,5,6-tetrachloro-1,2-benzoquinonebis(triphenylphosphine)platinum(II), these reactions being straightforward oxidative-addition reactions with displacement of triketoindane. Attempts to isolate organic products from these reactions only produced oils whose infrared spectra showed absorptions in the carbonyl region but from which no useful information could be deduced.

Hexafluorobut-2-yne reacted with the triketoindane complex at 60° to give hexafluorobut-2-ynebis(triphenylphosphine)platinum(0) with displacement of triketoindane. The reaction also proceeded at room temperature to give the hexafluorobut-2-yne complex along with two ring expanded products, which will be discussed in a later section. With hexafluoroacetone and tetracyanoethylene ring expanded, rather than displacement products were obtained.

The above observations and the fact that the triketoindane complex can be prepared from trans-stilbene-bis(triphenylphosphine)platinum(0) and diphenylacetylene-bis(triphenylphosphine)platinum(0) enables triketoindane to be fitted into a stability series for bis(triphenylphosphine)platinum complexes:

trans-stilbene < diphenylacetylene < triketoindane < hexafluorobut-2-yne.
At room temperature the triphenylarsine analogue of the triketoindane complex reacted with hexafluorobut-2-yne to give the displacement product hexafluorobut-2-ynebis(triphenylarsine)platinum(0) and a ring expanded product.

Tetrafluoroethylene and fumaronitrile appeared not to react with the diphenyltriketone complex at room temperature but at 60° reactions occurred to give tetrafluoroethylenebis(triphenylphosphine)platinum(0) and fumaronitrilebis(triphenylphosphine)platinum(0) respectively in straightforward displacement reactions. The reaction with hexafluorobut-2-yne at 60° gave the displacement product hexafluorobut-2-ynebis(triphenylphosphine)platinum(0) and two ring expansion products which were the sole products of the reaction at room temperature and will be discussed later.

Hexafluoroacetone reacted with the diphenyltriketone complex at room temperature to give the displacement product hexafluoroacetonebis(triphenylphosphine)platinum(0) and a ring expanded product.

Tetracyanoethylene yielded only a ring expanded product.

On the basis of this data it is possible to fit the diphenyltriketone complex into a stability series for the bis(triphenylphosphine)platinum complex:

\[ \text{trans-stilbene} < \text{diphenylacetylene} < \text{diphenyltriketone} < \text{(fumaronitrile, hexafluorobut-2-yne, tetrafluoroethylene, hexafluoroacetone)} \]
(iii) Reactions with oxygen and the reactions of the ketones and their hydrates with peroxobis(triphenylphosphine)platinum(II).

The four ketone complexes reacted slowly with atmospheric oxygen in the solid state, but rapidly in solution or benzene suspension. Elemental analysis and molecular weight data indicated that for the complexes of triketoindane, diphenyltriketone and diphenyltetraketone 1:1 adducts were formed with oxygen, but for the alloxan complex it was found to be impossible to obtain a pure sample of the oxygen adduct and even after several recrystallisations the white complex showed extremely broad absorptions in the carbonyl region of the infrared spectrum.

The 1:1 adduct formed between the triketoindane complex and oxygen was a white crystalline solid showing carbonyl absorptions at 1752 and $1675 \text{ cm}^{-1}$ and strong absorptions at 1315 and $1275 \text{ cm}^{-1}$ in the infrared spectrum. The same complex could be isolated from the reaction between triketoindane and peroxobis(triphenylphosphine)-platinum(II) and surprisingly from the reaction between ninhydrin and peroxobis(triphenylphosphine)platinum(II). This one complex isolated from these three reactions might be expected to have a five membered ring structure involving a peroxo group analogous to the systems formed between peroxobis(triphenylphosphine)platinum(II) and aldehydes and ketones. However, it has been shown that $\alpha$-diketones, when involved in this type of five membered ring structure
rearrange to give dicarboxylate complexes. When the α-diketone is glyoxal, a diketone which hydrates to give a monohydrate, the five membered ring system cannot be isolated, but only the dicarboxylate, which is probably formed via an unstable five membered ring intermediate, Figure 1.8.

![Diagram](image)

**Figure 1.8.**

(L=PPh₃; R=alkyl or aryl; R=H for glyoxal)

By analogy to the reaction with glyoxal it seems reasonable to expect triketoiandane to undergo a similar reaction to yield the dicarboxylate complex via an unstable peroxo five membered ring complex.

The strong absorptions in the infrared spectrum at 1315 and 1275 cm⁻¹ can be assigned to vsym(OCO) for the carboxylate complex and one of the bands in the carbonyl region (probably 1675 cm⁻¹) can be assigned to vas(OCO),
the other being due to the carbonyl adjacent to the aromatic system (1752 cm\(^{-1}\)).

These absorptions in the infrared spectrum fall reasonably well into the regions of characteristic absorptions for unidentate carboxylate groups bonded to platinum. Table II shows the values of \(\nu_{\text{sym}}(\text{OCO})\) and \(\nu_{\text{as}}(\text{OCO})\) for some unidentate carboxylate-bis(triphenylphosphine)platinum(II) complexes.

<table>
<thead>
<tr>
<th>Carboxylate complex</th>
<th>(\nu_{\text{as}}(\text{OCO}) \text{ cm}^{-1})</th>
<th>(\nu_{\text{sym}}(\text{OCO}) \text{ cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{PPh}_3)_2\text{Pt}(\text{OCOCH}_3)_2)(^{47})</td>
<td>1634,1597</td>
<td>1308,1299</td>
</tr>
<tr>
<td>((\text{PPh}_3)_2\text{Pt}(\text{OCOCF}_3)_2)(^{47})</td>
<td>1727,1700</td>
<td>1400</td>
</tr>
<tr>
<td>((\text{PPh}_3)_2\text{Pt}(\text{OCO})_2\text{C}_6\text{H}_4)(^{48})</td>
<td>1645</td>
<td>1332,1307</td>
</tr>
</tbody>
</table>

**Table II**

On this evidence the 1:1 adduct between oxygen and the triketoindane complex and between triketoindane (or ninhydrin) and peroxobis(triphenylphosphine)platinum(II) is assigned the dicarboxylate structure (XXXX) which is most probably formed via an unstable peroxyo five membered ring. The formation of the dicarboxylate complex involves the ring opening of the triketoindane five membered ring system.
This reaction is analogous to the reaction of 1,2-benzocyclobutadienequinone with peroxobis(triphenylphosphine)platinum to give the carboxylate complex (XXXI)\(^{49,50}\) (see Table II) which is probably also formed via an unstable peroxo five membered ring complex.

The reactions of triketoin dane and 1,2-benzocyclobutadienequinone with peroxobis(triphenylphosphine)platinum(II) therefore both lead to ring opening of the cyclic ketones.

Oxygen reacted rapidly with the diphenyltriketone
complex to give a white crystalline complex which showed absorptions in the carbonyl region of the infrared spectrum at 1640s, 1639m and 1624m cm\(^{-1}\) and strong absorptions at 1356 and 1326 cm\(^{-1}\) but no absorptions between 850 and 760 cm\(^{-1}\), the region in which \(\nu(0-0)\) absorptions occur in peroxy five membered ring complexes.

By analogy to the adduct formed between oxygen and the triketoindane complex this complex is assigned a dicarboxylate structure, one of the absorptions in the carbonyl region of the infrared spectrum being assignable to \(\nu_{as}(OCO)\) and the absorptions at 1356 and 1326 cm\(^{-1}\) to \(\nu_{sym}(OCO)\). Again the dicarboxylate is most likely formed via unstable peroxy five membered ring, which rearranges rapidly to give the dicarboxylate structure (XXXII).

\[
\begin{align*}
\text{L}_1\text{PtO} & \\
\text{L}_2\text{COCOPh} & \\
\text{CO} & \\
\phi_h & \\
\text{Ph} & \\
\downarrow & \\
\text{O}_2 & \\
\rightarrow & \\
\left[\text{L}_1\text{PtO_2C_cOPh}\right] & \\
\rightarrow & \\
\text{L}_1\text{OCOCOPh} & \\
\text{L}_2\text{OCOCOPh} & \\
\end{align*}
\]

(XXXII)(L=PPPh\(_3\))

The reaction of diphenyltriketone with peroxybis(triphenylphosphine)platinum(II) yielded a complex different to (XXXII) but which was a 1:1 adduct between diphenyltriketone and peroxybis(triphenylphosphine)platinum(II) and showed two absorptions in the carbonyl region of the infrared spectrum at 1696s and 1678s cm\(^{-1}\). There were no bands
assignable to $\nu_{\text{sym}}(\text{OCO})$ for an unidentate carboxylate group but there were weak absorptions at 812 and 788 cm$^{-1}$ either of which could be assigned to $\nu(0-O)$ in a peroxo five membered ring structure.$^{34,35}$

The presence of two carbonyl absorptions and the lack of absorptions assignable to $\nu_{\text{sym}}(\text{OCO})$ suggests a peroxo five membered ring structure involving a carbonyl group adjacent to the phenyl groups. Since this carbonyl group is less electrophilic than the central carbonyl group and does not hydrate an analogy can be drawn with the reaction of $\alpha$-diketones with peroxobis(triphenylphosphine)platinum(II) which gives peroxo five membered ring systems which rearrange slowly to dicarboxylate complexes.$^{38}$

The infrared data suggests that the complex has structure (XXXXIII) which would be expected to rearrange slowly to give a dicarboxylate complex identical to the one shown in structure (XXXXII).

![Diagram](image)

A sample of the complex was allowed to stand for several months after which the white solid had become pale
yellow. An infrared spectrum of the aged complex showed absorptions identical to those for the dicarboxylate (XXXXII) showing that slow rearrangement of the peroxo five membered ring system to the dicarboxylate had occurred.

The reaction of diphenyltriketone hydrate with peroxobis(triphenylphosphine)platinum(II) gave two white crystalline products.

The product in highest yield (41%) was identical to that obtained in the reaction between diphenyltriketone and peroxobis(triphenylphosphine)platinum(II), (XXXXIII). This reaction must initially involve formation of a peroxo five membered ring with a carbonyl group adjacent to phenyl and then loss of water from the unstable gem-diol system formed to give (XXXXIII), Figure 1.9.

\[
\text{L}_2\text{PtOO} + \text{PhCOC(OH)}_2\text{COPh} \xrightarrow{\Delta} \begin{array}{c}
\text{L} \\
\text{Pt}
\end{array} \begin{array}{c}
\text{O} \\
\text{O} \\
\text{C} \\
\text{Ph}
\end{array} + \text{H}_2\text{O}
\]

(XXXXIII)  

Figure 1.9.
The product formed in lowest yield (24%) was identical to that formed in the reaction between oxygen and the diphenyltriketone complex, (XXXXII). This reaction is analogous to that between ninhydrin and peroxobis(triphenylphosphine)platinum(II) which yields a product identical to that formed in the reaction between triketoindane and peroxobis(triphenylphosphine)platinum(II), (XXXX). That is, before (XXXXII) or (XXXX) can be formed water has to be displaced from the gem-diol hydrates to reveal the central electrophilic carbonyl groups which can then give the observed products.

Possible mechanism for formation of (XXXXII) in reaction of \((\text{PPh}_3)_2\text{PtO}_2\) with \(\text{PhCOC(OH)}_2\text{COPh}\).

(A similar mechanism can be envisaged for the reaction of ninhydrin with \((\text{PPh}_3)_2\text{PtO}_2\) to yield (XXXX).)

It seems unlikely that peroxobis(triphenylphosphine)platinum(II) is a strong enough nucleophile to displace water from the
ketone hydrates but this appears to be the only explanation available.

The diphenyltetraketone complex reacted with oxygen to give a white crystalline complex which showed absorptions in the carbonyl region of the infrared spectrum at 1684, 1641 and 1630 cm\(^{-1}\) and strong absorptions at 1324, 1316 and 1302 cm\(^{-1}\). By analogy to the oxygen adducts of the triketoindane and diphenyltriketone complexes this complex is assigned a dicarboxylate structure in which the absorptions in the infrared spectrum at 1324, 1316 and 1302 cm\(^{-1}\) are due to vsym(OCO) and one or more of absorptions in the carbonyl region due to vas(OCO). The dicarboxylate is again most likely formed via an unstable peroxo five membered ring structure which in this case can rearrange to give two possible carboxylates, (XXXXIVa) and (XXXXIVb).
Structure (XXXXIVa), the unsymmetrical dicarboxylate seems unlikely since the central carbonyl group of the carboxylate group involving three carbonyl groups would be electrophilic enough to hydrate to the gem-diol (cf. diphenyltriketone) and the lack of $\nu$(O-H) absorptions in the infrared spectrum precludes this. Hence the complex can be assigned structure (XXXXIVb), the symmetrical dicarboxylate.

A preliminary investigation of the reaction of diphenyltetraketonehydrate with peroxobis(triphenylphosphine)platinum(II) yielded a white crystalline complex in low yield (32%) which was shown to be identical to the product from the reaction of the diphenyltetraketone complex with oxygen. This reaction can presumably go by direct reaction with the carbonyl group $^1\text{CO}^2\text{CO}^3\text{Ph}$ to give an intermediate peroxo five membered ring complex, with loss of water or by displacement of water from the gem-diol and then reaction with the carbonyl group so formed (carbonyl group $^3\text{CO}^4\text{Ph}$) to again give an intermediate peroxo five membered ring complex with, in each case, rapid rearrangement to dicarboxylate (XXXXIVb).
Possible mechanisms for the formation of (XXXXIVb) in the reaction of $(\text{PPh}_3)_2\text{PtOO}$ with $\text{PhCOC(OH)}_2\text{COCOPh}$

$(L=\text{PPh}_3)$
The triphenylarsine analogue of the triketoindane complex reacted rapidly with oxygen in solution or benzene suspension and the white crystalline complex isolated was shown to be a 1:1 adduct with oxygen by elemental analysis and molecular weight determination. The infrared spectrum of the complex was very similar to that shown by the triphenylphosphine analogue with strong absorptions in the carbonyl region at 1755 and 1679 cm$^{-1}$ and absorptions at 1313 and 1271 cm$^{-1}$. A dicarboxylate structure (XXXX) ($L$=AsPh$_3$) is assigned to this complex in which the bands in the infrared spectrum at 1313 and 1271 cm$^{-1}$ are assigned to $\nu_{\text{sym}}$(OCO) and one of the bands at 1755 and 1679 cm$^{-1}$ to $\nu_{\text{as}}$(OCO).

Assuming that in the reactions of oxygen with the triketoindane, diphenyltriketone and diphenyltetraketone complexes the formation of the observed dicarboxylate complexes goes via an unstable peroxo five membered ring intermediate these can be regarded as reactions going by an initial ring expansion reaction of the ketone three membered ring systems.

(iv) **Reactions with ketones.**

Reactions with hexafluoroacetone will be dealt with under a separate heading.

The triketoindane complex did not react with diphenyltriketone and 9-fluorenone at room temperature or with degassed acetone, while under reflux. In oxygenated acetone a reaction occurred to produce the oxygen adduct (XXXX).
With triketoindane the triketoindane complex gave a bright yellow crystalline complex which elemental analysis and molecular weight determination showed was a 1:1 adduct between triketoindane and the triketoindane complex. The complex showed absorptions in the carbonyl region of the infrared spectrum at 1743\text{m} and 1706\text{s} cm\textsuperscript{-1} in contrast to absorptions at 1709\text{m} and 1678\text{s} for the triketoindane complex.

Hexafluoroacetone has been shown to ring expand hexafluoroacetone-platinum phosphine complexes\textsuperscript{28,26} but not the triphenylphosphine-hexafluoroacetone complex.\textsuperscript{1} The ring expansion reaction only appears to occur when the phosphine is basic enough to give increased electron density on platinum so that sufficient electron density is available on platinum for the incoming hexafluoroacetone molecule to co-ordinate and form, perhaps, a six co-ordinate intermediate which then rearranges to give the ring expanded product.

Triketoindane is almost certainly less electrophilic than hexafluoroacetone. Therefore there will be sufficient electron density on the platinum in the triketoindane complex to allow co-ordination of a second molecule of triketoindane so that ring expansion can occur. The resulting complex can have one of three structures, (XXXVa), (XXXVb) and (XXXVc).

\[
\begin{align*}
\text{(XXXVa)} & \quad \text{(XXXVb)} & \quad \text{(XXXVc)} \\
\text{(L=PPh}_3\text{)}
\end{align*}
\]
In ring expansion reactions of hexafluoroacetone complexes by hexafluoroacetone (see Section 1.1. Nickel, Palladium, Platinum) ring expansion occurs to give carbon to oxygen (head to tail) bonded five membered ring systems, analogous to structure (XXXXVc).

Structure (XXXXVa) can reasonably be eliminated as there would undoubtedly be strong repulsion between the $\pi$-systems of the aromatic rings and the polar carbonyl groups rendering the formation of this configuration from, say, a six co-ordinate intermediate unfavourable.

The structure (XXXXVb) would be expected to show $\nu(O-O)$ for the peroxo group in the region of 800 cm$^{-1}$ by analogy to the peroxo five membered ring complexes formed between peroxobis(triphenylphosphine)platinum(II) and aldehydes and ketones which show $\nu(O-O)$ in this region.\textsuperscript{34,35}  A lack of absorptions in the infrared spectrum between 859 and 776 cm$^{-1}$ suggests that structure (XXXXVb) can be eliminated.

The evidence, therefore, seems to indicate that structure (XXXXVc) can be assigned to the complex, but the complex undergoes some interesting reactions which suggest another possible structure.

Hexafluorobut-2-yne did not react with the bis-triketoindane complex at room temperature but at 60$^\circ$ both molecules of triketoindane were readily displaced to give hexafluorobut-2-ynebis(triphenylphosphine)platinum(0). At room temperature, the complex reacted with hexafluoroacetone to give red crystals of triketoindane and two bis(triphenyl-
phosphine)platinum complexes containing triketoindane and hexafluoroacetone in the ratios of 1:1 and 1:2. These two products could also be isolated from the reaction of the mono-triketoindane complex with hexafluoroacetone and are assigned five and seven membered ring structures, which will be discussed in a later section.

The reaction with hexafluorobut-2-yne indicates that both triketoindane molecules are reasonably readily displaced. That with hexafluoroacetone suggests that one molecule of triketoindane can be displaced readily facilitating the formation of the five and seven membered ring systems. The fact that the identical five and seven membered ring systems can be isolated from the reaction of the mono-triketoindane complex with hexafluoroacetone adds weight to this deduction.

It is possible that this type of reaction goes via breakdown of the five membered ring to give an intermediate of the type (XXXXVIa),

![Diagram](image)

(XXXXVIa) \(L = \text{PPh}_3\)

which can then react with hexafluoroacetone with
displacement of one molecule of triketoindane to give the observed five and seven membered ring structures (See Section (vii) or with hexafluorobut-2-yne to give (XXXXVIb),

\[ \text{(XXXXVIb) } (L=\text{PPh}_3) \]

which breaks down to give hexafluorobut-2-ynebis(tri-phenylphosphine)platinum(0). However, it is not possible to rule out (XXXXVIa) as a possible structure for the bis-triketoindane complex and an X-ray crystallographic study of this complex is presently being undertaken.

The reaction of the bis-triketoindane complex with excess trifluoroacetic acid gave in high yield (90%) the alcohol 2-hydroxy-1,3-indandione (XXXXVII) and bis(trifluoroacetate)bis(triphenylphosphine)platinum(II).

\[ \text{(XXXXVII)} \]

This reaction could occur by breakdown of the five membered
ring system via cleavage at the ether linkage or, perhaps, via the π-bonded intermediate (XXXXVIa). It is interesting to note that the reaction of trifluoroacetic acid with diphenylacetylenebis(triphenylphosphine)platinum(0) yields trans-stilbene and bis(trifluoroacetate)bis(triphenylphosphine)platinum(II) and a similar reaction of the acid with a π-ketone complex could occur here.

The diphenyltriketone complex did not react with diphenyltriketone to give a complex analogous to that formed between the triketoindane complex and triketoindane. Neither could a product be obtained in acetone at 70° or in strong ultraviolet radiation.

The dark red diphenyltriketone complex reacted with triketoindane to give a yellow crystalline product, which elemental analysis and molecular weight determination indicated to be a 1:1 adduct with triketoindane.

The yellow complex showed absorptions in the carbonyl region of the infrared spectrum at 1737, 1704, 1680 and 1658 cm⁻¹. If this complex is a ring expanded five membered ring complex, as seems likely, there are four possible structures, (XXXXVIIIa), b, c and d.
Structure (XXXVIIIId) can possibly be ruled out on steric grounds, the bulky groups attached to the carbon atoms making the formation of the structure unlikely.

The complex shows weak absorptions at 807 and 792 cm\(^{-1}\) in the infrared spectrum which are assignable to \(\nu(0-0)\) and hence (XXXVIIIb) must be considered to be a possible structure. The observation that hexafluoroacetone five membered ring systems have carbon to oxygen (head to tail) configurations implies, by analogy, that either of (XXXVIIIa) or (XXXVIIIc) is the most probable structure.

The triphenylarsine analogue of the triketoindane complex also reacted with triketoindane to give a bright yellow complex, which was shown to be a 1:1 adduct between the triphenylarsine triketoindane complex and triketoindane by elemental analysis and molecular weight determination. The infrared spectrum was almost identical to that of the triphenylphosphine analogue and hence can be given the
same structural assignments.

(v) Reactions with tetracyanoethylene.

The triketoindane complex reacted with tetracyanoethylene at room temperature or 60° to give a white crystalline complex and a yellow crystalline complex both of which were stable in solution.

Elemental analysis and molecular weight determination indicated that the white complex was a 1:1 adduct between the triketoindane complex and tetracyanoethylene. The infrared spectrum (nujol mull) showed v(C≡N) at 2229 cm⁻¹ and strong, sharp absorptions in the carbonyl region at 1741m and 1712 cm⁻¹ in contrast to absorption at 1708m, and 1670s cm⁻¹ for the triketoindane complex.

Tetracyanoethylene does not form a charge transfer adduct with ninhydrin and hence is less likely to form one with the bonded triketoindane system on steric grounds. This product is most probably a ring expanded product involving tetracyanoethylene and triketoindane in a five membered ring system. In this case there are two possible structures for the complex (XXXXIXa) or (XXXXIXb). An X-ray crystal structure study would appear to be the only possible way of distinguishing between these two structures.
The yellow crystalline complex was shown to be a 1:2 adduct between the triketoindane complex and tetracyanoethylene by elemental analysis and molecular weight determination. The infrared spectrum showed $\nu(C=\!N)$ at 2205 cm$^{-1}$ and strong sharp absorptions in the carbonyl region at 1744 cm$^{-1}$ and 1713 cm$^{-1}$. There was a strong absorption at 1618 cm$^{-1}$ and another absorption at 1544 cm$^{-1}$.

Again, it seems unlikely that this is a charge transfer complex. The strong band at 1618 cm$^{-1}$ occurs in the region for $\nu(C=\!N)$ absorptions, suggesting that the complex incorporates the fragment shown in Figure 1.10.

![Figure 1.10.](attachment:image.png)

The positions of the carbonyl absorptions in this complex are almost identical to the positions in the 1:1 adduct (1:1 adduct 1741 cm$^{-1}$ and 1712 cm$^{-1}$; 1:2 adduct 1744 cm$^{-1}$ and 1713 cm$^{-1}$). This suggests that tetracyanoethylene and triketoindane are in the same arrangement as in (XXXXIXa) or (XXXXIXb), any modification due to the presence of a second molecule of tetracyanoethylene being in a position in the structure having little effect upon the energy of the carbonyl absorptions. This would be the case if the fragment shown in Figure 1.10 were inserted in
the platinum-carbon(tetracyanoethylene) bond of (XXXIXa) or (XXXIXb) and very tentatively it is suggested that this is the case. In other words, the complex involves a seven membered ring which incorporates a cyano group of the tetracyanoethylene. Possible structures for the complex are (La) or (Lb) and (Lc) or (Ld).

\[
\begin{align*}
\text{(La);} & \quad \text{(Ld);} \\
\text{(Lb) (C and N reversed);} & \quad \text{(Lc) (C and N reversed)} \\
(X = (CN)C≡C(CN)_2; L = PPh}_3) \\
\end{align*}
\]

Tetracyanoethylene reacted very rapidly with the diphenyltriketone complex at room temperature to give a white crystalline complex in high yield (94%). Elemental analysis and molecular weight determination indicated that the complex was a 1:1 adduct between the diphenyltriketone complex and tetracyanoethylene (incorporating one molecule of methylene chloride).

The complex showed v(C≡N) at 2225 and 2210 cm\(^{-1}\) and a strong sharp absorption in the carbonyl region at 1665 cm\(^{-1}\) in the infrared spectrum. Again it seems unlikely
that this is a charge transfer complex and it is most probably an analogous ring expanded product, for which there are two possible structures, (L\text{Ia}) and (L\text{Ib}).

\begin{align*}
\text{(L\text{Ia})} & \quad \begin{array}{c}
\text{Pt} \\
\text{L} \\
\text{PhOC} \\
\text{COPh}
\end{array} \\
& \quad \begin{array}{c}
\text{C} \\
\text{C} \\
\text{CN}_2 \\
\text{CN}_2
\end{array} \\
& \quad \begin{array}{c}
\text{L'}
\end{array} \\
& \quad \text{Ph}_{3} \text{P}
\end{align*}

\begin{align*}
\text{(L\text{Ib})} & \quad \begin{array}{c}
\text{Pt} \\
\text{L} \\
\text{O} \\
\text{COPh}
\end{array} \\
& \quad \begin{array}{c}
\text{C} \\
\text{C} \\
\text{CN}_2 \\
\text{CN}_2
\end{array} \\
& \quad \begin{array}{c}
\text{L'}
\end{array} \\
& \quad \text{Ph}_{3} \text{P}
\end{align*}

\text{(L=PPh}_3\text{)}

(vi) \text{ Reactions with hexafluorobut-2-yne.}

As mentioned in Section (ii) hexafluorobut-2-yne reacts with the triketoindane complex at 60° to give hexafluorobut-2-ynebis(triphenylphosphine)platinum(0). However, when the triketoindane complex and hexafluorobut-2-yne were allowed to react at room temperature for two months three products could be isolated. The first two products were shown to be the 1:1 adduct between the triketoindane complex and triketoindane and hexafluorobut-2-ynebis(triphenylphosphine)platinum(0). This reaction is represented in Figure 1.11.

\begin{equation}
\begin{array}{c}
\text{2Pt} \\
\text{L} \\
\text{PhOC} \\
\text{COPh} \\
\text{C}
\end{array} + \text{C}_4\text{F}_6 \rightarrow \begin{array}{c}
\text{Pt} \\
\text{L} \\
\text{O} \\
\text{COPh} \\
\text{C}
\end{array} + \text{L}_2\text{PtC}_4\text{F}_6
\end{equation}

\text{Figure 1.11. (L=PPh}_3\text{)}
The scheme indicates that the triketoindane complex in the presence of hexafluorobut-2-yne is unstable with respect to the formation of the five membered ring system and the hexafluorobut-2-yne complex.

The third product isolated from the reaction was a yellow crystalline complex. Elemental analysis and molecular weight determination indicated that the complex was a 1:1 adduct between the triketoindane complex and hexafluorobut-2-yne.

An infrared spectrum showed strong absorptions in the carbonyl region at 1718 and 1704 cm\(^{-1}\) and weak absorptions at 1751 and 1744 cm\(^{-1}\) and strong absorptions between 1250 and 1100 cm\(^{-1}\) due to \(\nu(C-F)\).

The \(^{19}\)F n.m.r. spectrum showed two signals each due to different -CF\(_3\) environments. The signal at high field (-7.05 p.p.m.) was a well defined quartet due to coupling with three equivalent fluorines, the fluorine-fluorine coupling constant (J(F-F)15Hz) indicating a cis configuration for the -CF\(_3\) groups. The low field signal (-13.6 p.p.m.) was a complex multiplet which appeared to be a triplet of quartets, the triplet coupling being 19.5Hz. It was not possible to determine the relative intensities of the triplet components but, assuming that the signal is due to -CF\(_3\) on a carbon \(\sigma\)-bonded to platinum as seems likely, then the magnitude of the coupling suggests that it is due to two equivalent \(^{31}\)P nuclei rather than \(^{195}\)Pt. For the complex trans-(PPh\(_3\))\(_2\)-Pt[\(\text{C(CF}_3\)=CHCF\(_3\)](OCOCF\(_3\))\(^{51,53}\) the -CF\(_3\) group on the carbon
bonded to platinum shows a coupling due to $^{195}\text{Pt}$ of 84Hz and for the equivalent cis complex 90Hz.

On this evidence the complex is assigned a five membered ring structure, which incorporates hexafluorobut-2-yne and triketoindane in the five membered ring and which can have one of two structures, (LIIa) or (LIIb).

The apparent equivalence of the phosphine ligands could be due to a dissociation effect similar to that found in the complex $[\text{P(OPh)}_3]_2\text{PtC}_2\text{O}^{26}$ which shows a triplet resonance in the $^{19}\text{F}$ n.m.r. and has a low molecular weight in solution. A dissociation of the phosphite ligands presumably leads to averaging of $J(\text{P cis-F})$ and $J(\text{P trans-F})$ on the n.m.r. time scale. In chloroform the complex (LII) shows a rather low molecular weight (951; M 1041.9) which adds weight to this suggestion.

The chemical shifts of the $-\text{CF}_3$ groups in this complex (-7.05 and -13.6 p.p.m.) are very close to those in the analogous complex with diphenyltriketone.
(-7.42 and -15.3 p.p.m.) which has a structure analogous to (LIIb) on the basis of its reaction with hydrogen chloride. This strongly suggests that the complex with triketoindane has structure (LIIb).

One of the absorptions in the infrared spectrum in the region of 1600 cm\(^{-1}\) (1604w, 1598w and 1587w cm\(^{-1}\)) is assignable to \(v(C=C)\) for the complex.

The low yield of the complex (11%) made an investigation of its chemistry impracticable.

The triphenylarsine analogue of the triketoindane complex undergoes a similar reaction with hexafluorobut-2-yne but much more rapidly (2 days) suggesting that the complex with triphenylarsine involves a more reactive three membered ring system. Only two products could be isolated from the reaction, the 1:1 adduct formed between the triphenylarsine analogue of the triketoindane complex and triketoindane, and hexafluorobut-2-ynabis(triphenylarsine)-platinum(0). There was no evidence to suggest that ring expansion with hexafluorobut-2-yne to give a five membered ring system occurred in this reaction.

Hexafluorobut-2-yne reacted slowly at room temperature (seven days) with the diphenyltriketone complex to give two products, a white crystalline complex and a yellow crystalline complex.

Elemental analysis and molecular weight determination for the white complex indicated that it was a 1:1 adduct between hexafluorobut-2-yne and the diphenyltriketone complex.
In the infrared spectrum there was a strong absorption in the carbonyl region at 1676 cm\(^{-1}\) and strong absorptions between 1250 and 1100 cm\(^{-1}\) due to \(\nu(C-F)\).

The \(^{19}\)F n.m.r. spectrum was very similar to that for the 1:1 adduct between hexafluorobut-2-yne and the triketoiindane complex. There were two signals each due to different -CF\(_3\) environments. The signal at high field (-7.42 p.p.m.) was a well defined quartet (\(J(F-F)=16.5\) Hz) and the signal at low field (-15.33 p.p.m.) a complex multiplet, which appeared to be a triplet of quartets with a triplet coupling of 19.5 Hz. Again, the relative intensities of the triplet components could not be discerned but the low value of the coupling suggests that it is not due to \(^{195}\)Pt, but rather to two equivalent \(^{31}\)P nuclei, a dissociation effect averaging \(J(\text{Ptrans-F})\) and \(J(\text{Pcis-F})\). The molecular weight of the complex in benzene is rather low (997; M 1119.9) which adds weight to this suggestion.

On this evidence, the complex can be assigned one of the two ring expanded structures (LIIIb) or (LIIIa).
One of the absorptions in the region of 1600 cm\(^{-1}\) in the infrared spectrum (1593\(\nu\), 1588\(\nu\)\(w\), 1576\(\nu\)\(w\) cm\(^{-1}\)) is assignable to \(\nu(C=C)\).

The reaction of the complex in methylene chloride with gaseous hydrogen chloride yielded a white crystalline solid, which elemental analysis and molecular weight determination indicated was a 1:1 adduct between the complex and hydrogen chloride. An infrared spectrum of the complex showed absorptions in the carbonyl region at 1698\(m\) and 1676\(s\) cm\(^{-1}\), an absorption in the \(\nu(O-H)\) region at 3340 cm\(^{-1}\), an absorption due to \(\nu(Pt-Cl)\) at 301 cm\(^{-1}\) and strong absorptions due to \(\nu(C-F)\) between 1250 and 1100 cm\(^{-1}\). This data strongly suggests that the complex is derived from structure (LIIIb), hydrogen chloride having cleaved the platinum-oxygen bond to give ring opening with the formation of a platinum-chlorine bond and an \(-OH\) group.

The \(^{19}\)F n.m.r. spectrum showed two signals, the high field signal (−9.65 p.p.m.) being a well defined quartet (\(J(F-F)19.5\)Hz) and the signal to low field (−18.7 p.p.m.) a quartet of double-doublets. The low field signal is due to a \(-CF_3\) on a carbon, which is \(\sigma\)-bonded to platinum showing cis and trans \(^{31}\)P coupling (\(J(Pcis-F)3.0\)Hz, \(J(Ptrans-F)6.9\)Hz).

From this data, the complex is assigned the ring opened structure (LIV) with the phosphines in a cis configuration.

\[
\begin{array}{c}
\text{L}^+\text{Pt}^\text{Cl}^-\text{C}==\text{C}\text{COPh} \\
\text{L'}^+\text{Pt}^\text{Cl}^-\text{COPh}
\end{array}
\]

(LIV) (L=\(\text{PPh}_3\))
This complex can only be derived from structure (LIIIb) for the 1:1 adduct between the diphenyltriketone complex and hexafluorobut-2-yne and hence this complex can be assigned this structure.

One of the absorptions in the infrared spectrum in the region of 1600 cm\(^{-1}\) (1595\(^w\), 1588\(^vw\), 1580\(^w\), 1573\(^vw\) cm\(^{-1}\)) is assignable to \(\nu(C=C)\).

The complex (LIIIb) did not react with trifluoroacetic acid.

An analogous ring opening reaction of the five membered ring complex \(\text{L}_2\text{PdCR=CR=CR} (\text{L} = \text{AsPh}_3, \text{PPh}_3, \text{MePPh}_3; \text{R} = \text{CO}_2\text{Me})\) has been shown to take place\(^{54}\) on treatment with one equivalent of acid, to give (LV) in which the phosphines (or arsines) are in a trans configuration. The structure of this complex has been confirmed by an X-ray crystal structure study.

\[ \text{LV} \quad (\text{L} = \text{AsPh}_3, \text{PPh}_3, \text{MePPh}_3; \text{R} = \text{CO}_2\text{Me}) \]

The yellow crystalline complex obtained in the reaction of hexafluorobut-2-yne with the diphenyltriketone complex was shown to be a 1:1 adduct with hexafluorobut-2-yne by elemental analysis and molecular weight determination.
This second isomer isolated from this reaction most probably has structure (LIIIa).

Thus an infrared spectrum showed absorptions in the carbonyl region at 1647 and 1625 cm\(^{-1}\) and strong absorptions due to \(\nu(C-F)\) between 1350 and 1100 cm\(^{-1}\).

The \(^{19}F\) n.m.r. spectrum showed two signals due to two \(-CF_3\) environments. The high field signal (+1.2 p.p.m.) was a well defined quartet due to coupling with three equivalent fluorines, the magnitude of the coupling \((J(\text{F-F})13.3\text{Hz})\) indicating a \textit{cis} configuration for the \(-CF_3\) groups.\(^{52}\) The low field signal (-9.98 p.p.m.) was a quartet of triplets, the triplet coupling being 11.4Hz. As the coupling on the low field signal is most certainly too small for \(^{195}\text{Pt}\) coupling it is probably due to two equivalent \(^{31}\text{P}\) nuclei, again a dissociation effect averaging \(J(\text{Pcis-F})\) and \(J(\text{Ptrans-F})\). In this case coupling due to \(^{195}\text{Pt}\) was not observed in the \(^{19}F\) n.m.r. spectrum.

The signal to low field has a chemical shift which is characteristic for \(-CF_3\) on carbon \(\sigma\)-bonded to
platinum in complexes of the type \( L_2\text{Pt}(\text{CF}_3\text{C}≡\text{CHCF}_3)\) \( X\) \( (L=\text{PPh}_3, \text{AsPh}_3, \text{MePPh}_2, \text{Me}_2\text{PPh}, \text{Et}_2\text{PPh}; X=\text{OCOCF}_3, \text{Cl}, \text{Br}) \).\(^{53}\)

The large chemical shift between the \(-\text{CF}_3\) groups and the coupling between them, which indicates that they are in a cis configuration, suggests that hexafluorobut-2-yne is incorporated in a five membered ring system with diphenyltriketone. A comparison of the chemical shift of the well defined quartet (+1.18 p.p.m.) with that of the well defined quartet of the white 1:1 adduct (LIIIb) (-7.42 p.p.m.) suggests that the \(-\text{CF}_3\) group in the yellow 1:1 adduct is not as deshielded as the \(-\text{CF}_3\) group in the white 1:1 adduct. This situation occurs if the yellow 1:1 adduct has structure (LIIIa) in which the \(-\text{CF}_3\) group is protected from the highly electron withdrawing carbonyl groups of the diphenyltriketone fragment by oxygen. The white 1:1 adduct has structure (LIIIb) where the chemical shift of the \(-\text{CF}_3\) group will be influenced by the close proximity of the carbonyl groups.

These observations suggest that the yellow 1:1 adduct has structure (LIIIa).

In the infrared spectrum one of the absorptions in the region of 1600 cm\(^{-1}\) (1601vw, 1597w, 1584vw, 1570w cm\(^{-1}\)) can be assigned to \( \nu(\text{C}≡\text{C}) \).

This complex (LIIIa) in methylene chloride solution reacts with aqueous hydrogen chloride (1 mol equivalent) to give cis-dichlorobis(triphenylphosphine)platinum(II) (96%) and unreacted complex. The formation of the dichloride in this reaction rather than a ring opened
product analogous to (LIV) is probably due to the presence of the ether linkage which will be cleaved in the presence of HCl.

Similarly the 1:1 adduct between tetracyanoethylene and the diphenyltriketone complex (LI) (Section V) reacts with hydrogen chloride gas to yield the dichloride, which suggests by analogy to (LIllla) that the complex involves an ether linkage and has structure (Lla). Reaction of structure (LIB) with hydrogen chloride might be expected to yield a ring opened product analogous to (LIV). It is of course possible that structure (LIB) would react with hydrogen chloride to yield the dichloride.

When carbon monoxide is bubbled through a suspension of the white 1:1 adduct between the diphenyltriketone complex and hexafluorobut-2-yne in benzene a white crystalline complex can be isolated from the solution formed. Elemental analysis and molecular weight determination indicated that carbon monoxide had displaced one triphenylphosphine ligand to give a complex having structure (LVIla) or (LVIb).

![Chemical structures](image)

(LVIla)  (LVIib)  (L=PPh₃)
The infrared spectrum showed a strong absorption at 2083 cm\(^{-1}\) which can be assigned to v(CO) for the platinum carbonyl. In the organic carbonyl region there was a strong absorption at 1686 cm\(^{-1}\) and there were strong absorptions between 1300 and 1100 cm\(^{-1}\) due to v(C-F).

An \(^{19}\)F n.m.r. spectrum showed two signals due to two different -CF\(_3\) environments. The high field signal (-8.14 p.p.m.) was a quartet (J(F-F)14.3Hz) and the signal at low field (-9.05 p.p.m.) was a complex multiplet, which appeared to be a doublet of quartets with a doublet coupling of 8.3Hz due to a trans \(^{31}\)P nucleus. The magnitude of the coupling due to \(^{31}\)P is in the order of that observed due to the trans phosphine ligand in the complex (PPh\(_3\))\(_2\)Pt[C(CF\(_3\))=CHCF\(_3\)](OCOCF\(_3\))(J(P_{trans-F})7.8Hz).\(^{51,53}\) Satellite signals due to coupling with \(^{195}\)Pt were not observed.

This data indicates, therefore, that the complex has structure (LVIa), with the remaining triphenylphosphine ligand trans to carbon rather than oxygen.

One of the bands in the region of 1600 cm\(^{-1}\) (1595w, 1591vw, 1579vw cm\(^{-1}\)) can be assigned to v(C=C).

Carbon monoxide could not be displaced from (LVIa) by triphenylarsine even in refluxing toluene but methyldiphenylphosphine displaced carbon monoxide rapidly to give a white crystalline complex showing no absorptions in the infrared spectrum in the region of 2000 cm\(^{-1}\). Elemental analysis and molecular weight determination indicated that this was the mixed phosphine complex, which can have structure (LVIIa) or (LVIIb).
The infrared spectrum showed absorption in the carbonyl region at 1676 and 1668 cm\(^{-1}\) and strong absorptions between 1300 and 1100 cm\(^{-1}\) due to ν(C-F).

An \(^{19}\)F n.m.r. spectrum was very similar to that shown by (LIIIb), the high field signal (-6.88 p.p.m.) being a quartet (\(J(F-F)15\)Hz) and that at low field (-14.3 p.p.m.) a complex multiplet which appeared to be a triplet of quartets with a triplet coupling of 21Hz. The relative intensities of the triplet components could not be discerned.

The \(^1\)H n.m.r. showed a doublet at 8.6\(\tau\) due to P-Me\(\left(J(P-H)8\text{Hz}, J(Pt-H) \text{ not discernable}\right)\).

Complex (LVIIa) did not react with excess trifluoroacetic acid but with hydrogen chloride a white crystalline solid could be isolated, which showed weak bands in the infrared spectrum due to ν(O-H) and ν(Pt-Cl) but was shown to be mainly unreacted (LVIIa). This could be due to the formation of a ring opened product from which HCl is readily
eliminated to give back the five membered ring system, as shown in Figure 1.12.

(vii) **Reactions with hexafluoroacetone.**

Hexafluoroacetone reacted with the triketoindane complex at room temperature to give two products.

The first product was a yellow crystalline solid which was shown to be a 1:1 adduct between the triketoindane complex and hexafluoroacetone by elemental analysis and molecular weight determination. An infrared spectrum of the complex showed a strong absorption in the carbonyl region at 1705 cm$^{-1}$ and weaker absorptions at 1760 and 1733 cm$^{-1}$. There were strong bands between 1300 and 1100 cm$^{-1}$ due to v(C-F).

The $^{19}$F n.m.r. spectrum showed one signal, a singlet at +7.1 p.p.m.

This data accords with a structure in which hexafluoroacetone and triketoindane are present in a five
membered ring system in which hexafluoroacetone is bonded to platinum via the carbonyl oxygen rather than the carbon since no $^{31}\text{P}$ or $^{195}\text{Pt}$ coupling is seen on the signal due to C(CF$_3$)$_2$. There are two possible structures for the complex, (LVIIIa) and (LVIIIb).

Sterically structure (LVIIIb) would appear to be unfavourable due to the close proximity of the groups on the carbons (although a scale model of the fragment indicates that there is no actual contact interaction).

That known five membered ring systems formed in the ring expansion of hexafluoroacetone three membered ring complexes by hexafluoroacetone involve carbon to oxygen (head to tail) bonded systems infers, by analogy, that structure (LVIIIa) which contains a carbon to oxygen bonded system is the probable structure.

The reaction of the complex in methylene chloride with aqueous hydrogen chloride (one mol equivalent) gives
cis-dichlorobis(triphenylphosphine)platinum(II) and the 1:1 adduct formed between oxygen and the triketoindane complex (XXXX), (35%). In oxygenated methylene chloride solution the complex was stable.

Formation of the oxygen adduct (XXXX) in this reaction must occur via breakdown of the five membered ring system in the presence of HCl, to give hexafluoroacetone hydrate and the triketoindane complex which reacts with oxygen present in the system. A suggested mechanism for this reaction starting from structure (LVIIIa) is shown in Figure 1.13.

A similar mechanism applied to structure (LVIIIb) would be expected to give the triketoindane complex but also some hexafluoroacetonebis(triphenylphosphine)platinum(0) via nucleophilic attack at the electrophilic carbon of the
triketoindane fragment as illustrated in Figure 1.14.

![Chemical structure](image)

Figure 1.14. (L=PhP)

No hexafluoroacetonebis(triphenylphosphine)platinum(0)
was isolated from this reaction which again suggests that
the complex has structure (LVIIIa).

Reactions of the complex with gaseous hydrogen
chloride and excess trifluoroacetic acid yielded cis-
dichlorobis(triphenylphosphine)platinum(II) and
bistrifluoroacetatebis(triphenylphosphine)platinum(II)
respectively.

The second product isolated from the reaction of
hexafluoroacetone with the triketoindane complex was a
white crystalline solid which melted with the liberation
of a gas. Elemental analysis and molecular weight determination
indicated that the complex was a 1:2 adduct between the
triketoindane complex and hexafluoroacetone.
The infrared spectrum showed a strong absorption in the carbonyl region at 1732 cm\(^{-1}\) and many strong absorptions between 1350 and 1100 cm\(^{-1}\) due to \(\nu (C-F)\).

An \(^{19}\text{F}\) n.m.r. spectrum showed four quartet resonances centred on 5.98, 7.98, 15.6 and 17.8 p.p.m. each showing the same \(^{19}\text{F}-^{19}\text{F}\) coupling constant \((J(F-F)10.5\text{Hz})\). This n.m.r. spectrum can only be due to a fragment in which two hexafluoroacetone molecules are bonded via the carbon atoms. Presumably this fragment is contained in a seven membered ring system with triketoiindane in which case there are two possible structures, (LIXa) and (LIXb).

A scale model (framework model) of structures (LIXa) and (LIXb) showed that the seven membered ring is puckered, rendering all four \(-\text{CF}_3\) groups inequivalent. The coupling observed in the \(^{19}\text{F}\) n.m.r. spectrum is due to the inequivalent \(\text{gem-}\text{CF}_3\) groups coupling to give the observed quartet signals. It is interesting to note that
basically the $^{19}\text{F}\ n.m.r.$ spectrum consisted of two pairs of quartets (5.98, 7.98 p.p.m. and 15.6, 17.8 p.p.m.) each pair being due to the two \(-\text{CF}_3\) groups on one carbon.

In the infrared spectrum there is a weak absorption at 801 cm\(^{-1}\) which is assignable to \(\nu(\text{O} \cdots \text{O})\) and hence both (LXIa) and (LIXb) must be considered to be possible structures. An X-ray crystal structure study would appear to be the only way of distinguishing between the two structures.

The gas liberated at the melting point of this complex is undoubtedly hexafluoroacetone.

As mentioned in Section (iv) the bis-triketoindane complex, \((\text{PPh}_3)_2\text{Pt(triketoindane)}\), reacts with hexafluoroacetone with the displacement of one molecule of triketoindane to yield complexes identical to the 1:1 and 1:2 adducts formed between the triketoindane complex and hexafluoroacetone. However, one other product could also be isolated from the reaction. The product was a white crystalline solid which elemental analysis suggested was a 1:1 adduct between hexafluoroacetone and the triketoindane complex. An infrared spectrum of the complex showed a strong absorption at 1728 cm\(^{-1}\) and strong absorptions between 1350 and 1100 cm\(^{-1}\) due to \(\nu(\text{C} \cdots \text{F})\). Attempts to obtain an $^{19}\text{F}\ n.m.r.$ spectrum failed due to the small amount of the complex available (11%) and its apparent insolubility in most common organic solvents. This complex most probably contains a five membered ring system involving hexafluoroacetone and triketoindane, the presence
of a weak absorption in the infrared spectrum at 804 cm\(^{-1}\) suggests the presence of peroxyo linkage but this of course can only be a tentative suggestion.

The 1:1 adduct between the triketoindane complex and hexafluoroacetone (LVIII) reacted under vigorous conditions to give in low yield (33\%) the seven membered ring complex formed in the reaction between the triketoindane complex and hexafluoroacetone (LIX). This would appear to be a novel five to seven membered ring expansion reaction. However, it is possible that the reaction goes via dissociation of the five membered ring followed by recombination, to give the observed product. The fact that unreacted 1:1 adduct (38\%) and a low yield (7\%) of hexafluoroacetonebis-(triphenylphosphine)platinum(0) could be isolated from the reaction mixture appears to add weight to this suggestion, although for dissociation of the five membered ring system a larger yield of the hexafluoroacetone complex would have been expected since this is stable under the conditions of the reaction.

It is interesting to note that the five membered ring complex \((\text{PPh}_3)_2\overline{\text{PtOC(CF}_3)_2\text{OO}}\) does not ring expand under similar conditions to give the seven membered ring complex, \((\text{PPh}_3)_2\overline{\text{PtOC(CF}_3)_2\text{OC(CF}_3)_2\text{OO}}\). The seven membered ring complex is formed only in the reaction of peroxybis(triphenylphosphine)platinum(II) with excess hexafluoroacetone.\(^{34}\)

An analogous seven membered ring complex is formed during the reaction of the hexakis(trifluoromethyl)-
benzene complex \( \text{L}_2\text{Ni} \left[ \text{C}_6(\text{CF}_3)_6 \right] (\text{L}=\text{P}(\text{OMe})_3,\text{Me}_2\text{AsPh}) \), at room temperature with hexafluorobut-2-yne. The seven membered ring complex can be formally described as a nickelahexakis(trifluoromethyl)cyclohepta-cis,trans, cis-triene, \((\text{LX})\). An X-ray crystal structure study shows that there is a significant interaction between nickel and the central double bond of the triene system making the geometry about nickel approximately trigonal bipyramidal.

\[ \text{Ni} \quad \text{LX} \quad (\text{L}=\text{P}(\text{OMe})_3,\text{Me}_2\text{AsPh}) \]

Hexafluoroacetone and the diphenyltriketone complex reacted slowly at room temperature to yield two white crystalline solids. The second of these was hexafluoroacetonebis(triphenylphosphine)platinum(0) formed in a straightforward displacement reaction.

The first was shown to be a 1:1 adduct between hexafluoroacetone and the diphenyltriketone complex by elemental analysis and molecular weight determination. An \(^{19}\text{F}\) n.m.r. spectrum of a freshly prepared solution \((\text{CH}_2\text{Cl}_2)\) of the complex showed a 1:4:1 triplet (+14.5 p.p.m., \(J(\text{Pt-F})13.7\text{Hz}\)). However, on standing the solution showed an additional signal at +3.28 p.p.m. The new signal was
a doublet with $^{195}$Pt satellites ($J(_{\text{Pt-F}})_{\text{trans}}=11.3\text{Hz}, J(_{\text{Pt-F}})_{\text{F}}=70.5\text{Hz}$) and was assigned to hexafluoroacetonebis(triphenylphosphine)-platinum(0) ($\delta+3.28 \text{ p.p.m.}, J(_{\text{Pt-F}})_{\text{trans}}=11.3\text{Hz}, J(_{\text{Pt-F}})_{\text{F}}=70.5\text{Hz}$). This observation indicates that the 1:1 adduct decomposes in the presence of light to give the hexafluoroacetone complex. The solid is stable when stored in the dark but on exposure to light rapidly discolours to give a dirty yellow solid.

The signal at $+14.5 \text{ p.p.m.}$ is due to hexafluoroacetone bonded to platinum via oxygen, the small $J(_{\text{Pt-F}})$ and absence of phosphorus coupling precluding the carbon bonded case. Presumably hexafluoroacetone is involved in a five membered ring system with diphenyltriketone.

The infrared spectrum showed strong absorptions between 1300 and 1100 cm$^{-1}$ due to $\nu(C-F)$ and two strong absorptions at 1670 and 1648 cm$^{-1}$ due to $\nu(C=O)$. That there are two distinct carbonyl absorptions in the infrared spectrum suggests that it is not the central carbonyl group of diphenyltriketone incorporated in the five membered ring system but one adjacent to phenyl. It seems unlikely that the ring expansion reaction would give this product but probably not inconceivable since it is postulated that the absence of carbonyl absorptions in the infrared spectrum of the diphenyltriketone complex is due to a weak association between the carbonyl groups and platinum. This weak association could lead to the formation of an intermediate to ring expansion which involves diphenyltriketone bonded via a carbonyl group adjacent to phenyl. Collapse of this intermediate would lead to
the observed product.

There are two possible structures for the complex, (LXIa) and (LXIb).

![Structure (LXIa)](image1)

![Structure (LXIb)](image2)

(LXIa)  (LXIb)

(L=Ph3P)

A scale model (framework model) suggests that structure (LXIb) is unfavourable due to strong repulsions between the groups on carbon. Thus (LXIa) would seem to be the most likely structure by analogy to hexafluoroacetone five membered ring systems which have carbon to oxygen (head to tail) bonded configurations.

The π-ketonebis(triphenylphosphine)platinum(0) complexes of triketoinandane, diphenyltriketone, diphenyltetraeketone and alloxan appear to be much more reactive towards three to five membered ring expansion than the hexafluoroacetone analogue. While these complexes (with triketoinandane and diphenyltriketone) undergo ring expansion reactions with tetracyanoethylene and hexafluorobut-2-yn the analogous reactions for hexafluoroacetone complexes of nickel,
Palladium and platinum have not been reported.

Also the ring expansion reactions of the complexes with hexafluoroacetone and triketoindane has no parallel in the chemistry of hexafluoroacetonebis(triphenylphosphine)-platinum(0).

The ready reaction of the complexes with oxygen to give dicarboxylate complexes via a ring expanded five membered ring intermediate is a measure of their reactivity.

It would appear that the increase in reactivity over hexafluoroacetonebis(triphenylphosphine)platinum(0) is due to the nature of the ketones. Triketoindane, diphenyltriketone, diphenyltetraketone and alloxan although electrophilic enough to hydrate are undoubtedly less electrophilic than hexafluoroacetone. The result is a higher electron density on platinum making the formation of a transition state to ring expanded products more probable. Also since electron withdrawing groups are known to stabilise complexes of this kind, the ketones will form weaker bonds with platinum than hexafluoroacetone, again facilitating ring expansion.

This would seem to be the sole reason for the reactivity since hexafluoroacetonebis(triphenylphosphine)-platinum(0) is sterically less crowded than the ketone complexes, which involve bulky phenyl groups.

The formation of a seven membered ring complex in the reaction of hexafluoroacetone with the triketoindane complex and the apparent ring expansion of the 1:1 adduct between hexafluoroacetone and the triketoindane complex with hexafluoroacetone to give the same seven membered ring
complex are reactions of interest since complexes containing seven membered ring systems are rare at present and there has been no report of a reaction involving five to seven membered ring expansion.
1.3. **The reactions of some electrophilic ketones with zero-valent platinum complexes.**

The reaction of tetrakis(triphenylphosphine)platinum(0) with \(\Psi\)-isatin.

No reaction occurred between isatin (LXIIa) and tetrakis(triphenylphosphine)platinum(0) at room temperature, but when refluxed in benzene a dark red solution was formed from which red crystals were obtained by addition of ether.

The infrared spectrum of the complex showed no \(\nu\)(N-H) but a band at 2175 cm\(^{-1}\) in the region of \(\nu\)(Pt-H)\(^{56,57,58,59}\) and bands in the \(\nu\)(C=O) region at 1723 and 1674 cm\(^{-1}\) were observed. This suggested that oxidative-addition of isatin via the N-H bond to platinum(0) had occurred to give a hydrido-complex of platinum(II). Elemental analysis and molecular weight data confirmed this. The \(^1\)H n.m.r. spectrum of the complex showed a triplet resonance on the high field side of T.M.S. at 21.8\(\tau\) (J(Pt-H)14.5Hz). This signal can be assigned to the hydride resonance coupling to two equivalent \(^{31}\)P nuclei thus defining a **trans** configuration for the complex\(^{56,57,58,59}\) (LXIIb). Due to the limited solubility of the complex the satellite signals due to \(^{195}\)Pt\(-^1\)H coupling were not observed.
Table III shows some of the infrared data for the hydrido-platinum(II) isatin complex and for free isatin.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>$\nu$(C=O) cm$^{-1}$</th>
<th>$\nu$(N-H) cm$^{-1}$</th>
<th>$\nu$(Pt-H) cm$^{-1}$</th>
<th>Other bands cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(Isatin)L$_2$</td>
<td>Dark red</td>
<td>1723s 1674s</td>
<td>-</td>
<td>2175m</td>
<td>1608s 1596m 1583s</td>
</tr>
<tr>
<td>Isatin</td>
<td>Orange</td>
<td>1744m 1726s</td>
<td>3195w</td>
<td>-</td>
<td>1616s 1595m</td>
</tr>
</tbody>
</table>

**TABLE III**

Similar hydrido-complexes of platinum(II) have been prepared by the reaction of imides with zero-valent platinum complexes.\textsuperscript{60}

The imides succinimide, phthalimide, saccharin and parabanic acid are all weakly acidic and have pKa's ranging from 6.1 to 11.7. Isatin is undoubtedly weakly acid but as the N-H group has only one adjacent carbonyl group is probably not as acidic as the imides.
These imides (Figure 1.15.) all give trans hydrido-complexes of platinum(II) on refluxing in benzene with tetrakis(triphenylphosphine)platinum(0) and have structure (LXIII) illustrated by the hydride derived from succinimide.

Table IV gives a comparison of the spectral data for the hydrides derived from imides with that from isatin.
Analogous hydrido-complexes of platinum(II) have been prepared by the reactions of 5-chloro-, 5-bromo- and 5-phenyltetrazole with cis-dichlorobis(triphenylphosphine)-platinum(II) and hydrazine.61

5-Substituted tetrazoles behave as weak acids as they can exist in two tautomeric forms (Figure 1.16.).

![Figure 1.16.](image)

As the tautomeric forms suggest, the preparations lead to mixtures of two hydrides containing the $N_1$ and $N_2$ bonded
tetrazole, (LXIVa) and (LXIVb).

\[ \text{(LXIVa) (N}_2\text{ bonded)} \quad \text{(LXIVb) (N}_1\text{ bonded)} \]
\[(L=\text{PPh}_3; \ R = \text{Cl}, \text{Br}, \text{Ph}).\]

The mixtures of \(N_1\) and \(N_2\) bonded tetrazoles shows double triplets on the high field side of T.M.S. indicating that each isomer has a trans configuration as shown in (LXIVA) and (LXIVB).

The reaction of tetrakis(triphenylphosphine)platinum(O) with 5-substituted tetrazoles always led to the formation of the bis-tetrazolato complex rather than the hydride. The bis-tetrazolato complexes are assigned a trans configuration.

The reaction of trans-stilbenebis(triphenylphosphine)-platinum(O) with benzoyl cyanide.

The reaction of trans-stilbenebis(triphenylphosphine)-platinum with benzoyl cyanide yielded two products, a pale yellow crystalline solid and a white crystalline solid.

The pale yellow solid showed \(\nu(C\equiv N)\) at 2144 cm\(^{-1}\) and \(\nu(C=O)\) at 1629 cm\(^{-1}\) compared with \(\nu(C\equiv N)\) at 2225 cm\(^{-1}\) and \(\nu(C=O)\) at 1680 cm\(^{-1}\) for free benzoyl cyanide. The
strong ν(C=O) band at 1629 cm\(^{-1}\) appears in the region for metal acyl ν(C=O) absorptions,\(^{62,63,64}\) which suggests that the CO-CN carbon-carbon bond has cleaved with oxidative-addition to platinum(0) to give a platinum(II) complex. Elemental analysis for the complex indicated that its stoichiometry corresponded to Pt(PhCOCN)(PPh\(_3\))\(_2\). On this evidence the complex is formulated as a platinum(II) acyl complex having a cis or trans configuration, (LXVa) or (LXVb).

\[
\begin{align*}
\text{Pt} & \quad \text{CN} \\
\text{L} & \quad \text{COPh}
\end{align*}
\]

(LXVa) cis (L=PPh\(_3\))

\[
\begin{align*}
\text{Pt} & \quad \text{CN} \\
\text{PhOC} & \quad \text{L}
\end{align*}
\]

(LXVb) trans (L=PPh\(_3\))

Benzoyl chloride reacts with tris(triphenylphosphine)-platinum(0) in an analogous way to give Pt(COPh)Cl(PPh\(_3\))\(_2\) in which the benzoyl group shows strong characteristic absorptions in the infrared spectrum at 1614 cm\(^{-1}\) (ν(C=O)) and 890 cm\(^{-1}\). Table V shows a comparison of two characteristic absorptions of the benzoyl group in Pt(COPh)CN(PPh\(_3\))\(_2\) and Pt(COPh)Cl(PPh\(_3\))\(_2\).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Characteristic PhCO- absorptions cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(COPh)CN(PPh(_3))(_2)</td>
<td>1629s, ν(C=O); 883s</td>
</tr>
<tr>
<td>Pt(COPh)Cl(PPh(_3))(_2)</td>
<td>1614s, ν(C=O); 890s</td>
</tr>
</tbody>
</table>

**TABLE V**
Pt(COPh)Cl(PPh$_3$)$_2$ on heating to 210° loses carbon monoxide to give Pt(Ph)Cl(PPh$_3$)$_2$ in which the bands at 1614 and 890 cm$^{-1}$ have disappeared. Similarly the complex Pt(COPh)CN(PPh$_3$)$_2$ on melting (m.p. 187-189°) loses gas (carbon monoxide) and on heating for several minutes at 200° yields a white complex, which shows no absorptions at 1629 and 883 cm$^{-1}$ but still shows an absorption in the v(C≡N) region at 2120 cm$^{-1}$. This complex can most likely be formulated as Pt(Ph)(CN)(PPh$_3$)$_2$.

The reversible carbonylation reactions of several palladium and platinum alkyl and aryl complexes have been described$^{63}$ in which acyl complexes of the type trans-M(COR)X(PEt$_3$)$_2$, (M=Pd or Pt; X=Cl,Br or I; R=Me,Et or Ph) can be prepared by the action of carbon monoxide on alkyl or aryl complexes of the type MRX(PEt$_3$)$_2$. The acyl complexes when heated to approximately 140° lose carbon monoxide to yield the corresponding alkyl or aryl complex. Dipole moment measurements showed that the acyl complexes had a trans configuration, the benzoyl platinum complexes showing $v$(C=O) absorptions in the region of 1610-1613 cm$^{-1}$.

Analogous triphenylphosphine complexes could not be carbonylated and it has been suggested that this is due to the steric effect of the bulky triphenylphosphine,$^{62}$ which is also thought to account for the higher thermal stability of Pt(COPh)Cl(PPh$_3$)$_2$ over the triethylphosphine complexes. These effects are kinetic rather than thermodynamic and a comparison of the high thermal stability of Pt(COPh)Cl(PPh$_3$)$_2$ with the lower thermal stability of
the triethylphosphine complexes, with these effects in mind, led to the assignment of a trans configuration to Pt(COPh)Cl(PPh$_3$)$_2$ in keeping with the confirmed trans configuration of the triethylphosphine complexes.

Using the same argument the complex Pt(COPh)CN(PPh$_3$)$_2$ is tentatively assigned a trans configuration, although the position of the acyl $\nu$(C=O) at 1629 cm$^{-1}$ needs some explanation.

In free benzoyl cyanide $\nu$(C=O) occurs at 1680 cm$^{-1}$, but in the co-ordinated benzoyl group the energy of $\nu$(C=O) is lower, probably due to the ability of the metal to feed electron density onto the acyl group, giving a situation somewhere between the two extremes shown in Figure 1.17.

![Figure 1.17](image)

This electron density flow will occur via overlap of a metal d orbital with $\pi$-antibonding orbitals on the carbonyl group.

The ability of the metal to release electron density in this way will be influenced by the electron density on the metal which will be dependent on the $\pi$-acceptor properties of the ligands bonded to the metal. Hence a ligand with good $\pi$-acceptor properties will tend to inhibit
the flow of electron density from the metal onto the acyl group and so make the situation in the acyl group more near to (a) (Figure 1.17). It is clear, therefore, that as CN\(^-\) is a better \(\pi\)-acceptor than Cl\(^-\)\(^{65}\) there will be a resulting decrease in electron density on the metal and hence a shift of the acyl \(\nu(C=0)\) absorption to higher energy.

Table VI gives a comparison of the decarbonylation temperatures and \(\nu(C=0)\) absorptions for Pt(COPh)CN(PPh\(_3\))\(_2\) with some other benzoyl complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ligand trans to PhCO⁻</th>
<th>Decarbonylation temp. °C</th>
<th>(\nu(C=0)) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(COPh)CN(PPh(_3))(_2)</td>
<td>CN</td>
<td>200</td>
<td>1629</td>
</tr>
<tr>
<td>Pt(COPh)Cl(PPh(_3))(_2)</td>
<td>Cl</td>
<td>210</td>
<td>1613</td>
</tr>
<tr>
<td>Pt(COPh)I(PEt(_3))(_2)</td>
<td>I</td>
<td>140</td>
<td>1613</td>
</tr>
<tr>
<td>Pt(COPh)Br(PEt(_3))(_2)</td>
<td>Br</td>
<td>140</td>
<td>1613</td>
</tr>
<tr>
<td>Pt(COPh)Cl(PEt(_3))(_2)</td>
<td>Cl</td>
<td>140</td>
<td>1610</td>
</tr>
</tbody>
</table>

**TABLE VI**

The white crystalline solid showed no absorption in the \(\nu(C=0)\) region but \(\nu(C≡N)\) at 2135 cm\(^{-1}\) and from the microanalytical data was shown to be dicyanobis(triphenylphosphine)-platinum(II).

It is possible that this is formed in a disproportionation reaction between Pt(COPh)CN(PPh\(_3\))\(_2\) and benzoyl cyanide via a platinum(IV) intermediate, which is
unstable with respect to dicyanobis(triphenylphosphine)-platinum(II) and benzil. (Figure 1.18)

\[
\begin{align*}
\text{Pt} & \quad \text{CN} \\
\text{PhOC} & \quad \text{L} \\
+ \quad \text{PhCOCN} & \quad \rightarrow \\
\text{PhOC} & \quad \text{CN} \\
\text{L} \quad \text{Pt} & \quad \text{CN} \\
\end{align*}
\]

**Figure 1.18.** (L=PPh₃)

Since the dicyano-complex only shows one band due to \( \nu(\text{C≡N}) \) at 2135 cm\(^{-1} \) it can be assigned a \textit{trans} configuration (\textit{cis}, two bands 2141 and 2148 cm\(^{-1} \), nujol mull; \textit{trans} one band 2133 cm\(^{-1} \)). The complexes \( \text{Pt(COPh)(CN)(PPh₃)}_2 \) and \( \text{Pt(CN)}_2(PPh₃)_2 \) are formed via the cleavage of the CO-CN carbon-carbon bond and there are several other examples of C-CN carbon-carbon bond cleavage by low-valent metal complexes.

Cyanogen, NC.CN, which has a carbon-carbon bond energy estimated to be about 140Kcal/mol, reacts instantaneously at room temperature with the zero-valent
nickel, palladium and platinum phosphine complexes
ML₄ (M=Ni, L₂=1,2-bis(diphenylphosphino)ethane; M=Pd,
L₂=1,2-bis(diphenylphosphino)ethane or 1,3-bis(diphenyl-
phosphino)propane; M=Pt, L=triphenylphosphine) to give
the dicyano-complexes cis-M(CN)₂L₂. The ease with which
this strong carbon-carbon bond is cleaved is probably
accounted for by the stability of the dicyano-complexes
formed.

Tetrakis(triphenylphosphine)platinum(0) reacts with
1,1,1-tricyanoethane in refluxing benzene to give the
oxidative-addition product Pt(CN)[C(Me)(CN)₂](PPh₃)₂ formed via C-CN bond cleavage.

An analogous reaction occurs when the zero-valent
platinum-acetylene complex dicyanoacetylenebis(triphenyl-
phosphine)platinum(0) in acetone solution is exposed to
ultraviolet radiation. Rearrangement of the complex
occurs to give cyano(cyanoacetylido)bis(triphenylphosphine)-
platinum(II) a cyanoacetylide of platinum (II) formed
via C-CN bond cleavage. This is analogous to the
rearrangement which occurs for some π-olefin complexes
of platinum to give the σ-vinyl complex.
1.4. **Experimental**

The section is subdivided under headings for the appropriate ketone and a brief summary of infrared and n.m.r. data is given under such headings at the end of the section.

Melting points were measured on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded using nujol and where appropriate hexachlorobutadiene mulls on a Perkin Elmer 225 spectrometer between KBr(4000-400 cm\(^{-1}\)) and polythene (400-200 cm\(^{-1}\)) plates.

Fluorine magnetic resonance spectra were recorded at 56.4 MHz on a Varian Associates DA60 spectrometer or at 94.0 MHz on a J.E.O.L. JNM PS 100 spectrometer. Proton magnetic resonance spectra were recorded at 60 MHz on a Varian Associates T60 spectrometer.

Molecular weight determinations were carried out by Beller Mikkroanalytisches Laboratorium, 34 Göttingen, Theaterstrasse 23, West Germany and microanalysis by Dr. F. Pascher, Mikkroanalytisches Laboratorium, 53 Bonn, Burchstrasse 54, West Germany.

**Solvents**

Analar benzene and diethylether were dried by standing over sodium wire and were filtered before use. Other solvents were normal reagent grade and were used without further purification.

Benzene was degassed by refluxing under a stream of dry nitrogen for at least three days and was introduced
into reaction vessels under nitrogen, via a closed system. Solvents used for Carius tube reactions were 'pump-freeze' degassed under high vacuum and then distilled into the tube containing the reactant.

Ligands and other reagents

Ninhydrin was supplied by British Drug Houses and 0.5g quantities were dehydrated to give trikentoindone by heating at 130° for several hours. Diphenyltriketone hydrate was prepared from dibenzoylmethane supplied by Aldrich Chemical Co. by a standard literature method and was dehydrated to give diphenyltriketone by distillation under high vacuum.

Diphenyltetraketone was prepared by the oxidation of benzoylformoin in refluxing thionyl chloride and was recrystallised from benzene to give scarlet crystals. Diphenyltetraketone hydrate was obtained when a sample of diphenyltetraketone was allowed to stand in a moist atmosphere for several days. Benzoylformoin was prepared from ω-isonitrosoacetophenone supplied by Ralph N. Emanuel Ltd. by a standard literature method.

Alloxan hydrate was supplied by Koch-Light Laboratories and 0.5g quantities were dehydrated to give alloxan by heating at 150° under high vacuum.

The following reagents were purchased:
Hexafluoroacetone - Matheson Co.
Hexafluorobut-2-yne - Bristol Organics Ltd.
Tetracyanoethylene - Ralph N. Emanuel Ltd.
Fumaronitrile - Fluka Chemicals
Trifluoroacetic acid - Ralph N. Emanuel Ltd.
Triphenylphosphine, triphenylarsine - British Drug Houses
Tetrafluoroethylene was prepared by heating p.t.f.e. powder supplied by I.C.I. Ltd.
W-Isatin was supplied by British Drug Houses and was recrystallised from acetone-ethanol before use.
Benzoyl cyanide was supplied by Ralph N. Emanuel Ltd. and was distilled under high vacuum immediately before use.

**Complexes**

The following complexes were prepared by literature methods:

tetrakis(triphenylphosphine)platinum(O), \(^{75}\)
dichlorobis(triphenylphosphine)platinum(II), \(^{76}\)
trans-stilbenebis(triphenylphosphine)platinum(O), \(^{77}\)
diphenylacetylenebis(triphenylphosphine)platinum(O), \(^{78}\)
tris(triphenylphosphine)platinum(O), \(^{75}\)
peroxobis(triphenylphosphine)platinum(II), \(^{79}\)
tetrakis(triphenylarsine)platinum(O), \(^{75}\)
trans-chloro(carbonyl)bis(triphenylphosphine)iridium(I), \(^{80}\)
chlorotris(triphenylphosphine)rhodium(I). \(^{81}\)

All reactions were carried out at room temperature unless otherwise stated.
A. TRIKETOINDANE

1. The reaction of tetrakis(triphenylphosphine)-platinum(O) with triketoindane

Tetrakis(triphenylphosphine)platinum(O) (1g, 0.805 mmol) and triketoindane (0.13 g, 0.81 mmol) were stirred together in benzene (100 ml) under a nitrogen atmosphere for half an hour to produce a dark brown solution. The volume of the solution was reduced (to ca. 20 ml) by evaporation under reduced pressure and an excess of ether (ca. 100 ml) was added. Yellow crystals of stoichiometry triketoindane-bis(triphenylphosphine)platinum(O) were slowly deposited. These were filtered, washed with ether, dried in vacuo and stored under nitrogen. (0.6 g, 85%), m.p. 210-214°C decomp.

Found: C, 61.28; H, 4.13; O, 5.8; M 893, CHCl₃. C₄₅H₃₄O₃P₂Pt requires: C, 61.5; H, 3.87; O, 5.4%; M 879.6. ν(C=O) 1709m, 1678s cm⁻¹.

Infrared spectrum cm⁻¹: 1709m, 1678s, 1600w, 1585vw, 1571vw, 1478m, 1437s, 1432m, sh, 1322w, 1311vw, 1200m, 1188vw, 1177vw, 1155w, 1095s, 1027vw, 1018vw, 982m, 883vw, 856vw, 803vw, 769w, sh, 761m, 756m, 748m, 734m, 712m, 702s, 625vw, 573w, 552s, 536w, 526s, 520s, 511s.

The same general method was used for the reactions of trans-stilbenebis(triphenylphosphine)platinum(O) (1g, 1.105mmol) and diphenylacetylenebis(triphenylphosphine)platinum(O) (1g, 1.12mmol) with triketoindane (0.18g, 1.11mmol, and 0.18g, 1.12mmol respectively) to yield in each case
2. The reaction of tetrakis(triphenylphosphine)platinum(0) with ninhydrin,(triketoindane hydrate)

Tetrakis(triphenylphosphine)platinum(0) (1g, 0.805 mmol) and ninhydrin (0.143g, 0.81mmol) were stirred together in benzene (100 ml) under a nitrogen atmosphere for two hours to produce a dark brown solution. The volume of the solution was reduced (to ca. 20 ml) by evaporation under reduced pressure and an excess of ether (ca. 100 ml) was added. Yellow crystals were slowly deposited which were filtered, washed with ether, dried in vacuo and stored under nitrogen. These were shown to be triketoindanebis(triphenylphosphine)platinum(0) by infrared spectrum and melting point. (0.6g, 85%), m.p. 212-220° decomp. Found C,61.68; H,3.85. C_{45}H_{34}O_{3}P_{2}Pt requires: C,61.5; H,3.87%. ν(C=O) 1709m, 1678s cm⁻¹.

The same general method was used for the reactions of trans-stilbenebis(triphenylphosphine)platinum(0) (0.4g, 0.45mmol) and diphenylacetylenebis(triphenylphosphine)platinum(0) (0.25g, 0.278mmol) with ninhydrin (0.079g, 0.45mmol, and 0.05g, 0.28mmol respectively) to yield in each case triketoindanebis(triphenylphosphine)platinum(0) (0.3g, 77% and 0.22g, 90% respectively). In each case a yellow (rather than dark brown) solution was produced after the reaction time.
3. The reaction of triketoindanebis(triphenylphosphine) platinum(0) with hydrogen chloride.

Gaseous hydrogen chloride was bubbled through a stirred suspension of triketoindanebis(triphenylphosphine)-platinum(0) (0.49g, 0.556mmol) in benzene (50 ml) for five minutes. The white suspension formed was filtered and a further crop of the white solid obtained by reducing the volume of the filtrate by evaporation under reduced pressure. Recrystallisation from methylene chloride-ethanol yielded white crystals, which were shown to be cis-dichlorobis(triphenylphosphine) platinum(II) by infrared and far infrared spectra and melting point. (0.39g, 90%) m.p. 306-310° (lit. value, 310-312°). 76

4. The reaction of triketoindanebis(triphenylphosphine) platinum(0) with 3,4,5,6-tetrachloro-1,2-benzoquinone.

Triketoindanebis(triphenylphosphine) platinum(0) (0.25g, 0.284mmol) was stirred with 3,4,5,6-tetrachloro-1,2-benzoquinone (0.07g, 0.284mmol) in benzene (30 ml) for twelve hours under a nitrogen atmosphere. The yellow-orange solution formed was filtered and reduced in volume (to ca. 10 ml) by evaporation under reduced pressure. Addition of ethanol yielded a yellow solid, which was filtered. Recrystallisation from methylene chloride-ethanol gave yellow crystals, which were shown to be 3,4,5,6-tetrachloro-1,2-benzoquinonebis(triphenylphosphine) platinum(II) by infrared spectrum and melting point. (0.24g, 88%) m.p. 240° (lit. value 246°). 82
5. The reaction of triketoindanebis(triphenylphosphine)platinum(O) with oxygen.

A suspension of triketoindanebis(triphenylphosphine)platinum(O) (0.8g, 0.91mmol) in oxygenated benzene (100 ml) was shaken for five days. The white suspension formed was filtered, washed with a small portion of benzene and recrystallised from methylene chloride, benzene-ether to give white needles having a stoichiometry corresponding to a 1:1 adduct between oxygen and triketoindanebis(triphenylphosphine)platinum(O). These were filtered, washed with ether and dried in vacuo. (0.5g, 60%) m.p. 168-171°. Found: C, 58.81; H, 4.03, O, 8.65; M 1020, CHCl₃. C₄₅H₃₄O₅P₂Pt requires: C, 59.25; H, 3.76; O, 8.77%; M 911.82. v(C=O) 1752s, 1675s cm⁻¹.

Infrared spectrum cm⁻¹: 1752s, 1675s, 1583vw, 1568vw, 1480m, 1438s, 1433s, 1315m, 1298vw, 1275s, 1231w, 1188w, 1158w, 1147vw, 1113m, 1095s, 1072w, 1028vw, 1008w, 859m, 848w, 819w, 807vw, 776vw, 766m, 760m, sh, 758m, 748m, 720m, 712m, 706m, sh, 696s, 662vw, 634vw, 624vw, 560m, 544m, 532s, 527m, sh, 517m, 512s.

6. The reaction of peroxobis(triphenylphosphine)platinum(II) with triketoindane and ninhydrin.

Peroxobis(triphenylphosphine)platinum(II) (0.5g, 0.665mmol) and triketoindane (0.106g, 0.665 mmol) were stirred together in benzene (50 ml) under a nitrogen atmosphere for three hours. The white suspension formed was filtered, washed with a small portion of benzene and recrystallised
from methylene chloride, benzene-ether to give white crystals (needles) which were filtered, washed with ether and dried in vacuo. These were shown to be identical to the 1:1 adduct formed between triketoindanebis(triphenylphosphine)platinum(O) and oxygen by infrared spectrum and melting point. (0.3g, 50%) m.p. 170-172°. ν(C=O) 1752s, 1675s cm⁻¹.

The same product could be isolated when peroxo-bis(triphenylphosphine)platinum(II) (0.25g, 0.32mmol) was reacted with ninhydrin (0.059g, 0.332mmol) under the same conditions. (0.2g, 67%).

The 1:1 adduct between triketoindanebis(triphenylphosphine)platinum(O) and oxygen (0.45g, 0.51mmol) could be recovered unchanged after a suspension in iso-propylalcohol (B.P. 96.5°) had been refluxed for one day. (0.42g, 93%)

7. The reaction of triketoindanebis(triphenylphosphine)platinum(O) with triketoindane.

Triketoindanebis(triphenylphosphine)platinum(O) (0.25g, 0.284mmol) and triketoindane (0.055g, 0.29 mmol) were stirred together in benzene (20 ml) under a nitrogen atmosphere for two days. The bright yellow solution formed was filtered and reduced in volume (to ca. 10 ml) by evaporation under reduced pressure. Slow addition of ether led to the formation of yellow crystals (prisms) having a stoichiometry corresponding to a 1:1 adduct between triketoindanebis(triphenylphosphine)platinum(O) and
triketoindane. These were filtered, washed with ether and dried in vacuo. (0.2g, 68%), m.p. 157-161°. Found: C, 61.6; H, 4.31; O, 9.56; M 1030, CHCl₃. C₅₄H₃₈O₆P₂Pt requires: C, 62.4; H, 3.68; O, 9.23%; M 1039.9. ν(C=O) 1743m, 1728vw, 1706s cm⁻¹.

Infrared spectrum, cm⁻¹: 1743m, 1728vw, 1706s, 1596w, 1572vw, 1481m, 1336s, 1332m, sh, 1347vw, 1284vw, 1252m, 1184s, 1151m, 1112w, 1103m, 1096m, 1027vw, 1016w, 984m, 970s, 887vw, 859w, 776w, 758m, 746m, 732w, 724vw, 712s, 704m, sh, 696s, 672w, 626vw, 612w, 562m, 550m, 536s, 528m, 520m, 508m.

8. The reaction of triketoindanebis(triphenylphosphine)platinum(O) with diphenyltriketone and some other ketones.

Triketoindanebis(triphenylphosphine)platinum(O) (0.25g, 0.284mmol) was stirred with diphenyltriketone (0.076g, 0.29mmol) in benzene (20 ml) for two days. Addition of ether to the yellow solution formed gave yellow crystals, which were shown to be unreacted triketoindanebis(triphenylphosphine)platinum(O) by infrared spectrum and melting point. (0.2g, 80%), m.p. 214-220° decomp.

Similarly triketoindanebis(triphenylphosphine)platinum(O) (0.2g, 0.227mmol) was stirred with 9-fluorenone, (diphenylene ketone), (0.2g, 1.11mmol) in benzene (20 ml) under a nitrogen atmosphere at room temperature, and 60°, for twelve hours, after which only unreacted triketoindanebis(triphenylphosphine)platinum(O) could be recovered. (0.17g, 85%)
Triketoindanebis(triphenylphosphine)platinum(O) (0.26g, 0.295mmol) was refluxed in degassed acetone (50 ml) under a nitrogen atmosphere for six hours. The yellow solution formed was reduced in volume by evaporation under reduced pressure and addition of ether gave yellow crystals, which were shown to be unreacted triketoindanebis(triphenylphosphine)platinum(O) by comparison of the infrared spectrum with that of an authentic sample. (0.2g, 77%).

Triketoindanebis(triphenylphosphine)platinum(O) (0.2g, 0.227mmol) was shaken in oxygenated acetone (75 ml) for three days. The solvent from the resulting very pale yellow solution was removed completely by evaporation under reduced pressure, and the off-white residue was dissolved in methylene chloride. Addition of ether and slow reduction in volume by evaporation under reduced pressure yielded white needles, which were shown to be identical to the 1:1 adduct formed between triketoindanebis(triphenylphosphine)platinum(O) and oxygen by infrared spectrum and melting point. (0.19g, 90%), m.p. 172-174°. v(C=O) 1752s, 1675s cm\(^{-1}\).

9. The reaction of triketoindanebis(triphenylphosphine)platinum(O) with tetracyanoethylene.

Triketoindanebis(triphenylphosphine)platinum(O) (0.5g, 0.568mmol) and tetracyanoethylene (0.073g, 0.569mmol) were stirred together in benzene (50 ml) under a nitrogen atmosphere for two days. The pale yellow suspension formed was filtered, washed with ether and dried \textit{in vacuo}. (0.4g)
The product showed $\nu(C=\equiv N) 2230\text{ cm}^{-1}$, $\nu(C=O)$ 1744\text{ cm}^{-1}$, 1712\text{ s cm}^{-1}$ and bands at 1620\text{ s cm}^{-1}$ and 1588\text{ m cm}^{-1}$ in the infrared spectrum.

Recrystallisation from methylene chloride, ethanol-ether yielded a white solid, which was filtered and washed with ether, the filtrate and ether washings being bright yellow in colour. The white solid was recrystallised from methylene chloride, benzene-ether to give white needles having a stoichiometry corresponding to a 1:1 adduct between triketoindanebis(triphenylphosphine)platinum(0) and tetracyanoethylene. These were filtered, washed with ether and dried \textit{in vacuo}. (0.2g, 35%), m.p. 198-202°. Found: C, 60.8; H, 3.51; N, 5.54; O, 5.15; M 1078, CHCl$_3$. C$_{51}$H$_{34}$N$_4$O$_3$P$_2$Pt requires: C, 60.75, H, 3.40; N, 5.56; O, 4.7%; M 1007.9. $\nu(C=\equiv N) 2229\text{ m cm}^{-1}$, $\nu(C=O) 1741\text{ m cm}^{-1}$, 1712\text{ s cm}^{-1}$.

Infrared spectrum cm$^{-1}$: 2229\text{ m cm}^{-1}, 1741\text{ m cm}^{-1}, 1712\text{ s cm}^{-1}$. 1588\text{ vw}, 1584\text{ vw}, 1572\text{ vw}, 1485\text{ w}, 1480\text{ m}, 1439\text{ m}, 1434\text{ s}, 1336\text{ w}, 1315\text{ w}, 1269\text{ m}, 1187\text{ s}, 1161\text{ m}, 1149\text{ w}, 1105\text{ m}, 1096\text{ m}, 1090\text{ m}, 1072\text{ vw}, 1029\text{ m}, 1011\text{ vw}, 1003\text{ w}, 982\text{ vw}, 920\text{ w}, 880\text{ w}, 838\text{ m}, 792\text{ vw}, 776\text{ s}, 764\text{ m}, 752\text{ s}, 728\text{ m}, 712\text{ s}, 709\text{ s}, 703\text{ s}, 670\text{ vw}, 645\text{ m}, 625\text{ w}, 553\text{ s}, 535\text{ s}, 529\text{ s}, 523\text{ s}, 509\text{ m}, 504\text{ m}.

The yellow filtrate was reduced in volume by evaporation under reduced pressure to yield a yellow solid, which was recrystallised from methylene chloride, benzene-ether to give yellow needles having a stoichiometry corresponding to a 1:2 adduct between triketoindanebis(triphenylphosphine)platinum(0) and tetracyanoethylene. These
were filtered, washed with ether and dried in vacuo. (0.1g, 16%), m.p. 185-205° decomp. Found: C, 59.72; H, 3.0; N, 9.49; O, 4.36; M 1142, CHCl₃. C₅₇H₃₄N₈O₃P₂Pt requires: C, 60.02; H, 3.02; N, 9.85; O, 4.23%; M 1135.9. v(C≡N) 2205s cm⁻¹, v(C=O) 1744m, 1713s cm⁻¹.

Infrared spectrum cm⁻¹: 2205s, 1744m, 1713s, 1619s, 1614s, sh, 1588w, 1572vw, 1568vw, 1544m, 1530vw, 1443m, sh, 1440m, 1399s, 1383s, 1356vw, 1328s, 1252m, 1232w, 1184w, 1177w, 1144w, 1102s, 1097s, 1072vw, 1054w, 1050w, sh, 1026m, 959w, 930w, 906m, 857vw, 824m, 800m, 760s, 752s, 714s, 698s, 664m, 626w, 590vw, 559s, 536s, 524m, 517s, 509s.

Attempts to grow crystals of this compound for an X-ray crystallographic study failed to yield crystals of the required size.

10. The reaction of triketoiandebis(triphenylphosphine)platinum(O) with hexafluorobut-2-yne at 60°.

Hexafluorobut-2-yne (ca. 2 ml) was condensed into a Carius tube (-196°) containing triketoiandebis(triphenylphosphine)platinum(O) (0.25g, 0.284mmol) suspended in benzene (20 ml). The tube was sealed and shaken at 60° for one day. The solvent was completely removed from the pale yellow solution formed by evaporation under reduced pressure and the residue was dissolved in ether, filtered and reduced in volume. Addition of petrol (B.P. below 40°) yielded white crystals, which were filtered and dried in vacuo. These
were shown to be hexafluorobut-2-ynebis(triphenylphosphine)-platinum(0) by infrared and n.m.r. spectra and melting point (0.15 g, 60%), m.p. 212° (lit. value 215-216°). v(C=C) 1762 s cm⁻¹ (lit. value 1775 cm⁻¹).

11. The reaction of triketoindanebis(triphenylphosphine)platinum(0) with hexafluorobut-2-yne at room temperature.

Hexafluorobut-2-yne (ca. 2 ml) was condensed into a Carius tube (-196°) containing triketoindanebis(triphenylphosphine)platinum(0) (1 g, 1.136 mmol) suspended in benzene (ca. 25 ml). The tube was sealed and shaken at room temperature for two months, after which a yellow solid suspended in a yellow solution was filtered and washed well with ether. The yellow solid was recrystallised from methylene chloride-ether to yield bright yellow crystals, which were shown to be identical to the 1:1 adduct formed between triketoindanebis(triphenylphosphine)platinum(0) and triketoindane by infrared spectrum and melting point (0.35 g, 30%), m.p. 160-162°. v(C=O) 1743 m, 1728 v w, 1706 s cm⁻¹. The solvents were completely removed from the filtrate and ether washings by evaporation under reduced pressure and the residue was dissolved in methylene chloride. Addition of methanol and slow evaporation under reduced pressure gave a pale yellow solid, which was filtered and washed with petrol (B.P. below 40°). Recrystallisation from methylene chloride-methanol gave white crystals, which were shown to
be hexafluorobut-2-ynebis(triphenylphosphine)platinum(O)
by infrared spectrum and melting point. (0.25g, 25%)
m.p. 214° (lit. value 215-216°).^83

The filtrate and petrol washings were slowly
evaporated under reduced pressure to give a yellow solid,
which was filtered. Recrystallisation from benzene-ether,
petrol (B.P. below 40°) gave yellow crystals (needles)
having a stoichoimetry corresponding to a 1:1 adduct between
triketoindanebis(triphenylphosphine)platinum(O) and
hexafluorobut-2-yne. These were filtered, washed with petrol
(B.P. below 40°) and dried in vacuo. (0.13g, 11%), m.p.
164-168°. Found: C,56.66; H, 3.32; F, 11.14; M 951, CHCl₃.
C₄₉H₃₄F₆O₃P₂Pt requires: C,56.4; H,3.28; F,10.93%; M 1041.85.
ν(C=O) 1751w, 1744w, 1738vw,sh, 1718s, 1704s cm⁻¹.

Infrared spectrum cm⁻¹: 1751w, 1744w, 1738vw,sh,
1718s, 1704s, 1604w,1598w, 1587w, 1482m, 1440s, 1436m,sh,
1344vw, 1307w,sh, 1298m, 1288m, 1281w, 1242s, 1233s, 1182w,sh,
1178m, 1160s, 1136m,sh, 1125s, 1115m,sh, 1100s, 1088m,sh,
1028vw, 1016w, 994m, 921vw, 856vw, 838w, 820w, 774w, 768w,
762m, 756m, 749s, 743m, 732w, 712s, 703s, 697s,sh, 640w,sh,
636m, 628w, 548m, 536s, 531s, 527s, 506m.

The ¹⁹F n.m.r. spectrum in methylene chloride showed
two signals at $\delta$ - 7.05 p.p.m. (3F, quartet, $J(F-F)15$ Hz.)
and - 13.6 p.p.m. (3F, multiplet) relative to internal
C₆H₅CF₃. The multiplet appeared to be a triplet of
quartets with a triplet coupling of 19.5 Hz. The relative
intensities of the triplet components could not be discerned.
12. The reaction of triketoindanebis(triphenylphosphine)platinum(0) with hexafluoroacetone.

Hexafluoroacetone (ca. 1.5 ml) was condensed into a Carius tube (-196°) containing triketoindanebis(triphenylphosphine)platinum(0) (0.72g, 0.82mmol) suspended in benzene (25 ml). The tube was sealed and shaken at room temperature for three days, after which a yellow solid suspended in a pale yellow solution was filtered and washed with ether. Two further crops of the pale yellow solid were obtained by evaporation of the filtrate under reduced pressure and addition of ether. The three crops were combined and recrystallised from methylene chloride-ether to yield pale yellow crystals, having a stoichiometry corresponding to a 1:1 adduct between triketoindanebis(triphenylphosphine)platinum(0) and hexafluoroacetone. These were filtered, washed with ether and dried in vacuo. (0.53g, 62%), m.p. 210-220° decomp. Found: C,55.01; H,3.37; F,10.7; M 1020, CHCl₃. C₄₈H₃₄F₆O₄P₂Pt requires: C,55.2, H,3.28; F,10.9%; M 1045.84. ν(C=O) 1760vw, 1733m, 1705s cm⁻¹.

Infrared spectrum cm⁻¹: 1760vw, 1733m, 1705s, 1588w, 1569vw, 1480m, 1438s,sh, 1434s, 1346w, 1320w, 1276m, 1262w, 1243m, 1232w,sh, 1221s, 1208w, 1184m, 1174s, 1160w, 1148w, 1128s, 1118m,sh, 1102m, 1090m, 1072w, 1052w, 1024w, 1011w, 988s, 952w, 887w, 844m, 803vw, 786w, 762m, 756m, 752m, 748m, 742s, 728w, 720w, 714m, 705s, 700s, 656vw, 640m, 624vw, 566m, 556m, 550m, 540s, 532s, 522s, 513s, 504s, 470w.
The $^{19}$F n.m.r. spectrum in methylene chloride showed one signal, a singlet at $\delta + 7.1$ p.p.m. relative to internal C$_6$H$_5$CF$_3$.

The solvents from the filtrate and ether washings were completely removed by evaporation under reduced pressure and ether was added to the residue. A cream solid slowly precipitated and precipitation was completed by the slow addition of petrol (B.P. below 40°). The cream solid was filtered, washed with petrol (B.P. below 40°) and recrystallised from methylene chloride-methanol to give white crystals (prisms) having a stoichiometry corresponding to a 1:2 adduct between triketoindanebis(triphenylphosphine)-platinum(0) and hexafluoroacetone. These were filtered, washed with methanol and dried in vacuo. (0.26g, 26%)

m.p. 182-185° decomp. (gas evolved). Found: C,50.7; H,2.92; F,18.27; M 1203, CHCl$_3$. C$_{51}$H$_{34}$F$_{12}$O$_5$P$_2$Pt requires: C,50.5; H,2.83; F,18.79%; M 1211.9. v(C=O) 1732s cm$^{-1}$.

Infrared spectrum cm$^{-1}$: 1732s, 1601w, 1594vw, 1589vw, 1583vw, 1575vw, 1483m, 1441s, 1436s, 1325m, 1315s, 1289vw, 1272vw, 1249s,sh, 1244s, 1220s, 1215s, 1203s, 1192s, 1176s, 1166s, 1160m,sh, 1142m,sh, 1136m, 1125m, 1111s, 1100s, 1080w, 1029vw, 1020vw, 983vw,sh, 971m, 955w, 912w, 880vw, 864w, 826w, 801w, 772m, 760w, 754m, 745w, 738w, 726m, 712m, 696s, 643w, 624vw, 564m, 536s, 531m,sh, 520m, 508m.

The $^{19}$F n.m.r. spectrum in methylene chloride showed four signals at $\delta + 5.98$ p.p.m. (3F, quartet, $J$(F-F) 10.5Hz.), +7.98 p.p.m. (3F, broad quartet, $J$(F-F)$_{ca}$.10.5Hz.),
+ 15.6 p.p.m. (3F, quartet, J(F-F)10.5 Hz.) and + 17.8 p.p.m. (3F, quartet, J(F-F)10.5 Hz.) relative to internal C₆H₅CF₃.

13. The reaction of the 1:1 adduct formed between triketoinanebis(triphenylphosphine)platinum(O) and triketoinane with hexafluorobut-2-ynene.

Hexafluorobut-2-ynene (ca. 1.5 ml) was condensed into a Carius tube (-196°) containing Pt(triketoinane)₂(PPh₃)₂ (0.44g, 0.42mmol) and benzene (25 ml). The tube was sealed and shaken at 60° for four hours. The solvent from the yellow-green solution formed was completely removed by evaporation under reduced pressure and the residue was dissolved in ether and filtered. Addition of methanol and slow evaporation under reduced pressure gave a white solid, which was filtered. A second crop of the white solid was obtained from the filtrate in a similar way. Recrystallisation of the two crops from methylene chloride-methanol gave white crystals, which were shown to be hexafluorobut-2-ynene-bis(triphenylphosphine)platinum(O) by infrared spectrum and melting point. (0.26g, 70%), m.p. 213° (lit. value 215-216°).³³

14. The reaction of the 1:1 adduct formed between triketoinanebis(triphenylphosphine)platinum(O) and triketoinane with hexafluoroacetone.

Hexafluoroacetone (ca. 1.5 ml) was condensed into a Carius tube (-196°) containing Pt(triketoinane)₂(PPh₃)₂
(0.56g, 0.54mmol) and benzene (30 ml). The tube was sealed and shaken at room temperature for three days, after which a blue-green solution containing red crystals was formed. The red crystals were filtered, washed with benzene and dried in vacuo. These were shown to be triketoindane by infrared spectrum and melting point. (0.04g, 47%), m.p. 240-244° decomp. (lit. value 241-243° decomp.). The infrared spectrum showed no bands in the ν(O-H) region.

The filtrate was reduced in volume (to ca. 10 ml) by evaporation under reduced pressure and addition of ether yielded a pale yellow solid contaminated by red crystals of triketoindane. The mixture was filtered, washed with ether and recrystallised from methylene chloride-ether to give yellow crystals, which were shown to be identical to the 1:1 adduct formed between triketoindanebis(triphenylphosphine)platinum(O) and hexafluoroacetone by infrared spectrum and melting point. (0.24g, 43%), m.p. 190-210° decomp. ν(C=O) 1760vw, 1733m, 1705s cm\(^{-1}\).

The filtrate and ether washings were reduced in volume (to ca. 2 ml) by evaporation under reduced pressure and addition of ether yielded a pale yellow solid, which was filtered and washed with ether. Recrystallisation from methylene chloride-ether gave white crystals having a stoichiometry corresponding to a 1:1 adduct between triketoindanebis(triphenylphosphine)platinum(O) and hexafluoroacetone. These were filtered, washed with ether and dried in vacuo. (0.06g, 11%) m.p. 270-290° decomp.
without melting. Found: C, 54.17; H, 3.21; F, 9.99; C_{48}H_{34}F_6O_{4}P_2Pt requires: C, 55.2; H, 3.28; F, 10.9%. ν(C=O) 1728 s cm⁻¹.

Infrared spectrum cm⁻¹: 1728 s, 1608 w, 1600 vw, 1587 vw, 1572 vw, 1483 m, 1439 s, 1341 vw, 1312 m, 1292 m, 1278 s, 1223 s, 1212 s, 1191 vw, 1180 m, 1159 m, 1150 m, 1121 s, 1104 m, 1096 m, 1081 m, 1042 s, 1009 m, 972 s, 943 m, 902 m, 879 m, 804 vw, 778 m, 763 m, 752 m, 727 s, 714 m, 700 s, 623 w, 562 m, 549 m, 538 m, 526 m, 518 m, 504 m.

An attempt to obtain a ¹⁹F n.m.r. spectrum of the compound failed due to the small amount available and its apparent insolubility in most common solvents (CH₂Cl₂, C₆H₆, (CH₃)₂CO, tetrahydrofuran).

The solvents from the filtrate and ether washings were completely removed by evaporation under reduced pressure and to the residue ether was added. A white solid slowly precipitated, which was filtered. Two additional crops were obtained in this way and the combined crops were recrystallised from methylene chloride-methanol to give white crystals. These were shown to be identical to the 1:2 adduct formed between triketoindanebis(triphenylphosphine)-platinum(0) and hexafluoroacetone by infrared and n.m.r. spectra and melting point. (0.22g, 34%), m.p. 174-184° decomp. (gas evolved). ν(C=O) 1731 s cm⁻¹.
15. The reaction of the 1:1 adduct formed between triketoindanebis(triphenylphosphine)platinum(0) and triketoindane with trifluoroacetic acid.

To a stirred solution of Pt(triketoindane)\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (0.11g, 0.105mmol) in benzene (10 ml) was added trifluoroacetic acid (0.05g, 0.44mmol) in ether (10 ml). Immediately the yellow colour of the solution was discharged and a white solid was precipitated, which was filtered and washed with ether. Recrystallisation from a large volume of methylene chloride (ca. 50 ml) gave white needles, which were shown to be 2-hydroxy-1,3-indandione by mass spectra and melting point. These were filtered, washed with ether and dried \textit{in vacuo}. (0.03g, 90%), m.p. 160-165° (lit. value 156°).\textsuperscript{84} Mass peak in the mass spectrum 162 (M, 2-hydroxy-1,3-indandione, 162). Addition of petrol (B.P. below 40°) to the filtrate gave white needles which were shown to be bis(trifluoroacetate)bis(triphenylphosphine)platinum(II) by infrared spectrum and melting point. (0.08g, 80%), m.p. 220-225° (lit. value 230-235°).\textsuperscript{79}

16. The reaction of the 1:1 adduct formed between triketoindanebis(triphenylphosphine)platinum(0) and hexafluoroacetone with hexafluoroacetone.

Hexafluoroacetone (ca. 2 ml) was condensed into a Carius tube (-196°) containing Pt(triketoindane)(hexafluoroacetone)(PPh\textsubscript{3})\textsubscript{2} (0.5 g, 0.477mmol) and benzene (20 ml). The
tube was sealed and shaken at 70° for two days, after
which the yellow solution formed was reduced in volume
(to ca. 5 ml) by evaporation under reduced pressure. To
the residue, ether (ca. 60 ml) was added and the resulting
yellow solution was treated with activated charcoal at
room temperature, filtered and the volume of the resulting
pale yellow solution reduced (to ca. 20 ml) by evaporation
under reduced pressure. Petrol (B.P. below 40°) was added
to the precipitation point of the solution, which was
allowed to stand for twelve hours. The yellow solid formed
was filtered and washed with petrol (B.P. below 40°).
Recrystallisation from methylene chloride-ether gave yellow
crystals, which were shown to be unreacted \( \text{Pt(triketoindane)}-(\text{hexafluoroacetone})(\text{PPh}_3)_2 \) by infrared spectrum and melting
point. (0.19g, 38%), m.p. 190-210° decomp.

Addition of methanol to the filtrate and slow
evaporation under reduced pressure gave a white solid, which
was filtered and washed with methanol.

Recrystallisation from methylene chloride-methanol
yielded white crystals, which were shown to be identical
to the 1:2 adduct formed between triketoindanebis(triphenyl-
phosphine)platinum(0) and hexafluoroacetone by infrared
spectrum and melting point. (0.19g, 33%), m.p. 178-183°
decomp. (gas evolved). \( \nu(C=O) \) 1732s cm\(^{-1}\).

The filtrate was reduced in volume by evaporation
under reduced pressure to yield a white solid which was
filtered and washed with a small portion of ether. The
infrared spectrum of the solid indicated that it was a mixture of mainly hexafluoroacetonebis(triphenylphosphine)-platinum(O) and another product. Recrystallisation from methylene chloride-ether yielded a white crystalline solid, which was shown to be mainly hexafluoroacetonebis(triphenylphosphine)platinum(O) by comparing the infrared spectrum with that of an authentic sample.\(^\text{1}\) (0.03g, 7%).

17. The reaction of the 1:1 adduct formed between triketoindanebis(triphenylphosphine)platinum(O) and hexafluoroacetone with aqueous hydrogen chloride.

To a solution of Pt(triketoindane)(hexafluoroacetone)\((\text{PPh}_3)_2\) (0.12g, 0.115mmol) in methylene chloride (20 ml) was added 1.2 ml of 0.10022M hydrogen chloride in water (0.115mmolHCl). The mixture was shaken for three days, after which a small amount of white crystalline solid had precipitated. This was filtered and washed with ether. From the filtrate a further crop was obtained by addition of ether and slow reduction in volume by evaporation under reduced pressure. The two crops were combined and shown to be cis-dichlorobis(triphenylphosphine)platinum(II) by infrared spectra and melting point. (0.03g, 65%), m.p. 305-310° (lit. value 310-312).\(^\text{76}\)

The solvents from the filtrate were completely removed by evaporation under reduced pressure and addition of ether to the residue yielded an off-white solid. Recrystallisation
from chloroform-ether yielded white needles, which were shown to be identical to the 1:1 adduct formed between triketoindanebis(triphenylphosphine)platinum(0) and oxygen by infrared spectrum and melting point. (0.04g, 35%), m.p. 167-173°. ν(C=O) 1750s, 1674s cm⁻¹.

18. The reaction of the 1:1 adduct formed between triketoindanebis(triphenylphosphine)platinum(0) and hexafluoroacetone with trifluoroacetic acid and hydrogen chloride.

To a solution of Pt(triketoindane)(hexafluoroacetone)(PPh₃)₂ (0.2g, 0.192mmol) in methylene chloride (10 ml) was added excess trifluoroacetic acid (0.045g, 0.39mmol). Ether was added to the colourless solution formed and slow reduction in volume by evaporation under reduced pressure gave white crystals. These were shown to be bis(trifluoroacetate)bis(triphenylphosphine)platinum(II) by infrared spectrum and melting point. (0.13g, 70%), m.p. 220-223° (lit. value 230-235°).³⁹

Similarly after passing gaseous hydrogen chloride through a solution of Pt(triketoindane)(hexafluoroacetone)(PPh₃)₂ (0.1g, 0.096mmol) in methylene chloride (10 ml) only cis-dichlorobis(triphenylphosphine)platinum(II) could be isolated. (0.06g, 80%), m.p. 308-312° (lit. value 310-312°).³⁶
19. The reaction of trans-chloro(carbonyl)bis(triphenylphosphine)iridium(I) with triketoindane.

trans-Chloro(carbonyl)bis(triphenylphosphine)iridium(I) (0.5g, 0.64mmol) and triketoindane (0.103g, 0.645mmol) were stirred together in benzene (50 ml) under a nitrogen atmosphere for three days. The yellow solution formed was filtered and reduced in volume by evaporation under reduced pressure. The yellow crystals formed were shown to be unreacted trans-chloro(carbonyl)bis(triphenylphosphine)iridium(I) by infrared spectrum and melting point. (0.45g, 90%), m.p. 305° (lit. value 323-325°).

Similarly, when the reaction was repeated at 60° for two days only yellow crystals of trans-chloro(carbonyl)bis(triphenylphosphine)iridium(I) could be isolated.

20. The reaction of chlorotris(triphenylphosphine)-rhodium(I) with triketoindane.

Chlorotris(triphenylphosphine)rhodium(I) (0.5g, 0.54mmol) and triketoindane (0.0865g, 0.54mmol) were stirred together in benzene (50 ml) under a nitrogen atmosphere for twelve hours. The brick red suspension formed was filtered, washed with benzene and dried in vacuo. This was shown to be μμ'-dichlorotetakis(triphenylphosphine)dirhodium(I) by infrared and far infrared spectra and melting point. (0.3g, 83%), m.p. 124-130° decomp. ν(Rh-Cl) 300 cm⁻¹.
B. TRIKETOINDANE

1. The reaction of tetrakis(triphenylarsine)platinum(0) with triketoindane.

Tetrakis(triphenylarsine)platinum(0) (2g, 1.41mmol) and triketoindane (0.225g, 1.41mmol) were stirred together in benzene (150 ml) under a nitrogen atmosphere for one hour. The clear yellow solution formed was reduced in volume (to ca. 50 ml) by evaporation under reduced pressure and an excess of ether (ca. 150 ml) was added. Yellow crystals having a stoichiometry triketoindanebis(triphenylarsine)platinum(0) were slowly deposited. These were filtered, washed with ether, dried in vacuo and stored under nitrogen. (1.14g, 84%), m.p. 149-151°. Found: C,56.47; H,3.77; O,5.54; M 970, CHCl₃. C₄₅H₃₄O₃As₂Pt requires: C,55.8; H,3.54; O,4.96%; M 967.7. ν(C=O) 1712m, 1684s cm⁻¹.

Infrared spectrum cm⁻¹: 1712m, 1684s, 1600w, 1592vw, 1480m, 1335s, 1360s, 1345m, 1320w, 1308w, 1234vw, 1200m, 1184vw, 1179vw, 1154w, 1113vw, 1077m, 1065vw, 1026w, 1019vw, 978m, 881vw, 852w, 803w, 756m, 752m, 746s, 741m, 734s, 697s, 624vw, 620vw, 568m, 523vw, 488m, 473s.

The compound unless stored under nitrogen turned brown-yellow after several days.

Attempts at ligand exchange reactions on the compound using 1,2-bis(diphenylphosphine)ethane and methyldiphenylphosphine yielded only red intractable oils or red semi-solids, this probably being due to the ready
reaction of triketoneindane with phosphines. Triketoindane reacts with triphenylphosphine at room temperature to yield an orange crystalline adduct.

2. The reaction of tetrakis(triphenylarsine)platinum(0) with ninhydrin(triketoindanehydrate)

Tetrakis(triphenylarsine)platinum(0) (0.5g, 0.35mmol) and ninhydrin (0.0625g, 0.35mmol) were stirred together in benzene (50 ml) under an atmosphere of nitrogen for four hours. The clear yellow solution formed was reduced in volume (to ca. 20 ml) by evaporation under reduced pressure and an excess of ether (ca. 50 ml) was added. Yellow crystals were deposited, which were filtered, washed with ether, dried in vacuo and stored under nitrogen. These were shown to be triketoindanebis(triphenylarsine)platinum(0) by infrared spectrum and melting point. (0.25g, 74%), m.p. 151-153°. ν(C=O) 1712m, 1684s cm⁻¹.

3. The reaction of triketoindanebis(triphenylarsine)platinum(0) with oxygen.

A suspension of triketoindanebis(triphenylarsine)-platinum(0) (0.83g, 0.858mmol) in oxygenated benzene (100 ml) was shaken for one week. The white crystalline suspension formed was filtered and washed with benzene.

Recrystallisation from methylene chloride-ether gave white needles having a stoichiometry corresponding to a 1:1 adduct between triketoindanebis(triphenylarsine)platinum(0)
and oxygen. These were filtered, washed with benzene and dried in vacuo. (0.65g, 76%), m.p. 230-240° decomp.

Found: C, 53.91; H, 3.71; O, 7.99; M 1078, CHCl₃. C₄₅H₃₄O₅As₂Pt requires: C, 54.1; H, 3.43; O, 8.0%; M 999.68.

\( \nu(C=O) \) 1755s, 1679s cm\(^{-1}\).

Infrared spectrum cm\(^{-1}\): 1755s, 1679s, 1580vw, 1558vw, 1482m, 1436s, 1313m, 1296vw,sh, 1271s, 1226vw, 1188vw, 1184vw, 1156w, 1146vw, 1112m, 1080m, 1025vw, 1010w, 858w, 850w,sh, 818vw, 816vw, 776vw, 750s, 743s, 721m, 695s, 662vw, 638vw, 548w, 514vw, 485m, 472m, 464m.

4. The reaction of triketoindanebis(triphenylarsine)platinum(O) with triketoindane.

Triketoindanebis(triphenylarsine)platinum(O) (0.21g, 0.217mmol) and triketoindane (0.035g, 0.218mmol) were stirred together in benzene (20 ml) under a nitrogen atmosphere for four hours. The solvent was completely removed from the yellow solution formed by evaporation under reduced pressure and the yellow residue dissolved in methylene chloride and filtered. Addition of ether and slow reduction in volume by evaporation under reduced pressure gave, on standing, yellow crystals having a stoichiometry corresponding to a 1:1 adduct between triketoindanebis(triphenylarsine)-platinum(O) and triketoindane. These were filtered, washed with ether and dried in vacuo. (0.15g, 61%), m.p. 152-156°.

Found: C, 58.3; H, 3.77; O, 8.38; M 1135, CHCl₃. C₅₄H₃₈O₆As₂Pt requires: C, 57.5; H, 3.4; O, 8.52%; M 1127.8. \( \nu(C=O) \)
Infrared spectrum cm$^{-1}$: 1745m, 1733vw, 1711s, 1600w, 1584vw, 1484m, 1439s, 1244w, 1281vw, 1253m, 1184s, 1152m, 1079m, 1023vw, 1014w, 977m, 960m, 882vw, 859vw, 775vw, 766w, 755m, 744s, 730m, 698s, 687m, 669vw, 616w, 594vw, 572vw, 551vw, 531w, 488m, 474m, 464m.

5. The reaction of triketoindanebis(triphenylarsine)-platinum(O) with hexafluorobut-2-yne.

Hexafluorobut-2-yne (ca. 2 ml) was condensed into a Carius tube (-196°) containing triketoindanebis(triphenylarsine)platinum(O) (0.6g, 0.62mmol) and benzene (25 ml). The tube was sealed and shaken at room temperature for two days to produce a yellow-green solution, which was filtered and reduced in volume (to ca. 5 ml) by evaporation under reduced pressure. Addition of ether yielded a pale yellow solid, which was filtered and washed with several portions of ether. Recrystallisation from methylene chloride, benzene-ether yielded a yellow crystalline solid, which was shown to be identical to the 1:1 adduct formed between triketoindanebis(triphenylarsine)platinum(O) and triketoindane by infrared spectrum and melting point. (0.11g, 31%), m.p. 150-154°. ν(C=O) 1745m, 1733vw, 1711s cm$^{-1}$.

The solvent was removed completely from the filtrate and ether washings and addition of ether and petrol (B.P. below 40°) to the residue yielded a white solid, which was filtered and washed with petrol (B.P. below 40°). This
was shown to be hexafluorobut-2-ynebis(triphenylarsine)-platinum(0) by infrared and n.m.r. spectra. (0.42 g, 63%), ν(C=C) 1776s cm\(^{-1}\). (lit. value 1775 cm\(^{-1}\)).

C. **DIPHENYLTRIKETONE**

1. **The reaction of tetrakis(triphenylphosphine)-platinum(0) with diphenyltriketone(diphenylpropantrione).**

Tetrakis(triphenylphosphine)platinum(0) (1g, 0.805mmol) and diphenyltriketone (0.192g, 0.805mmol) were stirred together in benzene (50 ml) under a nitrogen atmosphere for one hour. The deep red solution formed was slowly reduced in volume by evaporation under reduced pressure to give dark red crystals (prisms) of stoichiometry diphenyltriketonebis(triphenylphosphine)platinum(0). These were filtered, washed with a small portion of benzene, dried in vacuo and stored under nitrogen. (0.56g, 73%), m.p. 159-161° (dark red crystals melt to colourless liquid). Found: C, 63.1; H, 4.21; O, 4.77; M 834, CHCl₃. \( \text{C}_{51} \text{H}_{40} \text{O}_{3} \text{P}_2 \text{Pt} \) requires: C, 63.9; H, 4.21; O, 5.01%; M 957.9.

Infrared spectrum cm\(^{-1}\): 1611w, 1592w, 1586vw, 1294s, 1256s, 1182m, 1156vw, 1128w, 1096w, 1069w, 1005m, 999w, 923vw, 877s, 808vw, 776w, 764w, 753m, 723s, 716m, 712m, 702s, 698s, 679m, 636w, 628vw, 624vw, 564m, 534s, 522m, 510m, 503w.

The compound, unless stored under nitrogen, slowly
faded in colour and after seven days had faded to pale pink.

The same general method was used for the reactions of trans-stilbenebis(triphenylphosphine)platinum(O) (1g, 1.11 mmol) and diphenylacetylenebis(triphenylphosphine)platinum(O) (0.72g, 0.802mmol) with diphenyltriketone (0.265g, 1.11mmol and 0.19g, 0.802mmol respectively) to yield in each case diphenyltriketonebis(triphenylphosphine)platinum(O), (0.95g, 89% and 0.56g, 73% respectively).

2. The reaction of tetrakis(triphenylphosphine)platinum-(O) with diphenyltriketone hydrate.

Tetrakis(triphenylphosphine)platinum(O) (1g, 0.805mmol) and diphenyltriketone hydrate (0.206g, 0.805mmol) were stirred together in benzene (50 ml) under a nitrogen atmosphere for four hours. The deep red solution formed was slowly reduced in volume by evaporation under reduced pressure to give dark red crystals, which were filtered, washed with a small portion of benzene, dried in vacuo and stored under nitrogen. These were shown to be diphenyltriketonebis(triphenylphosphine)platinum(O) by infrared spectrum and melting point. (0.59g, 77%), m.p. 157-159° (dark red crystals melt to colourless liquid).

3. The reaction of diphenyltriketonebis(triphenylphosphine)platinum(O) with oxygen.

A solution of diphenyltriketonebis(triphenylphosphine)-
platinum(0) (0.2g, 0.209mmol) in oxygenated benzene (70 ml) was shaken for twelve hours. The solvent from the resulting yellow solution was completely removed by evaporation under reduced pressure and the white residue was dissolved in methylene chloride. Addition of ether and slow evaporation under reduced pressure gave white crystals (needles) having a stoichiometry corresponding to a 1:1 adduct between diphenyltriketonebis(triphenylphosphine)platinum(0) and oxygen. These were filtered, washed with ether and dried in vacuo. (0.13g, 65%), m.p. 121-124°. Found: C, 61.27; H, 4.4; O, 8.2; M 724, CHCl₃. C₅₁H₄₀O₅P₂Pt requires: C, 61.9; H, 4.08; O, 8.08%; M 989.92. ν(C=O) 1683vw, 1640s, 1629m, 1624m, 1612w cm⁻¹.

Infrared spectrum cm⁻¹: 1683vw, 1640s, 1629m, 1624m, 1612w, 1576m, 1557vw, 1484m, 1481m,sh, 1440s, 1434s, 1356s, 1344m, 1336s, 1304m, 1224w, 1192vw, 1184vw, 1136vw, 1160vw, 1141vw, 1131w, 1102m, 1096m, 1067w, 1027w, 847w, 762w, 756w, 751m, 740w, 724m, 717m, 700s, 627vw, 563s, 536s, 528m, 520m, 509m.

4. The reaction of peroxobis(triphenylphosphine)-platinum(II) with diphenyltriketone.

Peroxobis(triphenylphosphine)platinum(II) (0.5g, 0.665mmol) and diphenyltriketone (0.16g, 0.67mmol) were stirred together in benzene (25 ml) under a nitrogen atmosphere for fifteen minutes. The resulting white suspension was filtered and washed with ether. Recrystallisation from
methylene chloride, benzene-ether gave white crystals (prisms) having a stoichiometry corresponding to a 1:1 adduct between peroxobis(triphenylphosphine)platinum(II) and diphenyltriketone. These were filtered, washed with ether and dried in vacuo, (0.59g, 90%), m.p. 128-131° decomp.

Found: C, 62.48; H, 4.44; O, 8.18; M (two results) 748, 698, CHCl₃. C₅₁H₄₀O₅P₂Pt requires: C, 61.9; H, 4.08; O, 8.08%; M 989.92. ν(C=O) 1696s, 1678s cm⁻¹.

Infrared spectrum cm⁻¹: 1696s, 1678s, 1595w, 1578vw, 1480m, 1436s, 1273m, 1184w, 1176w, 1165w, 1134m, 1109w, 1098s, 1074vw, 1042w, 1026w, 964w, 874s, 812w, 788vw, 772m, 754m, 749m, 713s, 699s, 686s, 658m, 641m, 621w, 592vw, 560s, 531s, 524m, 519m, 511m, 485w.

The infrared spectrum of this product indicated that it was different to the 1:1 adduct formed between diphenyltriketonebis(triphenylphosphine)platinum(O) and oxygen.

5. The reaction of peroxobis(triphenylphosphine)-platinum(II) with diphenyltriketone hydrate.

Peroxobis(triphenylphosphine)platinum(II) (0.5g, 0.665mmol) and diphenyltriketone hydrate (0.17g, 0.665mmol) were stirred together in benzene (20 ml) under a nitrogen atmosphere for fifteen minutes. The resulting dark orange solution was reduced in volume (to ca. 10 ml) by evaporation under reduced pressure and addition of ether yielded a white crystalline solid, which was filtered. Recrystallisation
from methylene chloride, benzene-ether gave white crystals (prisms), which were shown to be identical to the 1:1 adduct formed between peroxobis(triphenylphosphine)platinum(II) and diphenyltriketone by infrared spectrum and melting point. (0.27g, 41%), m.p. 130-132° decomp. v(C=O) 1696s, 1678s cm⁻¹.

The solvent was completely removed from the filtrate by evaporation under reduced pressure and the pale brown residue was dissolved in methylene chloride. Addition of methanol (ca. 5 ml) and petrol (B.P. below 40°) and slow reduction in volume to the precipitation point of the solution gave, on standing, an off-white solid, which was filtered. Recrystallisation from methylene chloride, benzene-ether gave white crystals (needles) which were shown to be identical to the 1:1 adduct formed between diphenyltriketone-bis(triphenylphosphine)platinum(0) and oxygen by infrared spectrum and melting point. These were filtered, washed with ether and dried in vacuo. (0.16g, 41%), m.p. 120-122°.

Found: C, 61.19; H, 4.26; O, 7.68. \( \text{C}_{51} \text{H}_{40} \text{O}_{5} \text{P}_{2} \text{Pt} \) requires: C, 61.9; H, 4.08; O, 8.08%. v(C=O) 1684vw, 1640s, 1628m, 1624m,sh, 1612w,sh cm⁻¹.

6. The reaction of diphenyltriketonebis(triphenylphosphine)platinum(0) with triketoindane.

Diphenyltriketonebis(triphenylphosphine)platinum(0) (0.27g, 0.282mmol) and triketoindane (0.0452g, 0.282mmol) were stirred together in benzene (25 ml) under a nitrogen atmosphere for thirty minutes. The volume of the yellow
solution formed was reduced (to ca. 5 ml) by evaporation under reduced pressure and addition of methylene chloride (ca. 10 ml) and ether and slow reduction in volume by evaporation under reduced pressure yielded a yellow crystalline solid, which was filtered. Recrystallisation from methylene chloride, benzene-ether gave yellow needles having a stoichiometry corresponding to a 1:1 adduct between diphenyltriketonebis(triphenylphosphine)platinum(O) and triketoindane (analysis indicated that the compound incorporated one molecule of methylene chloride). These were filtered, washed with ether, and dried in vacuo. (0.18g, 57%), m.p. 144-147°. Found (two results): C, 61.08, 61.57; H, 4.17, 3.98; O, 8.80, 8.11; M 1105, CHCl3. C60H44O6P2Pt.CH2Cl2 requires: C, 61.0; H, 3.86; O, 8.0%; M 1203. ν(C=O) 1737w, 1704s, 1680s, 1658m cm⁻¹.

Infrared spectrum cm⁻¹: 1737w, 1704s, 1680s, 1658m, 1596w, 1576vw, 1482m, 1440s, 1332vw, 1256m, 1241m, 1182vw, 1161vw, 1136vw, 1111vw, 1103w, 1096m, 1081w, 1068w, 1028w, 946vw, 924vw, 896w, 844w, 832m, 762m, 756m, 752m, 740m, 730m, 712s, 702s, 666w, 640w, 624vw, 583vw, 562w, 542m, 534s, 524s, 516m, 500w.

7. The reaction of diphenyltriketonebis(triphenylphosphine)platinum(O) with diphenyltriketone and acetone.

Diphenyltriketonebis(triphenylphosphine)platinum(O) (0.2g, 0.295mmol) and diphenyltriketone (0.0496g, 0.285mmol)
were stirred together in benzene (20 ml) for one day under an atmosphere of nitrogen after which there was no apparent reaction. The red suspension was filtered, washed with ether and shown to be unreacted diphenyltriketonebis(triphenylphosphine)platinum(0) by comparing the infrared spectrum with that of an authentic sample. (0.16g, 80%).

trans-stilbenebis(triphenylphosphine)platinum(0) (0.5g, 0.555mmol) and diphenyltriketone (0.132g, 0.555mmol) were sealed together in an evacuated Carius tube containing degassed acetone (30 ml). The tube was shaken for three days at room temperature and the deep red crystals formed were assumed to be diphenyltriketonebis(triphenylphosphine)-platinum(0). The tube was then shaken at 70° for two days and in strong ultra-violet radiation for two days, in each case, with no apparent reaction. The red crystalline suspension was filtered, washed with ether and shown to be diphenyltriketonebis(triphenylphosphine)platinum(0) by infrared spectrum and melting point. (0.52g, 98%), m.p. 156-158° (dark red crystals melt to a colourless liquid).

8. The reaction of diphenyltriketonebis(triphenylphosphine)platinum(0) with tetrafluoroethylene.

Tetrafluoroethylene (ca. 2 ml) was condensed into a Carius tube (-196°) containing diphenyltriketonebis(triphenylphosphine)platinum(0) (0.44g, 0.46mmol) and benzene (30 ml). The tube was sealed and shaken at 60° for one day. The pale orange solution formed was filtered and addition
of ether and slow evaporation under reduced pressure yielded a white crystalline solid, which was shown to be tetrafluoroethylenebis(triphenylphosphine)platinum(0) by infrared spectrum and melting point. (0.25g, 68%), m.p. 216-219° (lit. value 218-220°).

9. The reaction of diphenyltriketonebis(triphenylphosphine)platinum(0) with fumaronitrile.

Diphenyltriketonebis(triphenylphosphine)platinum(0) (0.2g, 0.209mmol) and fumaronitrile (0.0164g, 0.21mmol) were refluxed together in benzene (20 ml) under a nitrogen atmosphere for ten minutes. The yellow solution formed was treated with activated charcoal at room temperature and filtered to yield a pale yellow solution, from which the solvent was completely removed by evaporation under reduced pressure. The residue was dissolved in methylene chloride and addition of ether and slow reduction in volume by evaporation under reduced pressure yielded a white crystalline solid, which was filtered and washed with ether. This was shown to be fumaronitrilebis(triphenylphosphine)platinum(0) by infrared spectrum and melting point. (0.14g, 86%), m.p. 295-305°decomp. (lit. value 301°).

10. The reaction of diphenyltriketonebis(triphenylphosphine)platinum(0) with tetracyanoethylene.

Diphenyltriketonebis(triphenylphosphine)platinum(0) (0.3g, 0.314mmol) and tetracyanoethylene (0.04g, 0.313mmol)
were stirred together in benzene (50 ml) for one hour.
The white suspension formed was filtered and washed with ether. Recrystallisation from methylene chloride, benzene-ether gave white crystals, having a stoichiometry corresponding to a 1:1 adduct between diphenyltriketonebis(triphenylphosphine)platinum(O) and tetracyanoethylene (analysis results indicated that the product incorporated one molecule of methylene chloride). These were filtered, washed with ether and dried in vacuo. (0.33g, 94%), m.p. 169-174° decomp.
Found (two results): C, 59.6, 59.48; H, 3.56, 3.53; N, 4.88, 4.71; O, 4.09, 3.97; Cl (Incorporated CH2Cl2), 5.31; M 1166, CHCl3. C57H40N4O3P2Pt.CH2Cl2 requires: C, 59.5; H, 3.61; N, 4.78; O, 4.1; Cl 6.07%; M 1117.1 ν(C=O) 1677w, 1665s cm⁻¹ ν(C≡N) 2225w, 2210vw cm⁻¹.

Infrared spectrum cm⁻¹: 2225w, 2210vw, 1677w, 1665s, 1596w, 1588vw, 1579vw, 1480w, 1439s, 1434s, 1320vw, 1310vw, 1262m, 1218w, 1184w, 1160w, 1144m, 1104m, 1094w, 1064w, 1025vw, 918vw, 896w, 813w, 768w, sh, 774s, 732m, 711s, 702s, 697m, 690m, 673w, 648m, 554s, 532s, 525m, 516m, 506m.

11. The reaction of diphenyltriketonebis(triphenylphosphine)platinum(O) with hexafluorobut-2-yn with hexafluorobut-2-yn at 60°.

Hexafluorobut-2-yn, (ca. 2 ml) was condensed into a Carius tube (-196°) containing diphenyltriketonebis-(triphenylphosphine)platinum(O) (0.9g, 0.94mmol) and benzene (30 ml). The tube was sealed and shaken at 60° for two
hours to give a white suspension in a yellow solution, which was filtered and washed well with ether. Addition of ether to the filtrate and slow evaporation under reduced pressure yielded two further crops of the white solid. The three crops were combined and recrystallisation from methylene chloride, benzene-ether gave white crystals (plates) having a stoichiometry corresponding to a \textit{1:1 adduct} between diphenyltriketonebis(triphenylphosphine)platinum(O) and hexafluorobut-2-ynene. These were filtered, washed with ether and dried \textit{in vacuo}. (0.4g, 38%), m.p. 233-235°. Found (two results): C,58.27, 59.2; H,3.64, 3.77; F,9.60, 9.17; M 997, C₆H₆. C₅₅H₄₀F₁₄O₃P₂Pt requires: C,59.0; H,3.6; F,10.18%; M 1119.97. ν(C=O) 1676s cm⁻¹.

Infrared spectrum cm⁻¹: 1676s, 1593w, 1588vw, 1576w, 1480m, 1436s, 1308vw, 1272s,sh, 1264s, 1259s, 1249s, 1229s, 1212w, 1166s, 1160m, 1123s, 1098s, 1092m, 1086m, 1072vw, 1064vw, 1027w, 992w, 944vw, 863vw, 834w, 819w, 789vw, 760w,sh, 751m, 736s, 713m, 700s, 696s, 659w, 642m, 627vw, 608vw, 578vw, 551s, 531s, 517m, 510m.

The \textsuperscript{19}F n.m.r. spectrum in o-dichlorobenzene showed two signals at \( δ - 7.42 \) p.p.m. (3F, quartet, J(F-F)16.5Hz.) and \( - 15.3 \) p.p.m. (3F. multiplet) relative to internal C₆H₅CF₃. The multiplet appeared to be a triplet of quartets with a triplet coupling of 19.5 Hz. The relative intensities of the triplet components could not be discerned.

The volume of the filtrate was reduced (to ca. 5 ml) by evaporation under reduced pressure and addition of ether
yielded a white solid, which was filtered. Recrystallisation from ether-methanol gave white crystals, which were shown to be hexafluorobut-2-yne-bis(triphenylphosphine)platinum(O) by infrared spectrum and melting point. (0.1g, 12%), m.p. 210-212° (lit. value 215-216°). ν(C=C) 1762s cm⁻¹, (lit. value 1775 cm⁻¹).

The solvent was completely removed from the filtrate by evaporation under reduced pressure and addition of ether to the pale yellow residue yielded a yellow solid, which was filtered. Recrystallisation from methylene chloride-ether gave yellow crystals having a stoichiometry corresponding to a 1:1 adduct between diphenyltriketonebis(triphenylphosphine)-platinum(O) and hexafluorobut-2-yne. These were filtered, washed with ether and dried in vacuo. (0.15g, 14%), m.p. 260-266°. Found (two results): C, 60.01, 59.52; H, 3.98, 3.89; F, 9.29, 9.55; M 1092, C₆H₄O₃F₂P₂Pt requires: C, 59.0; H, 3.6; F, 10.18%; M 1119.97.

Infrared spectrum cm⁻¹: 1647w, 1625s, 1601w, sh, 1597w, 1584vw, 1570w, 1490m, 1479m, 1434s, 1348m, 1341m, 1331w, 1312w, 1301m, 1286m, 1238s, 1212m, 1202s, 1176m, 1164s, sh, 1158s, 1145s, 1119s, 1112m, sh, 1095s, 1076vw, 1066w, 1038w, 1026m, 980m, 940vw, 926vw, 856vw, 840m, 774w, 761m, 752m, 744m, 728w, 714s, 699s, 652vw, 644w, 624w, 580w, 559s, 550m, 536s, 527s, 523s, sh, 505s, 490vw.

The ¹⁹F n.m.r. spectrum in methylene chloride showed two signals at 5 + 1.18 p.p.m. (3F, quartet, J(F-F)13.3Hz.) and - 9.98 p.p.m. (3F, quartet of triplets) relative to
internal C$_6$H$_5$CF$_3$. The low field quartet appeared to be a quartet of triplets. The triplet coupling was 11.4 Hz.

12. The reaction of diphenyltriketonebis(triphenylphosphine)platinum(0) with hexafluorobut-2-yne at room temperature.

Hexafluorobut-2-yne (ca. 2 ml) was condensed into a Carius tube (-196°C) containing diphenyltriketonebis(triphenylphosphine)platinum(0) (1.2g, 1.25mmol) and benzene (30 ml). The tube was sealed and shaken at room temperature for seven days to give a white suspension in a yellow solution, which was filtered and washed with several portions of ether. The filtrate was reduced in volume (to ca. 5 ml) by evaporation under reduced pressure and addition of ether yielded a second crop of the white solid, which was filtered and washed with several portions of ether. The two crops were combined and recrystallisation from methylene chloride, benzene-ether yielded white crystals, which were shown to be identical to the white 1:1 adduct formed between diphenyltriketonebis(triphenylphosphine)platinum(0) and hexafluorobut-2-yne in the reaction at 60°C by infrared spectrum and melting point. (0.89g, 64%), m.p. 230-232°C. ν(C=O) 1676s cm$^{-1}$.

The solvents were completely removed from the filtrate by evaporation under reduced pressure and ether was added to the yellow residue to yield a yellow solid, which was filtered and washed with several portions of ether.
Recrystallisation from methylene chloride-ether gave yellow crystals, which were shown to be identical to the yellow 1:1 adduct formed between diphenyltriketonebis(triphenylphosphine)platinum(0) and hexafluorobut-2-yne in the reaction at 60° by infrared spectrum and melting point. (0.29g, 21%), m.p. 258-268°. Bands in the v(C=O) region 1648w, 1624s cm⁻¹.

Addition of methanol to the filtrate and reduction in volume (to ca. 10 ml) yielded a small quantity of white solid, which was shown to be the white 1:1 adduct between diphenyltriketonebis(triphenylphosphine)platinum(0) and hexafluorobut-2-yne by infrared spectrum. No hexafluorobut-2-ynebis(triphenylphosphine)platinum(0) could be isolated from the filtrate.

13. The reaction between diphenyltriketonebis(triphenylphosphine)platinum(0) and hexafluoroacetone.

Hexafluoroacetone (ca. 1.5 ml) was condensed into a Carius tube (-196°) containing diphenyltriketonebis(triphenylphosphine)platinum(0) (1g, 1.045mmol) and benzene (25 ml). The tube was sealed and shaken at room temperature for two weeks to give a white suspension in a pale yellow solution. The white solid was filtered, washed with ether and recrystallised from methylene chloride-methanol and methylene chloride-ether to give white crystals (needles) having a stoichiometry corresponding to a 1:1 adduct between diphenyltriketonebis(triphenylphosphine)platinum(0) and hexafluoroacetone. These were filtered, washed with ether
and dried in vacuo. (0.36g, 31%), m.p. 190-205° decomp.  
Found: C,57.79; H,3.64; F,10.09; M 962, C₆H₆.  C₅₄H₄₀F₆O₄
P₂Pt requires: C,57.6; H,3.58; F,10.14%; M 1124.  ν(C=O)
1670s, 1648s cm⁻¹.

Infrared spectrum cm⁻¹:  1670s, 1648s, 1596w, 1579w,  
1484m, 1480m, 1440s, 1434s, 1316vw, 1296vw, 1283vw, 1256m,  
1229m,sh, 1219s, 1200s, 1184m,sh, 1174vs, 1147vw, 1137w,  
1101m, 1096m, 1092m,sh, 1084s, 1044vw, 1027w, 969s, 954w,sh,  
842vw, 823w, 792vw, 776vw, 760s, 756m,sh, 748m, 739w, 727w,  
718m, 708s, 700s, 693s, 659w, 650w, 624w, 621w,sh, 584vw,  
553s, 584s, 523m, 514m.

The ¹⁹F n.m.r. spectrum in methylene chloride for a
freshly prepared solution showed one signal at δ + 14.5 p.p.m.  
(1:4:1 triplet, J(Pt-F)13.7 Hz.) and for a solution allowed  
to stand in light, two signals at δ + 3.28 p.p.m. (1:4:1  
triplet of doublets, J(Prans-F)11.3 Hz.,J(Pcis-F)not  
discernable, J(Pt-F)70.5 Hz.) and + 14.5 p.p.m. (1:4:1 triplet,  
J(Pt-F)13.7 Hz.) relative to internal C₆H₅CF₃.  The signal  
at δ + 3.28 p.p.m. is assigned to hexafluoroacetonebis(tri-  
phenylphosphine)platinum(O) (lit. values, δ + 3.28 p.p.m.  
relative to C₆H₅CF₃ determined for an authentic sample  
J(Ptrans-F) 11.3 Hz., J(Pt-F)70.5 Hz.).¹  In the solid state  
the white crystalline solid appears to decompose in the  
presence of light.

The volume of the filtrate was reduced (to ca. 10 ml)  
by evaporation under reduced pressure.  Addition of ether  
and a small volume of petrol (B.P. below 40°) gave white  
crystals, which were shown to be hexafluoroacetonebis(tri-
phenylphosphine)platinum(0) by infrared and n.m.r. spectra and melting point. (0.44g, 48%), m.p. 215° (lit. value 216-218°).\textsuperscript{1}

The $^{19}$F n.m.r. spectrum in methylene chloride showed one signal at δ + 3.28 p.p.m. (1:4:1 triplet of doublets) relative to internal $\text{C}_6\text{H}_5\text{CF}_3$.

$J(\text{Ptrans-F})$ 11.5Hz., $J(\text{Pcis-F})$ not discernable and $J(\text{Pt-F})$ 70.0 Hz. (lit values $J(\text{Ptrans-F})$ 11.3 Hz., $J(\text{Pt-F})$ 70.5 Hz.)\textsuperscript{1}

14. The reaction of the white 1:1 adduct formed between diphenyltriketonetris(triphenylphosphine)-platinum(0) and hexafluorobut-2-yne with hydrogen chloride.

Hydrogen chloride gas was bubbled through a stirred solution of Pt(PhCOCOCOPh)($C_4\text{F}_6$)($\text{PPh}_3$)$_2$ (0.18g, 0.161 mmol) in methylene chloride (20 ml) for five minutes. Addition of ether and a small volume of petrol (B.P. below 40°) and slow reduction in volume by evaporation under reduced pressure yielded a white crystalline solid. Recrystallisation from methylene chloride-ether, petrol (B.P. below 40°) gave white crystals having a stoichiometry corresponding to a 1:1 adduct between Pt(PhCOCOCOPh)($C_4\text{F}_6$)($\text{PPh}_3$)$_2$ and hydrogen chloride. These were filtered, washed with ether and dried in vacuo. (0.14g, 75%), m.p. 220-222°. Found: C,57.29; H,3.79, F,9.9; Cl,3.81; M 996, CHCl$_3$. $C_{55}H_{41}ClF_6O_3P_2Pt$ requires: C,57.15; H,3.58; F,9.86; Cl,3.07%. M 1156.4. $\nu$(C=O) 1698m, 1676s, cm$^{-1}$, $\nu$(O-H) 3340w cm$^{-1}$, $\nu$(Pt-Cl) 301s cm$^{-1}$. 
Infrared spectrum cm⁻¹: 3340w, 1698m, 1676s, 1595w, 1588vw, 1580w, 1573vw, 1554vw, 1482m, 1440s, 1435s, sh, 1400m, 1348s, 1344s, 1248s, 1240m, sh, 1190w, 1181w, 1162s, 1152s, 1143s, 1135s, 1124s, 1116m, 1108m, 1097m, 1092m, 1042w, 1023w, 944vw, 850vw, 844vw, 819w, 781w, 760w, sh, 754m, 748m, 732m, 711m, 698s, 657w, 630w, 624vw, 586vw, 562vw, 552w, 530s, 525m, 518m, 508w, 501w.

The $^{19}$F n.m.r. spectrum in methylene chloride showed two signals at δ - 9.65 p.p.m. (3F, quartet, J(F-F) 19.5 Hz.) and - 18.7 p.p.m. (3F, quartet of double doublets, J(Ptrans-F) 6.9 Hz., J(Pcis-F) 3.0 Hz., J(P-F) not discernable) relative to internal $\text{C}_6\text{H}_5\text{CF}_3$.

When Pt(PhCOCOCOPh)(C$_2$F$_2$)(PPh$_3$)$_2$ (0.2 g, 0.179 mmol) and excess trifluoroacetic acid (0.204 g, 1.79 mmol) were stirred together for twelve hours in methylene chloride only unreacted Pt(PhCOCOCOPh)(C$_2$F$_2$)(PPh$_3$)$_2$ could be isolated, identified by comparing the infrared spectrum with that of an authentic sample. (0.18 g, 90%).

15. The reaction of Pt(PhCOCOCOPh)(C$_4$F$_6$)(PPh$_3$) with hydrogen chloride and trifluoroacetic acid.

Hydrogen chloride gas was bubbled through a stirred solution of Pt(PhCOCOCOPh)(C$_4$F$_6$)(CO)(PPh$_3$) (0.13 g, 0.147 mmol) in methylene chloride (15 ml) for one hour. Addition of ether and slow reduction in volume by evaporation under reduced pressure yielded a white crystalline solid whose infrared spectrum showed weak bands in the v(O-H) and v(Pt-Cl) regions but was shown to be mainly unreacted.
Pt(PhCOCOCOPh)(C,F,)(CO)(PPh,) by comparing the infrared spectrum with that of an authentic sample. (0.12g).

When Pt(PhCOCOCOPh)(C,F,)(CO)(PPh,) (0.1g, 0.113mmol) and excess trifluoroacetic acid (0.13g, 1.14mmol) were stirred together for twelve hours only unreacted Pt(PhCOCOCOPh)(C,F,)(CO)(PPh,) could be isolated, identified by comparing the infrared spectrum with that of an authentic sample. (0.09g, 90%).

16. The reaction of the yellow 1:1 adduct formed between diphenyltriketonebis(triphenylphosphine)-platinum(O) and hexafluorobut-2-yne with aqueous hydrogen chloride.

To a solution of Pt(PhCOCOCOPh)(C,F,)(PPh,) (0.12g, 0.107mmol) in chloroform (15 ml) was added 1.10 ml of 0.10022M hydrogen chloride in water (0.107mmol HCl) and the mixture was shaken for two days. The solvent from the yellow solution was completely removed by evaporation under reduced pressure and addition of methanol yielded a white solid, which was filtered and washed with ether. This was shown to be cis-dichlorobis(triphenylphosphine)platinum(II) by infrared and far infrared spectra and melting point. (0.04g, 48%), m.p. 308-312° (lit. value 310-312°).76

The solvent was completely removed from the filtrate by evaporation under reduced pressure and addition of ether to the yellow residue yielded a yellow solid which was shown to be unreacted Pt(PhCOCOCOPh)(C,F,)(PPh,) by
infrared spectrum and melting point. (0.05g, 42%), m.p. 262-266°.

17. The reaction of the 1:1 adduct formed between diphenyltriketonebis(triphenylphosphine)platinum(0) and tetracyanoethylene with hydrogen chloride.

Hydrogen chloride gas was bubbled into a stirred solution of Pt(PhCOCOCOpH)(TCNE)(PPh\textsubscript{3})\textsubscript{2} (0.08g, 0.074mmol) in methylene chloride (15 ml) for a few minutes. Ether was added and slow reduction in volume under reduced pressure yielded a white crystalline solid, which was shown to be cis-dichlorobis(triphenylphosphine)platinum(II) by infrared spectrum and melting point. (0.056g, 96%), m.p. 311-314° (lit. value 310-312°).\textsuperscript{76}

18. The reaction of the white 1:1 adduct between diphenyltriketonebis(triphenylphosphine)platinum(0) and hexafluorobut-2-yne with carbon monoxide.

Carbon monoxide was bubbled through a vigorously stirred suspension of Pt(PhCOCOCOpH)(C\textsubscript{4}F\textsubscript{6})(PPh\textsubscript{3})\textsubscript{2} (0.17g, 0.157mmol) in benzene (25 ml). When a clear solution was formed, (ca. twenty minutes) an excess of petrol (B.P. below 40°) was added and carbon monoxide was passed for a further ten minutes while a white solid slowly precipitated. This was filtered and recrystallisation from methylene chloride-ether gave white crystals having a stoichiometry corresponding to Pt(PhCOCOCOpH)(C\textsubscript{4}F\textsubscript{6})(CO)(PPh\textsubscript{3}). These were filtered,
washed with ether and dried in vacuo. (0.11g, 82%), m.p. 259-261°. Found: C, 51.2; H, 2.91; F, 12.94; M 949, CHCl₃. C₃₈H₂₅F₆O₄P要求: C, 51.5; H, 2.85; F, 12.87%; M 885.67. ν(CO) 2083s cm⁻¹, ν(C=O) 1686s cm⁻¹.

Infrared spectrum cm⁻¹: 2083s, 1686s, 1595w, 1591vw, 1579vw, 1483m, 1440s, 1336vw, 1314vw, 1302vw, 1273s, 1259s, 1248s,sh, 1238s,sh, 1232s, 1192w, 1184w, 1176s, 1164m,sh, 1158m, 1153w, 1139s, 1130w,sh, 1116m, 1108m, 1103m, 1098m, 1090w, 1074vw, 1060vw, 1028w, 996w, 864w, 843w, 824w, 771w, 761m, 758m, 753m, 742s, 723m, 719m, 707m, 700s, sh, 697s, 686w, 664w, 646m, 624vw, 616vw, 604vw, 575m, 544m, 533m, 519m, 512m, 506m.

The ¹⁹F n.m.r. spectrum in methylene chloride showed two signals at 6 - 8.14 p.p.m. (3F, quartet, J(F-F) 14.3 Hz.) and - 9.05 p.p.m. (3F, multiplet) relative to internal C₆H₅CF₃. The multiplet appeared to be a doublet of quartets with a doublet coupling of 8.3 Hz. J(Pt-F) could not be discerned.

19. The reaction of Pt(PhCOCOCOPh)(C₄F₆)(CO)(PPh₃) with methyldiphenylphosphine.

To a stirred suspension of Pt(PhCOCOCOPh)(C₄F₆)(CO)(PPh₃), (0.17g, 0.192mmol) in benzene (10 ml) was slowly added a solution of methyldiphenylphosphine (0.04g, 0.2mmol) in ether (10 ml). The solvents were removed completely from the pale yellow solution formed by evaporation under reduced pressure and addition of ether to the residue yielded a pale yellow crystalline solid, which showed no ν(CO) band in the
2000 cm\(^{-1}\) region of the infrared spectrum. The pale yellow solid was dissolved in methylene chloride, treated with activated charcoal at room temperature and filtered. Addition of ether and slow reduction in volume by evaporation under reduced pressure yielded a white crystalline solid, which was twice recrystallised from methylene chloride-ether to give white crystals, having a stoichiometry corresponding to \(\text{Pt(PhCOCOCOPh)(C}_4\text{F}_6\text{MePPh}_2\text{PPh}_3\text{)}\). These were filtered, washed with ether and dried in vacuo. (0.15g, 75\%), m.p. 249-250\(^0\). Found: C, 56.86; H, 3.60; F, 10.67; M 1040, CHCl\(_3\). \(\text{C}_{50}\text{H}_{38}\text{F}_6\text{O}_3\text{P}_2\text{Pt}\) requires: C, 56.75; H, 3.62; F, 10.79\%; M 1057.89.

Infrared spectrum cm\(^{-1}\): 1676s, 1668s, 1595w, 1587vw, 1580w, 1568vw, 1560vw, 1485w, 1477w, 1356s, 1289vw, 1269s, 1252m,sh, 1235s, 1228s, 1181w, 1166s, 1157m, 1136m, 1127s,sh, 1121s, 1109m,sh, 1100m,sh, 1087m, 1027vw, 989vw, 944vw, 896m,sh, 890m, 883m, 861vw, 840w, 817w, 794vw, 761w,sh, 753m, 748m, 735s, 704m, 696s, 659w, 638w, 576vw, 530m, 517m, 496m.

The \(^{19}\text{F}\) n.m.r. spectrum in methylene chloride showed two signals at \(5 - 6.88\) p.p.m. (3F, quartet, \(J(\text{F-F})\) 15 Hz.) and - 14.3 p.p.m. (3F. multiplet) relative to internal \(\text{C}_6\text{H}_5\text{CF}_3\). The multiplet appeared to be a triplet of quartets with a triplet coupling of 21 Hz. The relative intensity of the triplet components could not be discerned.

The \(^{1}\text{H}\) n.m.r. spectrum in deuterochloroform showed a signal at 2.5\(\tau\) (phenyl protons, multiplet) and at 8.6\(\tau\) (methyl protons, doublet) \(J(\text{P-H})\) 8 Hz., \(J(\text{Pt-H})\) not discernible.
20. The reaction of Pt(PhCOCOCOPh)(C\textsubscript{4}F\textsubscript{6})(CO)(PPh\textsubscript{3})
with triphenylarsine.

Pt(PhCOCOCOPh)(C\textsubscript{4}F\textsubscript{6})(CO)(PPh\textsubscript{3}) (0.18g, 0.203mmol)
and triphenylarsine (0.0622g, 0.204mmol) were stirred
together in benzene (10 ml) for two days with no apparent
reaction. The solvent from the suspension was completely
removed by evaporation under reduced pressure and addition
of methylene chloride and ether to the residue yielded a
white crystalline solid, which was filtered and washed with
ether. This was shown to be unreacted Pt(PhCOCOCOPh)(C\textsubscript{4}F\textsubscript{6})
(CO)(PPh\textsubscript{3}) by comparing the infrared spectrum with that of
an authentic sample. (0.16g, 90%).

The reaction was repeated in refluxing toluene
using a large excess (ca. x 10) of triphenylarsine with the
same result.

21. The reaction of trans-chloro(carbonyl)bis(tri-
phenylphosphine)iridium(I) with diphenyldiketone.

trans-Chloro(carbonyl)bis(triphenylphosphine)iridium(I)
(0.5g, 0.64mmol) and diphenyldiketone (0.153g, 0.64mmol)
were stirred together in benzene (25 ml) under a nitrogen
atmosphere for twelve hours. The yellow solution with
yellow suspended solid was reduced in volume (to ca. 10 ml)
and the yellow solid filtered. This was shown to be unreacted
trans-chloro(carbonyl)bis(triphenylphosphine)iridium(I) by
comparing the infrared spectrum with that of an authentic
sample. (0.4g, 80%). \( \nu(CO) \) 1960 cm\(^{-1} \) (lit. value 1950 cm\(^{-1} \)).
The reaction was repeated in refluxing benzene with the same result.

22. The reaction of chlorotris(triphenylphosphine)-rhodium(I) with diphenyltriketone.

Chlorotris(triphenylphosphine)rhodium(I) (0.5g, 0.54mmol) and diphenyltriketone (0.13g, 0.545mmol) were stirred together in benzene (30 ml) under a nitrogen atmosphere for one day. The brick red suspension formed was shown to be \(\mu'\)-dichlorotetrakis(triphenylphosphine)dichlororhodium(I)\(^{81}\) by infrared and far infrared spectra and melting point. (0.3g, 83%), m.p. 128-138\(^{\circ}\)decomp., \(\nu\)(Rh-Cl) 300 cm\(^{-1}\).

D. DIPHENYLTRIKETONE

1. The reaction of tetrakis(triphenylphosphine)-platinum(0) with diphenyltriketone.

Tetrakis(triphenylphosphine)platinum(0) (1g, 0.804mmol) and diphenyltriketone (0.214g, 0.804mmol) were stirred together in benzene (50 ml) under a nitrogen atmosphere for one hour to produce an orange suspension in an orange solution. The suspension was filtered yielding an orange solid having a stoichiometry corresponding to diphenyltriketonebis(triphenylphosphine)platinum(0). This was washed with ether, dried \textit{in vacuo} and stored under nitrogen. (0.39g, 49%).

\begin{itemize}
  \item Found: C, 63.0; H, 3.9; O, 6.8; M 978, CHCl
  \item \(\text{C}_{52}\text{H}_{40}\text{O}_{4}\text{P}_{2}\text{Pt}\) requires: C, 63.3; H, 4.08; O, 6.49%; M 985.93.
\end{itemize}
\[ \nu(C=O) 1670\text{s cm}^{-1}. \]

Infrared spectrum cm\(^{-1}\): 1670s, 1609w, 1596m, 1585vw, 1572m, 1493s, 1439s, 1355m, 1229vw, 1319m, 1311m, 1281s, 1274s,sh, 1228w, 1215m, 1188m, 1170s, 1161m, 1099s, 1074w, 1065vw, 1028m, 978vw, 953s, 947s, 866s, 857m,sh, 808w, 778vw, 764s, 752s, 736s, 729s, 716s,sh, 712s, 701vs, 690vs, 670m, 643s, 624w, 618w, 557vs, 539vs, 534s, 520s, 511s, 492w, 465vw, 456w.

2. The reaction of diphenyltetraketonebis(triphenylphosphine)platinum(0) with oxygen.

Diphenyltetraketonebis(triphenylphosphine)platinum(0) (0.18g, 0.183mmol) was shaken in oxygenated benzene (50 ml) for two weeks to produce a pale yellow solution. The solvent was completely removed by evaporation under reduced pressure and the residue was dissolved in methylene chloride. Addition of ether and petrol (B.P. below 40\(^\circ\)) and slow reduction in volume by evaporation under reduced pressure yielded a white solid, which was filtered and recrystallised from methylene chloride-ether to give white crystals having a stoichiometry corresponding to a 1:1 adduct between diphenyltetraketonebis(triphenylphosphine)platinum(0) and oxygen. These were filtered, washed with ether and dried in vacuo. (0.13g, 70\%), m.p. 138-140\(^\circ\). Found: C,61.5; H,3.8; O,9.08; M 979, CHCl\(_3\). \(C_{52}H_{40}O_{6}P_{2}Pt\) requires: C,61.35; H,3.96; O,9.43%; M 1017.9. \[ \nu(C=O) 1684m, 1641s, 1630m, \text{cm}^{-1}. \]

Infrared spectrum cm\(^{-1}\): 1684m, 1641s, 1630m, 1598vw, 1584vw, 1576w, 1480m, 1440m, 1433s, 1352w, 1324s, 1316m,sh, 1302w,
3. A preliminary investigation into the reaction of peroxobis(triphenylphosphine)platinum(II) with diphenyltetraketone hydrate.

Peroxobis(triphenylphosphine)platinum(II) (0.41g, 0.545mmol) and diphenyltetraketone hydrate (0.16g, 0.545mmol) were stirred together in benzene (25 ml) under a nitrogen atmosphere for two hours. The dark brown solution formed was treated with activated charcoal at room temperature and filtered to give a yellow solution. The volume was reduced (to ca. 10 ml) and addition of ether and petrol (B.P. below 40°) gave a pale yellow solid, which was filtered. Several recrystallisations from methylene chloride-ether gave white crystals, which were shown to be identical to the 1:1 adduct formed between diphenyltetraketonebis(triphenylphosphine)-platinum(0) and oxygen by infrared spectrum and melting point (0.18g, 32%), m.p. 142-144°. ν(C=O) 1686m, 1640s, 1631m cm⁻¹.

E. ALLOXAN

1. The reaction of trans-stilbenebis(triphenylphosphine)platinum(0) with alloxan.

trans-Stilbenebis(triphenylphosphine)platinum(0) (1g, 1.11mmol) and alloxan (0.158g, 1.11mmol) were stirred
together in benzene (150 ml) under a nitrogen atmosphere for three days, after which the buff coloured suspended solid formed was filtered. Rapid recrystallisation from chloroform, methylene chloride-ether yielded buff coloured crystals having a stoichiometry corresponding to alloxanbis(triphenylphosphine)platinum(0). These were filtered, washed with benzene, dried in vacuo and stored under nitrogen. (0.7g, 73%).

Found: C,55.77; H,3.67; N,3.12; O,7.24; M 1088, CHCl₃. C₄₀H₃₂N₂O₄P₂Pt requires: C,55.75; H,3.74; N,3.25; O,7.43%; M 861.75. ν(C=O) 1739w,sh, 1716s, 1694m, 1682m,sh, 1648s cm⁻¹, ν(N-H) 3160m, 3047m, cm⁻¹.

Infrared spectrum cm⁻¹: 3160m, 3047m, 1739w,sh, 1716s, 1694s, 1682m,sh, 1648s, 1581vw, 1567vw, 1480m, 1476m,sh, 1441m, 1433s, 1370s, 1312vw, 1252m, 1231m, 1184vw, 1156w, 1105m, 1094m, 1070vw, 1038vw, 1025vw, 867w, 844w, 805w, 776w, 771w,sh, 767m, 760w, sh, 754w,sh, 747m, 722vw, 712m, 699s, 647vw, 624vw, 558w,sh, 547m, 531s, 522s, 511m, 503s, 544m.

Similarly diphenylacetylenebis(triphenylphosphine)-platinum(0) (0.5g, 0.557mmol) and alloxan (0.079g, 0.557mmol) under the same conditions yielded alloxanbis(triphenylphosphine)platinum(0). (0.4g, 83%).

2. The reaction of trans-stilbenebis(triphenylphosphine)-platinum(0) with alloxan hydrate.

trans-Stilbenebis(triphenylphosphine)platinum(0)
(0.5g, 0.556mmol) and alloxan hydrate (0.089g, 0.556mmol) were stirred together in benzene (75 ml) under a nitrogen atmosphere for three days, after which the buff coloured suspension formed was filtered and shown to be an impure sample of alloxanbis(triphenylphosphine)platinum(0). Rapid recrystallisation from chloroform, methylene chloride-ether yielded an almost pure sample of alloxanbis(triphenylphosphine)platinum(0) identified by comparing the infrared spectrum with that of a sample prepared from alloxan. (0.32g, 66%). \( \nu(C=O) 1734w,sh, 1714s, 1694m, 1682m, 1648s \ cm^{-1}. \ \nu(N-H) 3160m, 3047m, \ cm^{-1}. \)

Alloxanbis(triphenylphosphine)platinum(0) was shown to react with oxygen and hexafluoroacetone to give white and yellow solids respectively, but the purity of the products appeared to be very low and they showed very broad absorptions in the \( \nu(C=O) \) region of the infrared spectrum.

F. **ISATIN**

The reaction of tetrakis(triphenylphosphine)platinum(0) with isatin.

Tetrakis(triphenylphosphine)platinum(0) (0.5g, 0.402mmol) and isatin, (0.06g, 0.405mmol) were refluxed together in benzene (50 ml) under a nitrogen atmosphere for twelve hours. The red solution formed was reduced in volume (to ca. 10 ml) and addition of ether and further reduction in volume gave on standing dark red crystals having a stoichiometry corresponding to \( \text{Pt(isatin)(PPh}_3)_2 \). These were filtered,
washed with ether and dried in vacuo. (0.3g, 86%), m.p. 218-220°. Found: C, 60.56; H, 3.99; N, 1.78; M 834, CHCl₃.

C₄₄H₃₅NO₂P₂Pt requires: C, 61.0; H, 4.05; N, 1.62%; M 866.

ν(C=O) 1723s, 1674s cm⁻¹, ν(Pt-H) 2175 cm⁻¹.

Infrared spectrum cm⁻¹: 2175m, 1723s, 1674s, 1608s, 1596m, sh, 1583s, 1565vw, 1480m, 1482s, 1326m, 1307m, 1296w, 1269w, 1221m, 1188w, sh, 1182w, 1156w, 1142w, 1095s, 1026w, 973vw, 917m, 868vw, 840m, 824w, 760s, 748m, 743m, 729vw, 717s, 699s, 673vw, 624w, 552vw, 528s, 524s, sh, 516m, sh, 509m, 488vw, 477w.

The ¹H n.m.r. spectrum in deuterochloroform showed two signals: 2.6τ (multiplet, phenyl protons), 21.8τ (1:2:1 triplet, Pt-H, J(Pt-H) 14 Hz., J(Pt-H) not observed) relative to internal T.M.S.

G. BENZOYL CYANIDE

The reaction of trans-stilbenebis(triphenylphosphine)platinum(O) with benzoylcyanide.

trans-Stilbenebis(triphenylphosphine)platinum(O) (1g, 1.11mmol) and benzoylcyanide (0.146g, 1.11mmol) were stirred together in benzene (30 ml) under a nitrogen atmosphere for twelve hours. The orange solution formed was reduced in volume (to ca. 10 ml) by evaporation under reduced pressure and addition of ether and a small volume of petrol (B.P. below 40°) yielded a pale yellow solid. Recrystallisation from methylene chloride, benzene-ether, petrol (B.P. below 40°) gave pale yellow crystals (prisms) having a stoichiometry Pt(PhCOCN)(PPh₃)₂. These were filtered, washed with ether
and dried in vacuo. (0.3g, 32%), m.p. 187-189°.

Found: C,61.79; H,4.26; N,1.65. \( \text{C}_{44} \text{H}_{35} \text{NOP}_2 \text{Pt} \)
requires: C,62.15; H,4.16; N,1.65%. \( \nu (\text{C}=\text{O}) \) 1629s cm\(^{-1}\),
\( \nu (\text{C}=\text{N}) \) 2144w cm\(^{-1}\).

Infrared spectrum cm\(^{-1}\): 2144w, 1629s, 1590w, 1576w,
1569w, 1478s, 1437s,sh, 1432s, 1301vw, 1184m, 1156m, 1096s,
1070vw, 1024vw, 976vw, 883s, 774w, 762m, 750m, 744m, 710s,
697s, 692s,sh, 681w, 648s, 625vw, 620vw, 543s, 528s, 520s,
514m, 503m.

Gas was evolved at the melting point of this product
and a sample when heated at 200° for several minutes yielded
a white solid whose infrared spectrum showed no \( \nu (\text{C}=\text{O}) \) but
\( \nu (\text{C}=\text{N}) \) at 2120 cm\(^{-1}\).

Infrared spectrum cm\(^{-1}\): 2120w, 1604vw, 1590vw,
1572w, 1482m, 1442s, 1437s, 1424w, 1316vw, 1184vw, 1160vw,
1120vw, 1101s, 1072vw, 1028vw, 763m, 752m, 737m, 717s, 699s.

The filtrate was treated with activated charcoal
at room temperature and filtered. The solvents were completely
removed from the pale yellow solution formed by evaporation
under reduced pressure and the white residue was dissolved
in methylene chloride. Addition of ether and slow evaporation
under reduced pressure yielded a white solid. Recrystallisation
from methylene chloride, benzene-ether gave white crystals
having a stoichiometry corresponding to Pt(CN)_2(PPh_3)_2.
These were filtered, washed with ether and dried in vacuo.
(0.15g, 35%), m.p. 330°. Found: C,58.6 H,3.99. \( \text{C}_38 \text{H}_{30} \text{N}_2 \text{P}_2 \text{Pt} \)
requires: C,59.0; H,3.92%. \( \nu (\text{C}=\text{N}) \) 2135 cm\(^{-1}\).

Infrared spectrum cm\(^{-1}\): 2135m, 1584vw, 1568vw, 1480m,
1339s, 1334s, sh, 1330w, 1306w, 1182w, 1155w, 1098s, 1095m, sh,
1067vw, 1024w, 755s, 717m, 700s, 648vw, 622vw, 530s, 518s,
511m, 489w.
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<th>m.p. ( ^\circ C )</th>
<th>INFRARED SPECTRUM ( \text{cm}^{-1} )</th>
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<tr>
<td>((\text{PPh}_3)_2\text{Pt}(\text{T}))</td>
<td>Yellow</td>
<td>210-214 dec.</td>
<td>1709m 1678s</td>
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<tr>
<td>((\text{PPh}_3)_2\text{Pt}(\text{T})(\text{O}_2))</td>
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<td>168-171</td>
<td>1752s 1675s vsym(OCO) 1315m, 1275s</td>
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<td>((\text{PPh}_3)_2\text{Pt}(\text{T})_2)</td>
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<td>157-161</td>
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<td>((\text{PPh}_3)_2\text{Pt}(\text{T})(\text{TCNE}))</td>
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<td>198-202</td>
<td>1741m 1712s v(C≡N) 2229m</td>
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<tr>
<td>((\text{PPh}_3)_2\text{Pt}(\text{T})(\text{TCNE})_2)</td>
<td>Yellow</td>
<td>185-205 dec.</td>
<td>1744m 1713s v(C≡N) 2205s</td>
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(T) = Triketoin; (Dtri) = Diphenyltriketone; (Dteta) = Diphenyltetraketone; (Allox) = Alloxan.
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<th>m.p.°C</th>
<th><strong>INFRARED SPECTRUM cm⁻¹</strong></th>
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<td>(PPh₃)₂Pt(T)(C₄F₆)</td>
<td>Yellow</td>
<td>164-168</td>
<td>v(C=O) 1751w 1744w 1718s 1704s</td>
<td>-7.05 p.p.m. (g,3F) -13.6 p.p.m. (m,3F)</td>
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<td>(PPh₃)₂Pt(T) [(CF₃)₂CO]</td>
<td>Yellow</td>
<td>200-220</td>
<td>v(C=O) 1733m 1705s</td>
<td>+7.1 p.p.m. (s,6F)</td>
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<td>(PPh₃)₂Pt(T) [(CF₃)₂CO]₂</td>
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<td>v(C=O) 1732s</td>
<td>+5.98 p.p.m. (g,3F) +7.98 p.p.m. (g,3F) +15.6 p.p.m. (g,3F) +17.8 p.p.m. (g,3F)</td>
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<td>(PPh₃)₂Pt(T) [(CF₃)₂CO]</td>
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<td>v(C=O) 1728s</td>
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<td>2-Hydroxy-1,3-indandione</td>
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<td>Ninhydrin</td>
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<td>1722w, 1746s, 1718s</td>
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<tr>
<td>Diphenyltriptylène</td>
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<td>1326</td>
<td>v(O=O)</td>
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<td>812w or 788vw</td>
<td>v(C=O)</td>
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<td>225w</td>
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<td>(PPh(_3))(_2)Pt(Dt(_3))((C(_4)F(_6))) (Yellow)</td>
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<td>(PPh(_3))(_2)Pt(Dt(_3))((C(_4)F(_6))(HCl)) (Yellow)</td>
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**INFRARED SPECTRUM cm\(^{-1}\)**

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**Other bands**

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<td>COLOUR</td>
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</tr>
<tr>
<td>(PPh₃)₂Pt(CN)(Ph)</td>
<td>White</td>
</tr>
<tr>
<td>(PPh₃)₂Pt(CN)₂</td>
<td>White</td>
</tr>
<tr>
<td>PhCOCN</td>
<td>White</td>
</tr>
</tbody>
</table>

¹⁹F n.m.r. spectra measured relative to CF₃C₆H₅

¹H n.m.r. spectra measured relative to TMS
CHAPTER TWO
2.1. Introduction

**Vinyl isomerisation reactions of platinum-olefin complexes.**

The isomerisation of a platinum-olefin complex to the corresponding vinyl complex was first observed when the olefin complex \((\text{PPh}_3)_2\text{Pt}(\text{CFClCF}_2)\) was heated to just below its melting point (m.p. 206-208° decomp.) At this temperature the **trans**-vinyl complex \(\text{trans-}(\text{PPh}_3)_2\text{Pt}(\text{CFClCF}_2)\text{Cl}\) \(^{87,40}\) is formed which exhibits \(\text{v}(C=C)\) at 1735 cm\(^{-1}\).

The tetrachloroethylene complex \((\text{PPh}_3)_2\text{Pt}(\text{CCI}_2\text{CCl}_2)\), \(^{88,89}\) prepared by the reaction of tetrachloroethylene with tetrakis(triphenylphosphine)platinum(0) in benzene at 105°, also isomerises, in refluxing ethanol, to the perchlorovinyl complex **cis**-\((\text{PPh}_3)_2\text{Pt}(\text{CCI}_2\text{CCl}_2)\text{Cl}\) \(^{89}\) (\(\text{v}(\text{Pt-Cl})\) 307 cm\(^{-1}\) and \(\text{v}(C=C)\) 1550 cm\(^{-1}\)). This isomerisation reaction does not proceed in refluxing benzene, dichloromethane or acetone indicating that the isomerisation is solvent dependent. However, if tetracyanoethylene or tetrachloroethylene is present in a benzene solution vinyl isomerisation of the tetrachloroethylene complex does occur. Triphenylphosphine inhibits the isomerisation which is apparently caused by the presence of tetrachloroethylene in benzene solution.

The reactions of trichloroethylene and **trans**-dichloroethylene with tetrakis(triphenylphosphine)platinum(0) in benzene at 105° lead directly to the formation of the vinyl complexes \(^{89}\) \(\text{trans-}(\text{PPh}_3)_2\text{Pt}(\text{CHCl}_2)\text{Cl}\) and **trans**-
These reactions probably proceed via olefin complex intermediates, which undergo vinyl isomerisation under the reaction conditions.

Thus the reactions of the olefins with trans-stilbenebis(triphenylphosphine)platinum(0) under mild conditions (room temperature) yield the olefin complexes \((\text{PPh}_3)_2\text{Pt(CClCCl}_2)\) and \((\text{PPh}_3)_2\text{Pt(} \text{trans-CCl}_2\text{CHCl})\), which readily undergo vinyl isomerisation reactions, \((\text{PPh}_3)_2\text{Pt-(CHClCCl}_2)\) isomerising in ethanol to give \textit{cis}-(\text{PPh}_3)_2\text{Pt-(CHClCCl}_2)\text{Cl}\) and \((\text{PPh}_3)_2\text{Pt(} \text{trans-CHClCHCl})\) in refluxing methylene chloride to give a mixture of \textit{cis} and \textit{trans}-(\text{PPh}_3)_2\text{Pt(CHCHCl)Cl}\).

In contrast to these results, tribromoethylene reacts with trans-stilbenebis(triphenylphosphine)platinum(0) to give the vinyl complex \((\text{PPh}_3)_2\text{Pt(C}_2\text{Br}_2\text{H})\text{Br}\) probably via an olefin complex intermediate. It thus appears that Br migration from the olefin onto platinum occurs more readily than Cl migration and this possibly is a consequence of the weaker C-Br bond.

The olefin complexes \((\text{PPh}_3)_2\text{Pt(CFCF}_2)\)\(^{87,40}\) and \((\text{MePPh}_2)_2\text{Pt(CFCF}_2)\)\(^{40}\) prepared by the reaction in benzene of chlorotrifluoroethylene with tetrakis(triphenylphosphine)platinum(0) and tetrakis(methyldiphenylphosphine)platinum(0) both isomerise in refluxing n-butanol to give the vinyl complexes \textit{trans}-(\text{PPh}_3)_2\text{Pt-(CFCF}_2)\text{Cl} v(C=C) 1735 cm\(^{-1}\) and \textit{trans}-(\text{MePPh}_3)_2\text{Pt(CFCF}_2)\text{Cl}, v(C=C) 1727 cm\(^{-1}\), respectively.
In keeping with the observed reactivity of tribromoethylene towards vinyl complex formation\(^90\) the olefin complexes \((\text{PPh}_3)_2\text{Pt}(\text{CFBrCF}_2)\)\(^40\) and \((\text{MePPh}_2)_2\text{Pt}-(\text{CFBrCF}_2)\)\(^92\) formed in the reactions of bromotrifluoroethylene with tetrakis(triphenylphosphine)platinum(O) and tetrakis(methyldiphenylphosphine)platinum(O) appear to undergo vinylisation reactions more readily than the analogous chlorotrifluoroethylene olefin complexes. The isomerisation of \((\text{PPh}_3)_2\text{Pt}(\text{CFBrCF}_2)\) to give the vinyl complex trans-\((\text{PPh}_3)_2\text{Pt}(\text{CFCF}_2)\text{Br}\)\(^40\) occurs quantitatively and more rapidly than the corresponding chlorotrifluoroethylene complex. Similarly \((\text{MePPh}_2)_2\text{Pt}(\text{CFBrCF}_2)\) isomerises in ethanol at room temperature to give the vinyl complex trans-\((\text{MePPh}_2)_2\text{Pt}(\text{CFCF}_2)(\text{OAc})\)\(^92\) in contrast to the analogous chlorotrifluoroethylene complex which only isomerises in refluxing n-butanol.

These observations suggest that the rate determining step in these vinylisation reactions involves heterolytic cleavage of carbon-bromine or carbon-chlorine bonds.\(^92\) Weight is added to this deduction by the following experiments.

The olefin complex \((\text{MePPh}_2)_2\text{Pt}(\text{CFBrCF}_2)\) does not isomerise in acetone solution, however in the presence of the nucleophile ethylene the vinylisation reaction occurs. Also in acetone solution in the presence of silver acetate the vinyl complex \((\text{MePPh}_2)_2\text{Pt}(\text{CFCF}_2)(\text{OAc})\)\(^92\) is formed, presumably \(\text{Ag}^+\) facilitates the cleavage of the
C-Br bond by the formation of AgBr. Similarly the olefin complex \((\text{PPh}_3)_2\text{Pt}(\text{CFBrCF}_2)\) only undergoes vinylisation in refluxing n-butanol but in acetone in the presence of silver acetate the vinyl complex \((\text{PPh}_3)_2\text{Pt}(\text{CFCF}_2)(\text{OAc})\) is formed, again \(\text{Ag}^+\) facilitates the cleavage of C-Br by AgBr formation. In an analogous manner the rate of aquation of the complex \(\text{Co(NH}_3)_5\text{Br}^{2+}\) is greatly increased in the presence of \(\text{Ag}^+\).

The reaction of tetrachloroethylene with trans-stilbenebis(triphenylphosphine)platinum(0) yields the olefin complex \((\text{PPh}_3)_2\text{Pt}(\text{CCl}_2\text{CCl}_2)\) but the analogous reaction of diphenylacetylenebis(triphenylarsine)platinum(0) with tetrachloroethylene in benzene and at room temperature yields only the vinyl complex \((\text{AsPh}_3)_2\text{Pt}(\text{CClCCl}_2)\text{Cl.}\)

Chlorotrifluoroethylene and bromotrifluoroethylene react with tetrakis(triphenylphosphine)platinum(0) to yield the olefin complexes which only isomerise to vinyl complexes in refluxing n-butanol. In contrast the olefins react with tetrakis(triphenylarsine)platinum(0) in benzene at 40° to yield the vinyl complexes \((\text{AsPh}_3)_2(\text{CFCF}_2)\text{Cl}\) and \((\text{AsPh}_3)_2\text{Pt}(\text{CFCF}_2)\text{Br.}\) In the light of past observations it is not surprising, therefore, that tetrachloroethylene, chlorotrifluoroethylene and bromotrifluoroethylene react with \((\text{AsPh}_3)_2\text{PtCO}_3\) in ethanol at 40° to yield vinyl rather than olefin complexes.

The above observations indicate that the triphenylarsine ligand enhances the vinylisation reaction as does
the methyldiphenylphosphine ligand in the complex
\((\text{MePPh}_2)_2\text{Pt(CFBrCF}_2)\) which isomerises more readily than
\((\text{PPh}_3)_2\text{Pt(CFBrCF}_2)\).

It is possible to prepare the olefin complexes
\((\text{AsPh}_3)_2\text{Pt(CFClCF}_2)\) and \((\text{AsPh}_3)_2\text{Pt(CFBrCF}_2)\) by the reaction
of the appropriate olefin with tetrakis(triphenylarsine)-
platinum(0) in benzene at room temperature. The olefin
complexes readily isomerise to the vinyl complexes in
ethanol.

There is no evidence to suggest that the olefin
complex \((\text{PPh}_3)_2\text{Pt(CF}_2\text{CF}_2)\) undergoes vinyl isomerisation
and although triphenylarsine enhances vinylisation reactions
the olefin complex \((\text{AsPh}_3)_2\text{Pt(CF}_2\text{CF}_2)\) does not isomerise
to the vinyl complex in refluxing ethanol or n-butanol\(^{95}\),
presumably because the high C-F bond strength inhibits
such a reaction.

However, when the tetrafluoroethylene complex
\((\text{PPh}_3)_2\text{Pt(CF}_2\text{CF}_2)\) is treated with lithium iodide in
benzene-ethanol at 95\(^\circ\) the vinyl complex \((\text{PPh}_3)_2\text{Pt(CFCF}_2)\text{I}\)
is formed, the high lattice energy of the lithium
fluoride liberated providing a driving force for the
reaction.

The olefin trans-1,2-dicyano-1,2-bis(trifluoro-
methyl)ethylene reacts with trans-stilbenebis(triphenyl-
phosphine)platinum(0) to give the vinyl complex
\((\text{PPh}_3)_2\text{Pt[trans-C(CF}_3\text{)C(CF}_3\text{)CN]}\text{CN}\)\(^{96}\) which again is probably
formed via an olefin complex intermediate.
Results in preparative work suggest that these vinylisation reactions may go via some ionic mechanism which involves the heterolytic cleavage of the C-Cl or C-Br bond. Kinetic studies of the vinylisation reactions of the olefin complexes \((\text{PPh}^3)_2\text{Pt}(\text{CCl}_2\text{CCl}_2)\)\(^{97,98}\) and \((\text{PPh}^3)\text{Pt}(\text{CHClCCl}_2)\)\(^{91}\) gives a fuller understanding of mechanisms by which these reactions go.

For the vinylisation reaction of \((\text{PPh}^3)_2\text{Pt}(\text{CCl}_2\text{CCl}_2)\) in 98% ethanol (2% methylene chloride) plots of logarithms of olefin concentration vs. time are straight lines for at least 70% of complete reaction indicating that the isomerisation follows simple first-order kinetics. Activation parameters were obtained by measuring the first-order rate constant in 98% ethanol at various temperatures and are as follows:

\[
\Delta H = 21.4^{±1.0}\text{K cal mol}^{-1}, \quad \Delta S = -9^{±4}\text{ e.u.}
\]

The small negative value of \(\Delta S\) suggests that \(\Delta V\) for the isomerisation is similarly small and negative.\(^{99}\)

It was found that triphenylphosphine had negligible effect on the rate (in ethanol) and that when the isomerisation was carried out in the presence of tetracyanoethylene none was incorporated into the vinyl complex.

In ethanol-methylene chloride solvent mixtures the rate of the reaction was shown to decrease as the proportion of ethanol in the mixture was decreased.

These observations indicated that the isomerisation proceeds by one of two mechanisms or by a mechanism combining
the characteristics of the two mechanisms.\textsuperscript{97}

(1) An intramolecular mechanism.

(2) Loss of chloride from tetrachloroethylene ligand followed by rearrangement of the carbonium ion and nucleophilic attack of the chloride at platinum.

The two mechanisms are illustrated in Figure 2.1.

To distinguish between these two mechanisms the rates of isomerisation of the olefin complex was determined in a range of single and mixed solvents having different "ionising powers."\textsuperscript{100}

The expression $\log_{10} \frac{k}{k_0} = mV^{101,102}$ has been shown to relate the rate constant $k$ for a reaction in a
particular solvent to the rate constant $k_0$ in a standard solvent for a variety of unimolecular reactions conducted in a range of single and mixed solvents. The parameter $Y$ is characteristic of the solvent and can be described as "ionising power", and $m$ is characteristic of the compound. Solvolysis of tert-butylchloride in 80% EtOH/H$_2$O proceeds by a mechanism approximating to SN1(lim) and for this particular situation the $Y$ and $m$ parameters are given the values $Y=0$ and $m=1$.

For the vinylisation of $(\text{PPh}_3)_2\text{Pt(CCl}_2\text{CCl}_2)$ a plot of $Y$ vs. log $k$ resulted in a straight line whose slope $m$ was 0.88. This $m$ value of 0.88 is similar to $m$ values observed for SN1 solvolysis of typical organic halides.

This result indicates that the rate determining step in the vinylisation reaction involves heterolytic cleavage of a C-Cl bond resulting in the formation of an ion-pair (contact or solvent separated) or liberation of chloride ion into solution. Presumably this first rate-determining step is then followed by rapid nucleophilic attack of chloride at platinum with the breaking of a Pt-C bond, resulting in the formation of the observed vinyl complex.

If the mechanism were purely intramolecular a plot of $Y$ vs. log $k$ could still yield a linear plot but the observed solvent dependence would not be expected and the value of $m$ would be much lower.

In order to extend the above treatment to "poorly ionising" solvents such as benzene the expression due to
Brownstein, \( \log_{10} \frac{X}{X_0} = RS^{103} \) was used since \( Y \) values for such solvents are not obtainable due to experimental problems (i.e. tert-BuCl does not react in such solvents). For this expression spectroscopic, kinetic and equilibrium data have been used to elucidate the solvent parameter \( S \) and so extend the concept of solvent parameters to enable correlation with frequency (i.e. n.m.r., i.r., u.v. and visible frequencies), rate or equilibrium constants to be made for "poorly ionising" solvents. In the expression \( x \) is the observed frequency, rate or equilibrium constant for the reaction in a given solvent and \( x_0 \) is the analogous value in a reference solvent (EtOH, for which \( S \) is defined as 0.000). The parameter \( R \) is characteristic of the sensitivity of a given reaction to solvent effects and is obtained from the slope of the plot of \( \log_{10} x \) vs. \( S \). The \( R \) value obtained for the solvolysis of tert-butyl chloride which proceeds via a mechanism approximating to \( \text{SN}_1(\text{lim}) \) is 36.

For the vinylisation reaction of \( (\text{PPh}_3)_2\text{Pt}(\text{CCl}_2\text{CCl}_2) \) a plot of logarithms of the first order rate constants vs. \( S \) values gave a reasonable linear correlation for hydroxylic solvents but the point for benzene was at a significant distance from the straight line. This suggests that in benzene that the isomerisation proceeds by a different mechanism. Since in benzene the isomerisation in the presence of tetrachloroethylene is inhibited by addition of triphenylphosphine \( ^{89} \) it is possible that this
mechanism involves an equilibrium dissociation of one triphenylphosphine ligand.

From the plot the R value for the isomerisation was shown to be 18 which approaches the values obtained for SN1 solvolysis of organic halides.

This kinetic data indicates that the rate determining step for the vinyl isomerisation of \((\text{PPh}_3)_2\text{Pt}(\text{CCl}_2\text{CCl}_2)\) in hydroxylic solvents is close to SN1(lim) solvolysis of the tetrachloroethylene ligand and involves a carbonium ion intermediate. That is the isomerisation goes mainly via ionic mechanism (2) and has little intramolecular character (mechanism (1)).

A kinetic study of the vinylisation reaction of \((\text{PPh}_3)_2\text{Pt}(\text{CCLIHCCl}_2)\) indicates that for more than 50% of complete reaction the reaction goes by simple first-order kinetics. The rate constants for a range of solvents were determined and plots of logarithms of these vs. Y and S solvent parameters gave linear correlations which yielded m and R values of 0.6 and 10 respectively.

A comparison of m and R values for the vinylisation reactions of \((\text{PPh}_3)_2\text{Pt}(\text{CCl}_2\text{CCl}_2)\) and \((\text{PPh}_2)_2\text{Pt}(\text{CHClCCL}_2)\) with those for tert-butyl chloride are shown in Table I.

<table>
<thead>
<tr>
<th>Compound</th>
<th>m</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{PPh}_3)_2\text{Pt}(\text{CHClCCL}_2))</td>
<td>0.6</td>
<td>10</td>
</tr>
<tr>
<td>((\text{PPh}_3)_2\text{Pt}(\text{CCl}_2\text{CCl}_2))</td>
<td>0.88</td>
<td>18</td>
</tr>
<tr>
<td>tert-BuCl</td>
<td>1.0</td>
<td>36</td>
</tr>
</tbody>
</table>

**Table I**
It appears that the intramolecular mechanism plays a much more important role in the vinylisation reaction of \((\text{PPh}_3)\_2\text{Pt(CHClCCl}_2\text{)}\) since the lower values \(m\) and \(R\) indicate less solvent dependence than for the vinylisation of \((\text{PPh}_3)\_2\text{Pt(CCl}_2\text{CCl}_2\text{)}\). Hence the mechanism can probably be regarded as being one combining the characteristics of the intramolecular mechanism (1) and the ionic mechanism (2), or one involving parallel intramolecular and ionic mechanisms. This is in contrast to the almost purely ionic mechanism observed for the tetrachloroethylene complex.

The rate of vinylisation of the trichloroethylene complex is observed to be considerably faster than for the tetrachloroethylene complex (trichloroethylene complex \(\text{EtOH, 35}^\circ\ k = 1.9 \times 10^{-2}\text{sec}^{-1}\); tetrachloroethylene complex, \(\text{EtOH, 35}^\circ\ k = 5.4 \times 10^{-5}\text{sec}^{-1}\)). This is probably partly due to the different electronegativities and hence inductive effects of hydrogen and chlorine. That is chloride will more readily leave a carbon atom to which hydrogen is attached than one to which chlorine is attached. Also olefin complexes are stabilised by electron withdrawing groups on the olefin and hence it would be expected that tetrachloroethylene would form a more stable olefin complex than trichloroethylene. Since during the isomerisation part of the olefin breaks away from platinum it seems reasonable to expect the tetrachloroethylene complex to isomerise more slowly.
2.2. Results and Discussion.

The vinyl isomerisation reaction of bromotrifluoroethylene-bis(triphenylarsine)platinum(0) to bromo(trifluorovinyl)-bis(triphenylarsine)platinum(II).

Only kinetic studies of the vinylisation reactions of olefin complexes involving triphenylphosphine as ligand have so far been accomplished.\(^{91,97,98}\)

In the light of the observation that triphenylarsine as ligand appears to enhance vinylisation reactions\(^{94}\) a kinetic study of the vinylisation reaction of an olefin complex involving triphenylarsine as ligand seemed worthwhile.

The olefin complexes \((\text{AsPh}_3)_2\text{Pt} (\text{CFCICF}_2)\) and \((\text{AsPh}_3)_2\text{Pt} (\text{CFBrCF}_2)\)\(^{94}\) can be prepared by the reaction of the appropriate olefin on tetrakis(triphenylarsine)platinum(0) in benzene at room temperature and both olefin complexes isomerise readily in ethanol at 40°. At 35° in ethanol the half-lives of the vinylisation reactions are approximately 24 hours and 4 hours respectively. Since the complex \((\text{AsPh}_3)_2\text{Pt} (\text{CFBrCF}_2)\) has the more convenient half-life a kinetic study of the vinyl isomerisation of the complex was undertaken with a view to obtaining information regarding the mechanism.

For the isomerisation plots of logarithms of vinyl complex concentration vs. time were straight lines for over 70% of complete reaction and hence the isomerisation
follows simple first-order kinetics.

The first-order rate constants for the isomerisation were determined in a range of solvents at 35° and the average rate constants and the standard errors of the means are shown in Table II. It is worth noting that difficulty was experienced in obtaining consistent values for the rate constant in specific solvents, this especially being the case for MeOH, EtOH and n-PrOH, which have large values for the standard error of the mean. This inconsistency could not be removed even when great care was taken in the recrystallisation of (AsPh₃)₂Pt(CFBrCF₂) and the drying and purification of solvents. This problem made the accurate determination of activation parameters for the isomerisation in one solvent impracticable.

A preliminary inspection of the average rate constants indicates that the isomerisation to the vinyl complex is less solvent dependent than are the vinyl isomerisations of either (PPh₃)₂Pt(CCl₂CCl₂) or (PPh₃)₂Pt(CHClCCl₂). Thus the average rate constants for the isomerisation of (AsPh₃)₂Pt(CFBrCF₂) in MeOH and n-ProH only differ by a factor of 1.3 whereas for (PPh₃)₂Pt(CCl₂CCl₂) and (PPh₃)₂Pt(CHClCCl₂) the rate constants for the same two solvents differ by factors of 12 and 4 respectively.

Table III shows the average rate constants for the range of solvents used together with the solvent parameters Y and S for the solvents.

The treatment applied to the isomerisations of (PPh₃)₂Pt(CCl₂CCl₂) and (PPh₃)₂Pt(CHClCCl₂) to assess
Average first-order rate constants for the isomerisation of \((\text{AsPh}_3)_2\text{Pt}(\text{CFBrCF}_2)\) in a range of solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>No. of kinetic runs (n) at 35(^\circ)</th>
<th>Average rate constant (x 10^4) k (\text{AV.} x 10^4)</th>
<th>Standard error of mean S.E.A. (\sigma / n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>3</td>
<td>1.30</td>
<td>±0.35</td>
</tr>
<tr>
<td>EtOH</td>
<td>3</td>
<td>1.63</td>
<td>±0.40</td>
</tr>
<tr>
<td>n-ProOH</td>
<td>3</td>
<td>1.01</td>
<td>±0.38</td>
</tr>
<tr>
<td>iso-ProOH</td>
<td>4</td>
<td>0.53</td>
<td>±0.03</td>
</tr>
<tr>
<td>n-BuOH</td>
<td>4</td>
<td>0.66</td>
<td>±0.07</td>
</tr>
<tr>
<td>t-BuOH</td>
<td>2</td>
<td>0.28</td>
<td>±0.01</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>5</td>
<td>0.77</td>
<td>±0.10</td>
</tr>
<tr>
<td>T.H.F.</td>
<td>1</td>
<td>3.59</td>
<td>-</td>
</tr>
<tr>
<td>Dioxan</td>
<td>1</td>
<td>0.71</td>
<td>-</td>
</tr>
<tr>
<td>EtOH/10%H(_2)O</td>
<td>1</td>
<td>0.75</td>
<td>-</td>
</tr>
<tr>
<td>n-ProOH/10%H(_2)O</td>
<td>1</td>
<td>0.34</td>
<td>-</td>
</tr>
</tbody>
</table>

\(a\) - Confidence limits from S.E.M. and \(n\) via standard \(t\) tables.

Table II
Average first order rate constants for isomerisation of \((\text{AsPh}_3)_2\text{Pt(CFBrCF}_2\text{)}\) and solvent parameters \(Y\) and \(S\).

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Average rate constant (x \times 10^4)</th>
<th>(Y)</th>
<th>(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>1.3</td>
<td>-1.09</td>
<td>0.05</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.63</td>
<td>-2.03</td>
<td>0.0</td>
</tr>
<tr>
<td>n-PrOH</td>
<td>1.01</td>
<td>-2.3^a</td>
<td>-0.016</td>
</tr>
<tr>
<td>iso-PrOH</td>
<td>0.53</td>
<td>-2.73</td>
<td>-0.041</td>
</tr>
<tr>
<td>n-BuOH</td>
<td>0.66</td>
<td>-</td>
<td>-0.024</td>
</tr>
<tr>
<td>t-BuOH</td>
<td>0.28</td>
<td>-3.26</td>
<td>-0.105</td>
</tr>
<tr>
<td>CHCl(_3)</td>
<td>0.77</td>
<td>-</td>
<td>-0.20</td>
</tr>
<tr>
<td>T.H.F.</td>
<td>3.59</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dioxan</td>
<td>0.71</td>
<td>-</td>
<td>-0.179</td>
</tr>
<tr>
<td>EtOH/10%H(_2)O</td>
<td>0.75</td>
<td>-0.75</td>
<td>-</td>
</tr>
<tr>
<td>n-PrOH/10%H(_2)O</td>
<td>0.34</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

^a Estimated from \(Z\) and \(E_T\) values 100,105

Table III
dependence on solvent involved plotting logarithms of first-order rate constants for the range of solvents vs. Y and S solvent parameters. From these plots m and R values were obtained. The m and R values were compared with those for tert-butyl chloride which is considered to react via SN1(lim) solvolysis reaction and hence from the comparison the character (i.e. whether ionic or intramolecular) of the rate determining step for the isomerisations was determined. A similar treatment was applied to the results obtained for the isomerisation of (AsPh₃)₂Pt(CFBrCF₂).

Plots of logarithms of the first-order rate constants vs. Y and S solvent parameters gave reasonable straight line correlations and these are shown in Figure 2.2 and Figure 2.3 respectively. It will be noticed for the plot of log₁₀ k vs. S that the points for CHCl₃ and dioxan, non-hydroxylic and "poorly ionising" solvents appear to be at a significant distance from the straight line. A possible explanation for this lies in the differences between the inorganic system here being studied and the organic systems from which the S solvent parameter values are derived. It is possible that here there are in fact two correlations, one for hydroxylic solvents and one for non-hydroxylic solvents, each lying on separate straight lines. This situation arises for the complex W(CO)₄(Bipy) in which the frequency of the tungsten to bipyridine charge transfer band in the visible region is solvent dependent. For the complex, a plot of frequencies of maximum
Variation of $\log_{10} k_{AV}$ with $Y$ for isomerisation of $(\text{AsPh}_3)_2\text{Pt}($CFBrCF$_2)$ in a range of solvents.

**Solvent:**

1. MeOH
2. EtOH
3. n-PrOH
4. iso-PrOH
5. t-BuOH

**Figure 2.2.**
Variation of $\log_{10} k_{AV}$ with $S$ for isomerisation of $(\text{AsPh}_3)_2\text{Pt(CFBrCF}_2) \text{ in a range of solvents.}$

Solvent:
(1) MeOH
(2) EtOH
(3) n-PrOH
(4) iso-PrOH
(5) n-BuOH
(6) t-BuOH
(7) CHCl$_3$
(8) Dioxan

Figure 2.3.
absorption vs. $E$ values (a measure of "solvating power"
derived from spectroscopic measurement) for a range of
solvents gave two separate correlations, one for
hydroxylic solvents (MeOH, EtOH, nPrOH etc.) and one
for non-hydroxylic solvents (MeNO$_3$, MeCN, Me$_2$CO, CH$_2$Cl$_2$
etc.)

The plots of $\log_{10}k$ vs $Y$ and $S$ solvent parameters
yielded $m$ and $R$ values of $0.32 \pm 0.12$ and $4.89 \pm 1.24$
respectively. The corresponding values for (PPh$_3$)$_2$Pt(CCl$_2$CCl$_2$)
and (PPh$_3$)$_2$Pt(CHClCCl$_2$) were recalculated by the same
method used to calculate those for (AsPh$_3$)$_2$Pt(CFBrCF$_2$) and the
three sets of values together with their limits are shown
in Table IV. Included in this table are values for
tert-butyl chloride and tert-butyl bromide for comparative
purposes.

It will be noticed that the limits for $m$ and $R$
values for (AsPh$_3$)$_2$Pt(CFBrCF$_2$) reflect the apparent
inconsistency shown in the first order rate constants
for particular solvents, the limits for these values being
larger than for the corresponding $m$ and $R$ values for
(PPh$_3$)$_2$Pt(CCl$_2$CCl$_2$) and (PPh$_3$)$_2$Pt(CHClCCl$_2$). However, the
values indicate that the vinyl isomerisation reaction
of the olefin complex (AsPh$_3$)$_2$Pt(CFBrCF$_2$) proceeds by a
mechanism which is less solvent dependent than the
corresponding reactions of (PPh$_3$)$_2$Pt(CCl$_2$CCl$_2$) and
(PPh$_3$)$_2$Pt(CHClCCl$_2$). That is, assuming that the
isomerisation of (AsPh$_3$)$_2$Pt(CFBrCF$_2$) goes via either ionic
mechanism (1) or intramolecular mechanism (2) (See Figure 2.4)
Values of m and R for isomerisation of olefin complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>m</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>(AsPh\textsubscript{3})\textsubscript{2}Pt(CFBrCF\textsubscript{2})</td>
<td>0.32 ± 0.12</td>
<td>4.89 ± 1.24</td>
</tr>
<tr>
<td>(PPh\textsubscript{3})\textsubscript{2}Pt(CClHCCl\textsubscript{2})</td>
<td>0.54 ± 0.07</td>
<td>10.21 ± 0.5</td>
</tr>
<tr>
<td>(PPh\textsubscript{3})\textsubscript{2}Pt(CCl\textsubscript{2}CCl\textsubscript{2})</td>
<td>0.86 ± 0.07</td>
<td>17.95 ± 0.99</td>
</tr>
<tr>
<td>cf. tert-BuCl</td>
<td>1.0</td>
<td>36</td>
</tr>
<tr>
<td>tert-BuBr</td>
<td>0.924\textsuperscript{107}</td>
<td>-</td>
</tr>
</tbody>
</table>

**Table IV**
the m and R values indicate that the mechanism is one which is predominantly intramolecular in character.

(1) Ionic mechanism.

For a mechanism which is ionic in character a greater solvent dependence would be observed and the values for m and R would be expected to be larger (cf. \((\text{PPh}_3)_2\text{Pt-}

\text{CCl}_2\text{CCl}_2\)).

A preliminary investigation of the kinetics of isomerisation of the olefin complex in alcohol-water solvent mixtures yielded some rather unexpected results. Table II includes the first-order rate constants determined in EtOH/10%H_2O and n-PrOH/10%H_2O (0.75 x 10^{-4} and 0.34 x 10^{-4} respectively). These rate constants are significantly smaller than those obtained in pure EtOH and n-PrOH
(1.63 \times 10^{-4} \text{ and } 1.01 \times 10^{-4} \text{ respectively}). Since EtOH/10\%H_2O and n-PrOH/10\%H_2O solvent mixtures are considered to have a higher "ionising power" than pure EtOH and n-PrOH respectively the SN1(lim) solvolysis of tert-butyl chloride (and tert-butyl bromide) is faster in these solvent mixtures (reflected in Y value for EtOH/10\%H_2O of -0.75; Y value for EtOH is -2.03). The rate of isomerisation of (AsPh_3)_2Pt(CFBrCF_2) shows a correlation with Y values although only small differences in rate are observed with increase in "ionising power" of the solvent indicating a high intramolecular character for the isomerisation. Hence it would be expected that the rates of isomerisation in EtOH/10\%H_2O and n-PrOH/10\%H_2O would show an increase (although small) over the rates in pure EtOH and n-PrOH.

It is possible that for the isomerisation of (AsPh_3)_2Pt(CFBrCF_2) in these solvent mixtures there is some effect specifically involving water which causes the observed decrease in rate. That is for these solvent mixtures the bulk solvent parameters are not applicable to this isomerisation. This effect is not observed for the isomerisation of the olefin complex (PPh_3)_2Pt(CCl_2CCl_2) which shows a good correlation between \( \log_{10} k \) and Y solvent parameter values for aqueous methanol (MeOH/10\%, 20\%, 30\% water) and an increase in rate with increasing % of water present in the mixtures is observed.

The effect observed for (AsPh_3)_2Pt(CFBrCF_2) could
be due to the intramolecular character of the isomerisation (the mechanism for the isomerisation of (PPh$_3$)$_2$Pt(CCl$_2$CCl$_2$) is predominantly ionic) for which some specific solvation effect involving water hinders the intramolecular migration of Br onto platinum. Since water has a higher "solvating power" than, say, methanol it will be more difficult for the migrating Br to displace and hence it is possible that selective solvation of the olefin complex by water in these solvent mixtures leads to the observed decrease in rate.

The slowing effect on the rate of the isomerisation by water could possibly be seen as the explanation for the inconsistencies in the rate constants determined for particular solvents. However, this seems very unlikely since several runs were usually carried out using one batch of dried and purified solvent, which between runs was stored in a dry atmosphere.

Another possible explanation for the inconsistencies in rate constants is that the mechanism of isomerisation of (AsPh$_3$)$_2$Pt(CFBrCF$_2$) includes a certain amount of radical character. In this case the slowing of isomerisation in the aqueous alcohols can be seen as a quashing of the radical contribution to the rate in the "highly ionising" mixed solvents. However, little evidence to suggest that this is the case could be obtained. Thus, when the isomerisation was carried out in the presence of a radical initiator there was only a marginal increase in rate of isomerisation over a reference kinetic run. The
isomerisation was carried out in oxygenated ethanol and methanol with the result that there was only a marginal decrease in the rate over the rates for reference kinetic runs carried out in degassed ethanol and methanol. Increasing the intensity of light reaching the cells during a kinetic run (by increasing the slit width in the spectrophotometer) had no effect upon rate.
2.3. **Experimental.**

Bromotrifluoroethylenebis(triphenylarsine)platinum(0) and chlorotrifluoroethylenebis(triphenylarsine)platinum(0) were prepared by the literature method\(^8\) and were recrystallised from methylene chloride-ether and dried *in vacuo*. Purity was checked by infrared spectrum and melting point before use.

Solvents were dried and purified by standard methods.\(^{108}\) Tetrahydrofuran and dioxan were passed down alumina columns immediately before use.

The bromotrifluoroethylene olefin complex has $\lambda_{\text{max}} = 230$ μm; the vinyl complex has $\lambda_{\text{max}} = 230,257$ μm. The chlorotrifluoroethylene complex has $\lambda_{\text{max}} = 231$ μm; the vinyl complex has $\lambda_{\text{max}} = 231,253$ μm. Absorbance readings in kinetic runs for $(\text{AsPh}_3)_2\text{Pt}(\text{CFBrCF}_2)$ were measured every ten minutes at 265 μm. At this wavelength there was the maximum increase in absorbance during the vinylisation reaction.

For kinetic runs saturated solutions ($\approx 10^{-4}\text{M}$) of $(\text{AsPh}_3)_2\text{Pt}(\text{CFBrCF}_2)$ were prepared in the solvents at 35° and these were usually found to yield the required initial absorbance reading. For methanol and tetrahydrofuran it was found to be necessary to dilute the saturated solutions. For chloroform for each kinetic run a solution having approximately the same initial absorbance was prepared.

Kinetic runs were conducted in 1 cm cells in the
thermostated cell compartment of a Unicam SP800A spectrophotometer.

Results were computed on Elliot 4130 and Digital pdpl1 computers. Rate constants were calculated from 
\[ \log(A - A_t) \] (A = absorbance at complete reaction; \( A_t \) = absorbance at time t) and time using an unweighted least mean squares programme.

Values of m and R (for the three olefin complexes \((\text{AsPh}_3)_2\text{Pt(CFBrCF}_2)\), \((\text{PPh}_3)_2\text{Pt(CCl}_2\text{CCl}_2)\) and \((\text{PPh}_3)_2\text{Pt(CHClCCl}_2)\)) were calculated from \(\log_{10}kAV\). and Y and S solvent parameter values using again an unweighted least mean squares programme. For \((\text{AsPh}_3)_2\text{Pt(CFBrCF}_2)\) the value for 
\(\text{EtOH}/10\%\text{H}_2\text{O}\) was ignored in the calculation of m and the values for \(\text{CHCl}_3\) and dioxan in the calculation of R.
50. G.F. Everitt, personal communication.
That I have put aside and crossed out so much, indeed almost everything I wrote this year, that hinders me a great deal in writing. It is indeed a mountain, it is five times as much as I have in general ever written and by its mass alone it draws everything that I write away from under my pen to itself.

Franz Kafka, 1910.
SUMMARY

The introduction to the first chapter contains a review of the complexes formed during the reactions of hexafluoroacetone and related electrophilic molecules with low-valent metal complexes of the Group VIII transition metals. The reactivity of the complexes is described. The remainder of the chapter is concerned with the preparation of some π-bonded ketone complexes of platinum of general formula $L_2Pt(\text{ketone})$ ($L$ = triphenylphosphine, triphenylarsine). The reactions of the ketone complexes with oxygen and a series of electrophilic unsaturated molecules demonstrates that the complexes are more reactive towards ring expansion than the corresponding hexafluoroacetone platinum complex. Reactions of the ketones with peroxobis(triphenylphosphine)platinum are described. Also included in this chapter are the reactions of isatin and benzoyl cyanide with zero-valent platinum complexes.

The introduction to the second chapter contains a brief review of olefin to vinyl isomerisation reactions of platinum olefin complexes and a description of results obtained during kinetic studies of such reactions. The second part of the chapter contains results obtained from a kinetic study of the vinyl isomerisation of the olefin complex bromotrifluoroethylenebis(triphenylarsine)-platinum to bromo(trifluorovinyl)bis(triphenylarsine)platinum(II)