

FLUORINE CONTAINING PHOSPHINE COMPLEXES  
OF THE PLATINUM METALS

A thesis presented for the  
Degree of Doctor of Philosophy

in the  
Faculty of Science

by

MICHAEL JOHN HACKER

University of Leicester  
September 1972

UMI Number: U393212

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



UMI U393212

Published by ProQuest LLC 2015. Copyright in the Dissertation held by the Author.  
Microform Edition © ProQuest LLC.

All rights reserved. This work is protected against  
unauthorized copying under Title 17, United States Code.



ProQuest LLC  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106-1346

X753069600

THESIS  
430240  
9373

The work described in this thesis has been carried out by the author in the Department of Chemistry of the University of Leicester between October 1969 and September 1972; it has not been, nor is being concurrently, presented for any other degree.

Parts of this have been, or are in the process of being, published:-

' Insertion of Carbon Disulphide into a Metal-Fluorine Bond: Crystal Structure of  $[\text{Pt}(\text{S}_2\text{CF})(\text{PPh}_3)_2]^+ \text{HF}_2^-$  . '

J.A.Evans, M.J.Hacker, R.D.W.Kemmitt, D.R.Russell  
& J.Stocks.  
J.Chem.Soc. (D). 1972, 72.

' Preparation and Reactivity of some Halogen Bridged Complexes of Rhodium. '

D.M.Barlex, M.J.Hacker, & R.D.W.Kemmitt.  
J.Organometallic.Chem - in press.

' The Relative Stabilities of Tetrafluoroethylene and Hexafluoro butyne Adducts of  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$  (X= F, Cl) '

M.I.Bruce, J.Burgess, M.J.Hacker, R.D.W.Kemmitt,  
C.T.Mortimer, (Mrs) J.L.McNaughton, G.Shaw & F.G.A.  
Stone.  
J.Organometallic.Chem. - in press.

' Carbonatobis(triphenylarsine)platinum(II): A Convenient Source of Bis(triphenylarsine)platinum(0) for Olefin Complex Synthesis. '

M.J.Hacker & R.D.W.Kemmitt.  
J.Chem.Soc. (A) - in press.



Mike Hacker

September '72

VAL

&

DUDLESTON

I would like to express my sincere thanks to my supervisor Dr.R.D.W.Kemmitt for his constant help, encouragement, and ebullient, and often uncontrollable, enthusiasm during the progress of this work. I should also like to thank other members of this department: Dr.J.Burgess for much help and discussion of the work concerning the kinetic study, Dr.J. Evans and Dr.D, Russell for the single crystal study, to Miss.G.Warren, not only for the preparation of many starting materials, but also for her ability to endure three years working on the same bench, (usually all of it ); and to my fellow research students, whose particular brand of rampant cynicism helped to provide some rationality in the face of chemical intuition or simple pig-headedness.

My thanks go to Dr.M.Dove of the University of Nottingham for obtaining the  $F^{19}$  NMR spectra, and to Mrs.J.Mc Nau-ghton of the University of Keele for the D.S.C. thermochemical data.

To my parents I must give special thanks for the unending encouragement without which none of this would have been possible.

A research grant from the S.R.C. is gratefully acknowledged.

While an extensive chemistry exists for the chloro, and, to a lesser extent, the bromo and iodo phosphine, and related organometallic complexes of the platinum metals the corresponding fluoro complexes are virtually unknown; and as a consequence, have received little attention. In this study we have attempted to synthesise such complexes by various routes and to study and compare their chemistry with that of the other halogen complexes.

There has been some controversy concerning the formulation of the product obtained from the reaction of tetrakis-(triphenylphosphine)platinum(0) with liquid hydrogen fluoride. We have reinvestigated this reaction and provided conclusive evidence for the presence of a cationic species  $[\text{PtF}(\text{PPh}_3)_3]^+$  containing a platinum-fluorine bond, into which, as a crystal study has shown, the carbon disulphide molecule can be inserted; the first reported insertion reaction into a M-F bond of this type.

The fluoro derivative of Vaska's complex, and its rhodium analogue, have been synthesised by simple halide exchange using silver fluoride; as a consequence of these reactions we have found a simple high yield route to hitherto unknown mixed donor ligand complexes of the type  $\text{RhX}(\text{CO})\text{LL}'$  ( $\text{X} = \text{Cl}, \text{Br}$ ;  $\text{L} = \text{PPh}_3, \text{AsPh}_3$ ;  $\text{L}' = \text{PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{P}(\text{OPh})_3$ ) by halogen bridge cleavage of the dimeric precursors  $[\text{RhX}(\text{CO})\text{L}]_2$ . The inability to synthesise the corresponding fluorine bridged complex precluded investigation of similar reactions to obtain fluoro complexes of that type.

The iridium-fluorine bond in fluorocarbonylbis-(triphenylphosphine)iridium(I) has been shown to readily undergo halide exchange, either directly or simultaneously, and in competition with, oxidative addition of addenda containing other halogens; and, in polar solvents, displacement.

The adduct with sulphur dioxide appears to be less stable than the corresponding chloro, bromo, and iodo adducts. However, as a quantitative thermodynamic study has shown, the adducts with tetrafluoroethylene and hexafluorobut-2-yne are more stable than those of the other halogen derivatives; the trend for the stabilities of reversible decomposition for the complete series

of these compounds  $\text{IrX}(\text{CO})(\text{PPh}_3)_2\text{L}^*$  ( $\text{X}=\text{F}, \text{Cl}, \text{Br}; \text{L}^*=\text{C}_2\text{F}_4, \text{C}_4\text{F}_6$ ) is in the opposite direction to that predicted on the basis of series of related compounds.

Attempts to isomerise the  $\pi$  bonded tetrafluoro-ethylene in complexes of the type  $\text{PtL}_2(\text{C}_2\text{F}_4)$  ( $\text{L}=\text{PPh}_3, \text{AsPh}_3$ ) to yield trifluorovinyl complexes containing a platinum-fluorine bond, in an analogous reaction to that observed for the fluoro-chloro/bromo olefins, were unsuccessful; but led to the investigation of the chemistry of carbonatobis(triphenylarsine) platinum(II) as a clean easy precursor of bis(triphenylarsine) platinum(0) for the synthesis of olefin and acetylene complexes of the type  $\text{Pt}(\text{AsPh}_3)_2\text{Cf}; (\text{Cf}=\text{olefin}, \text{acetylene})$ .

A kinetic study of the oxidative addition of methylfluorosulphonate to Vaska's complex has been made and compared with data obtained for other molecules.

" Common sense is the most widely shared commodity in the world, for every man is convinced that he is well supplied with it "

DESCARTES.

Le Discours de La Méthode.

## CHAPTER ONE

### I.1. INTRODUCTION.

### I.2. REVIEW OF PLATINUM GROUP PHOSPHINE COMPLEXES CONTAINING METAL-FLUORINE BONDS.

### I.3. RESULTS AND DISCUSSION

#### I.3.1. Preparative methods.

#### I.3.2. Reaction of hydrogen fluoride with platinum complexes.

##### I.3.2.1 Stock's data.

##### I.3.2.2. Dixon's data.

##### I.3.2.3. Reinvestigation of $PtP_x$ ( $x = 3, 4; P = PPh_3$ ) with hydrogen fluoride<sup>x</sup>.

##### I.3.2.4. New $F^{19}$ N.M.R. data.

#### I.3.3. Reaction of $[PtF(PPh_3)_3]^+$ with carbon disulphide.

##### I.3.3.1 Stock's data.

##### I.3.3.2. Crystallographic data.

### I.4. EXPERIMENTAL.

### I.5. APPENDICES.

#### I.5.1 Analytical data.

#### I.5.2. Infrared data.

## I.I. INTRODUCTION.

Phosphine complexes of the transition metals are well characterised, particularly those of platinum<sup>1</sup> which have been known for over a century. The most stable phosphine complexes are those from the right hand side of the transition metal series, as shown by a modified form of the classification by Ahrland and associates<sup>2</sup>, based on the ability to form stable complexes with group V ligands of the type  $MR_3$  ( $M = P, As, Sb$ ). The classification is, however, not a sharp one and more definite is the tendency to form the most stable phosphine complexes along the diagonal towards platinum and gold; as for example the affinities of sets of ligands to  $Ag(I)$  have shown<sup>3</sup>.

The fact that the most stable phosphine complexes are derived mainly from salts of elements to the right hand side of the series is due, in part, to the character of the ligands. Phosphines act as  $\sigma$  bond donors and  $\pi$  bond acceptors, vacant 3d orbitals of the phosphorus being capable of interacting with filled non-bonding d orbitals of the transition metal. In many cases, the acceptor character may be at least as important as the donor property. This is illustrated by the ability to synthesise complexes of trifluorophosphine, where much reduced donor ability must be more than compensated for by increased electron affinity of the vacant 3d phosphorus orbitals; so much so, that trifluorophosphine shows a greater similarity to carbon monoxide than to tertiary phosphines as a ligand<sup>4</sup>.

Equally, the most stable complexes are those in

which the metal has its lowest energy orbitals completely occupied by electrons and its high energy orbitals vacant. The high ligand field strength of tertiary phosphines ensures this, inhibiting promotion of electrons from low to high energy orbitals.

The phosphine metal halide complexes are some of the most stable complexes known for a given metal and, as a consequence of both their number and dispersion throughout the transition metal series, have been extensively studied.

## I.2. REVIEW.

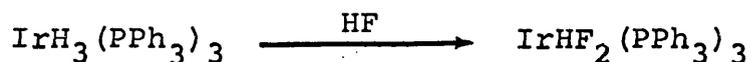
Phosphine metal fluoride complexes, or in fact any complexes containing metal fluorine bonds with ligands other than fluorine, oxygen or other halogen atoms, are virtually unknown and have received little attention.

Trifluorophosphine complexes containing metal fluorine bonds were prepared by Moissan<sup>5</sup> from the reaction of pentafluorophorus(V) on platinum metal. Chatt<sup>4</sup> has suggested that the complex should be written as  $\text{PtF}_2(\text{PF}_3)$  in view of the similarities of trifluorophosphine and carbon monoxide; and that it is dimeric with fluorine bridging groups, analagous to Schutzenberger's complex  $\left[ (\text{PCl}_3)\text{PtCl}_2 \right]_2$ <sup>6</sup>.

The first alkyl and aryl complexes containing metal fluorine bonds were prepared by Muetterties<sup>7</sup> from the reaction of tungsten hexafluoride with triphenylphosphine, which gave an ionic product formulated as  $\left[ \text{WF}_5(\text{PPh}_3) \right]^+ \text{F}^-$ .

Moss's<sup>8</sup> study of the reactions of tertiary

phosphine metal hydrides with anhydrous hydrogen fluoride yielded difluorohydridotris(triphenylphosphine)iridium(III),  $\text{IrHF}_2(\text{PPh}_3)_2$ , from the reaction



and complexes formulated as  $\text{PtF}_2(\text{PPh}_3)_2$  and  $\text{PdF}_2(\text{PPh}_3)_2$  from phosphine complexes, postulated at the time as,  $\text{PtH}_2(\text{PPh}_3)_4$ <sup>9</sup> and  $\text{PdH}_2(\text{PPh}_3)_4$ <sup>8</sup>. Later work has shown that these hydrido complexes were in fact the zero valent complexes  $\text{Pt}(\text{PPh}_3)_4$ <sup>10</sup> and  $\text{Pd}(\text{PPh}_3)_4$ <sup>11</sup>, and that the formulation of the product from the reaction of tetrakis(triphenylphosphine)-platinum(0) with hydrogen fluoride was also incorrect<sup>12</sup>.

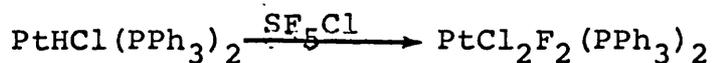
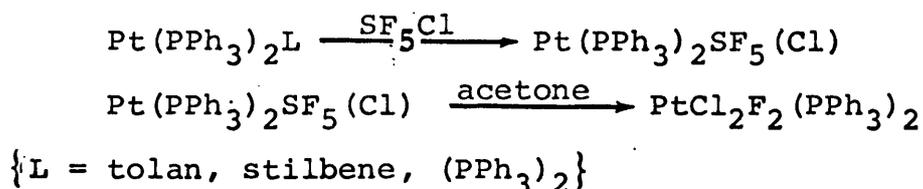
Mc Avoy<sup>13</sup> reported the synthesis of phosphine metal fluoride complexes of ruthenium and osmium using similar reactions and extended his work to a study of the chemistry of the complex formulated as  $\text{PtF}_2(\text{PPh}_3)_2$ , reporting reactions with carbon monoxide, triphenylphosphite and other compounds.<sup>14</sup>

A further extension of this work was made by Stocks<sup>12</sup> who reinvestigated the reaction of tetrakis(triphenylphosphine)platinum(0) with liquid hydrogen fluoride and extended this to trialkyl and triaryl phosphine complexes of platinum, palladium, nickel, rhodium and iridium. In most cases no reaction occurred and starting materials were isolated.

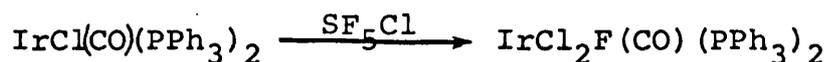
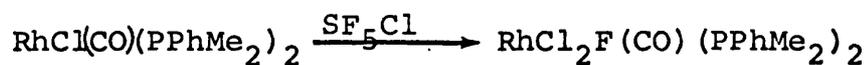
It has been reported that several phosphine complexes containing fluorine with other halogens have been obtained as by-products from some reactions.

Clark<sup>15</sup> isolated chlorofluorobis(triethyl-phosphine)platinum(II) as a minor product in the reaction of trans-hydrido-chlorobis(triethylphosphine)platinum(II) with trifluoroethylene.

Stocks<sup>12</sup> isolated several such complexes as major products from attempts at synthesis of complexes containing the pentafluorosulphur group using sulphur chloride pentafluoride; or as decomposition products from such isolated derivatives. The mechanism of these reactions is unclear.



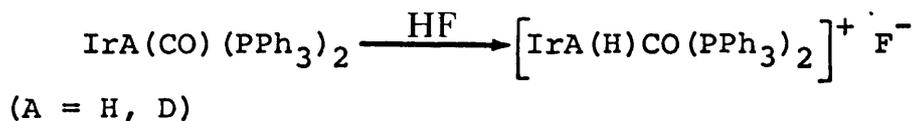
The complex  $\text{PtCl}_2\text{F}_2(\text{PPh}_3)_2$  had previously been obtained from the reaction of tetrakis(triphenylphosphine)platinum(0) with 1,1,2 trifluoro 3,3,3 trichloroprop-2-ene<sup>16</sup>.



Vaska<sup>17</sup> studied the reactions of gaseous hydrogen fluoride with crystals of the complex trans- $\text{IrX}(\text{CO})-(\text{PPh}_3)_2$  (X = Cl, Br, I) and observed only partial reaction, producing adducts of the type  $\text{IrF}(\text{H})\text{X}(\text{CO})(\text{PPh}_3)_2$ , while

hydrogen chloride and hydrogen bromide (and their deuterated analogues) reacted quantitatively.

Ionic fluoride complexes have also been prepared from the reaction of gaseous hydrogen fluoride with crystals of the hydrido and deuterio complexes  $\text{IrA}(\text{CO})(\text{PPh}_3)_2$ <sup>18</sup>.

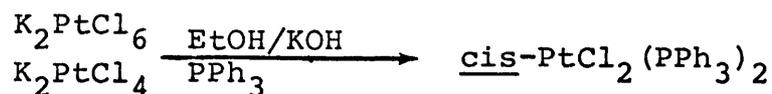


Stocks<sup>12</sup> isolated a compound formulated as cis-fluorochlorobis(triphenylphosphine)platinum(II) from the reaction of cis-dichlorobis(triphenylphosphine)platinum(II) with liquid hydrogen fluoride. This, however, may equally be formulated as an ionic bridged chloride dimer, a suggestion that has been indicated by  $\text{F}^{19}$  n.m.r. spectroscopy; although Stocks reported the complex to be a non conductor in nitromethane.

### I.3. RESULTS AND DISCUSSION.

I.3.I. One reason why complexes containing metal fluorine bonds, or binary fluorides in general, have been so little studied in comparison to the other halogen compounds is probably due to the absence of easy, convenient synthetic routes.

Halide phosphine complexes, for example, can be synthesised by very simple reactions, often from the binary metal halide or simple halide complex.

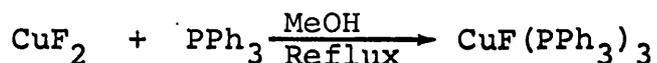


In some cases the presence of water is necessary, for example, the synthesis of Vaska's complex using dimethyl-formamide\*

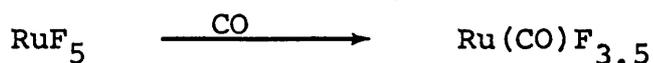


will only occur using the hydrated salt; the anhydrous salt being unreactive. The corresponding fluorides or fluoro complexes of these and related metals are in general unknown, unstable or very easily hydrolysed.

The only phosphine complex containing a metal fluorine bond synthesised by direct route has been  $\text{CuF}(\text{PPh}_3)_3$  in 46% yield by Jardine<sup>19</sup> et al. using the reaction



An ionic carbonyl fluoride  $[\text{Ru}(\text{CO})_2\text{F}]^+ [\text{RuF}_6]^-$  has been prepared by the reaction<sup>20</sup>



The routes then available are direct fluorination either by fluorine or a suitable precursor; or halide exchange. Direct fluorination using elemental fluorine is

usually unsuccessful. The extremely powerful oxidising nature of fluorine usually results in complete oxidation of all components in the solid state; whilst reaction in solution is virtually impossible, either because suitable solvents are oxidised, often explosively, or those few that are inert to fluorine, such as the saturated fluorinated -chlorinated hydrocarbons, are very poor solvents.

Halide exchange reactions have provided by far the most direct and easy routes to metal fluorine phosphine complexes, and exchange of a coordinated chlorine atom by the use of a suitable fluorinating agent has been used for the complexes discussed. The halide exchange is presumably an equilibrium, but by careful choice of fluorinating agents the chloride addendum is removed or precipitated from the system, displacing the equilibrium and ensuring complete reaction.

Using anhydrous hydrogen fluoride, the hydrogen chloride formed is lost from the system due to both its much lower boiling point ( $-84.9^{\circ}\text{C}$ ; 760mm.) compared to hydrogen fluoride ( $+19.54^{\circ}\text{C}$ ; 760mm.) and its very low solubility in anhydrous hydrogen fluoride.

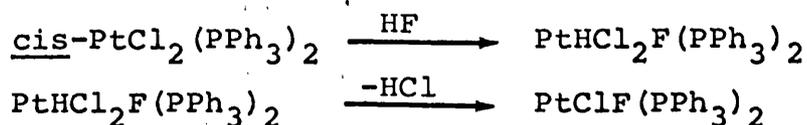
Binary fluorides of large metal ions such as thallium, caesium and silver have also been used. Here, the high lattice energy of the corresponding chlorides compared to their fluorides, together with their insolubility in the systems used, result in complete exchange. Halide exchange using silver fluoride has been used independently by several workers to prepare the fluoro derivative of Vaska's complex and its rhodium analogue  $\text{MF}(\text{CO})(\text{PPh}_3)_2$

(M = Rh<sup>21</sup>, Ir<sup>22</sup>). The Russian workers<sup>21</sup> simply reacted freshly prepared solid silver fluoride with refluxing solutions of chlorocarbonylbis(triphenylphosphine)rhodium(I) in benzene, while Vaska<sup>22</sup> generated silver fluoride in situ from a saturated solution of ammonium fluoride in methanol and silver carbonate.

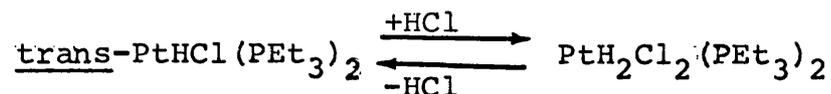
In our study, we have found that the optimum conditions for the synthesis of the fluoro complexes MF(CO)(PPh<sub>3</sub>)<sub>2</sub> (M = Rh, Ir) are achieved by vigorously shaking a benzene solution of the chloro complexes MCl(CO)(PPh<sub>3</sub>)<sub>2</sub> with a saturated aqueous solution of silver fluoride, containing a few percent of hydrogen fluoride, for one to two minutes. Quantitative precipitation of finely divided silver chloride, which darkens rapidly in light, occurs within seconds; producing on work up, a high yield of the fluoro complex.

### I.3.2. Reactions of hydrogen fluoride with platinum complexes.

Stocks<sup>12</sup> isolated a white crystalline solid from the reaction of anhydrous liquid hydrogen fluoride with cis-dichlorobis(triphenylphosphine)platinum(II) and from a study of its chemistry assigned it as cis-chlorofluorobis-(triphenylphosphine)platinum(II); the reaction presumably involving the addition of hydrogen fluoride to form a six coordinate platinum(IV) complex, followed by loss of hydrogen chloride to give the postulated product.

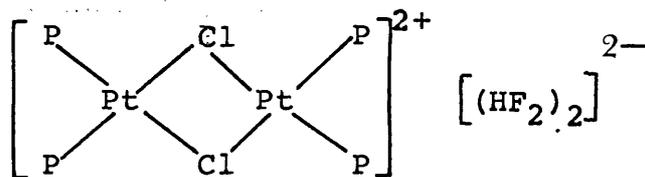


Chatt et al.<sup>23</sup> have shown that the addition of hydrogen chloride to trans-hydrido-chlorobis(triethyl-phosphine)platinum(II) gives dihydrodichlorobis(triethyl-phosphine)platinum(IV), which loses hydrogen chloride even in the solid state.



More recently the complex dihydrodichlorobis(triphenyl-phosphine)platinum(IV) has been isolated from the reaction of trans-hydrido-chlorobis(triphenylphosphine)platinum(II) with hydrogen chloride<sup>24</sup>.

Stocks's product ( PtClF(PPh<sub>3</sub>)<sub>2</sub> ) was reported to be a non conductor in nitromethane. We have found, however, that the F<sup>19</sup> n.m.r. spectra of the product from the same reaction indicates the presence of the hydrogen difluoride ion and may be formulated as an ionic bridged species.



I.3.2.I. As a consequence of the result obtained by Stocks, indicating the apparent easy cleavage of the platinum fluorine bond in the complex PtClF(PPh<sub>3</sub>)<sub>2</sub> by chlorinated solvents to yield cis-dichlorobis(triphenylphosphine)platinum-(II), he decided to reinvestigate the synthesis and reactions of the 'difluoride complex' PtF<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.

Mc Avoy had reported that if solutions of cis-PtF<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> in chlorinated solvents were kept for several hours, the solvent became fluorinated and dichloro-bis(triphenylphosphine)platinum(II) was formed (isomer not specified); yet all products from the reactions were recrystallised from dichloromethane.

Hence, it was decided to attempt recrystallisation of the product from the reaction of tetrakis(triphenyl-phosphine)platinum(0) with liquid hydrogen fluoride from some other non chlorinated solvents. The crude product, after washing with benzene and diethyl ether, was found to be readily soluble in acetone and was recrystallised by precipitation from acetone/ether to yield a white, highly crystalline product. Elemental analysis on the compound recrystallised in this way, however, differed significantly from those obtained by Mc Avoy<sup>14</sup>, who in fact did not quote any analytical data for fluorine, and that required for PtF<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. Particularly large differences were found for the platinum analysis.

	<u>Pt analysis.</u>
Calculated for PtF <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	25.75 %
Found by Mc Avoy	25.9 %
Calculated for PtCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	24.68 %
Found by Stocks	18.2 %

Hence, the proposed reaction scheme:



was reinvestigated by Stocks who found that:<sup>12</sup>

(A) One mole of the zero valent complex tetrakis(tri-phenylphosphine)platinum(0) after reaction with liquid hydrogen fluoride should yield two moles of free tri-phenylphosphine. However, in several separate quantitative determinations less than one mole was isolated and the yields of  $\text{PtF}_2(\text{PPh}_3)_2$  based on the above equation were also in excess of 100%.

(B) Reactions of tris(triphenylphosphine)platinum(0) with liquid hydrogen fluoride yielded an identical product and no free triphenylphosphine was isolated from the reaction.

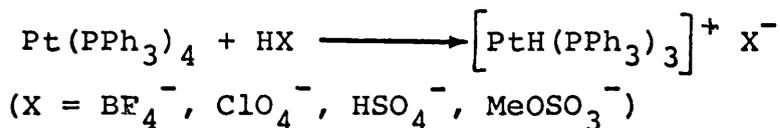
(C) Reaction of the complex with excess lithium chloride yielded cis-dichlorobis(triphenylphosphine)platinum(II) and free triphenylphosphine.

These facts indicated that the complex contained three and not two molecules of triphenylphosphine and elemental analysis suggested the formulation as  $\text{PtF}_3(\text{PPh}_3)_3$ .

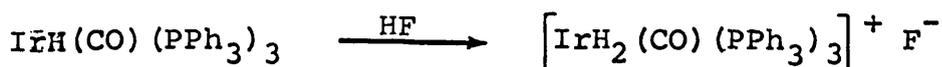
(D) Conductivity measurements indicated the complex to be ionic with a conductance similar to that of a univalent electrolyte in similar solvents.

(Mc Avoy did not report any conductivity data for the complex he obtained.)

Cariati, Ugo and Bonati, in a study of the reactions of zerovalent phosphine complexes of platinum with inorganic acids<sup>24</sup> isolated ionic hydride complexes of the type,



Vaska<sup>18</sup> obtained an ionic complex with fluoride as the counter ion, from the reaction of hydridocarbonyltris-(triphenylphosphine)iridium(I) with gaseous hydrogen fluoride,



excess hydrogen fluoride generating the hydrogen difluoride ion,



(E) The platinum complex from the reaction showed no platinum hydride absorption in its i.r. spectrum although it is sometimes obscured or very weak.

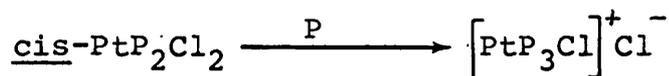
(F) Addition of solutions of alkali metal salts of large anions such as tetraphenylborate or tetrafluoroborate to solutions of the complex produced immediate precipitates which after recrystallisation were found to analyse as  $[\text{PtF}(\text{PPh}_3)_3]^+ \text{X}^-$ , (X =  $\text{BF}_4^-$ ,  $\text{BPh}_4^-$ ).

Stocks suggested that the formulation of the complex as a hydride such as  $[\text{PtH}(\text{PPh}_3)_3]^+ (\text{H}_2\text{F}_3)^-$  unlikely and postulated it as a fluoride complex, fluorotris(triphenyl-phosphine)platinum(II) hydrogen difluoride  $[\text{PtF}(\text{PPh}_3)_3]^+ (\text{HF}_2)^-$ .

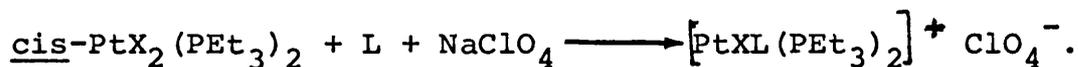
Related series of ionic complexes of this type

have been previously synthesised.

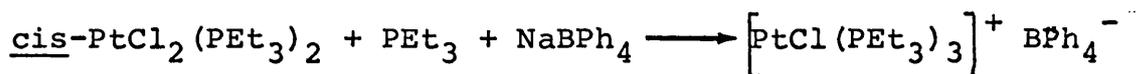
Grim *et al.*<sup>25</sup> have prepared complexes of the type  $[\text{PtXP}_3]^+ \text{Y}^-$ , (X = Cl, Y = Cl, P = PPh<sub>2</sub>Me; X = Cl, Y = Cl, BPh<sub>4</sub>, P = PPh<sub>2</sub>Pr) via:



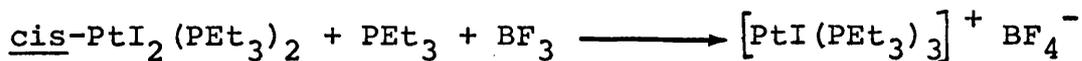
Church and Mays<sup>26</sup> prepared  $[\text{PtXL}(\text{PET}_3)_2]^+ \text{ClO}_4^-$ , (X = Cl, Br, L = PPh<sub>3</sub>, PET<sub>3</sub>, P(OPh)<sub>3</sub>, P(OMe)<sub>3</sub>) via



Clark and Dixon<sup>27</sup> as part of a study of palladium and platinum cations, have synthesised the  $[\text{PtP}_3\text{X}]^+$  cation by the reaction of dihalodiphosphineplatinum(II) complexes with excess phosphines in the presence of sodium tetraphenylborate,



and also<sup>28</sup> from the reaction with boron trifluoride.



I.3.2.2. During the later part of 1970 we received a private communication from Dixon<sup>29</sup> who had been working on the same reaction. Many of his results were similar to those found by Stocks<sup>12</sup> and confirmed his suggestion as to the composition of the complex; however, the structural

formulation suggested by Dixon was different.

Dixon had found that:

- (A) Reaction of one mole of tetrakis(triphenylphosphine) platinum(0) with excess liquid hydrogen fluoride always resulted in the liberation of approximately one mole of triphenylphosphine.
- (B) He was unable to detect hydrogen gas from the reaction by mass spectrometry.
- (C) Analytical data for a sample recrystallised by very slow precipitation from a nitromethane solution with diethyl ether, indicated a composition corresponding to  $\text{Pt}(\text{HF})_3(\text{PPh}_3)_3$ .
- (D) A suspension of the complex in water can be titrated as an approximately dibasic acid.
- (E) A conductance of  $62.5 \text{ ohm}^{-1}\text{cm}^2$  for a  $10^{-3}\text{M}$ . solution of the complex in nitromethane at  $25^\circ\text{C}$  is typical of a 1:1 electrolyte, although low enough to suggest that ionisation is not complete.
- (F) The i.r. spectrum of the product was found to be very similar to that of the starting material, tetrakis(triphenylphosphine)platinum(0), except for a very broad band at approximately  $1800 \text{ cm}^{-1}$ .

Similar absorptions have been previously observed in the spectra of triphenylphosphonium fluoride  $[\text{PPh}_3\text{H}]^+ \text{F}^-$  and of solutions of hydrogen fluoride in donor organic solvents. In the first case the peak was assigned to a phosphorus-hydrogen stretch which had been modified by a

very strong hydrogen bond to fluorine; and in the second to a solvated  $\text{HF}_2^-$  ion, although the other absorptions normally associated with this species were not observed<sup>31</sup>.

- (G)  $\text{F}^{19}$  N.M.R. spectra of the complex in nitromethane at  $-40^\circ\text{C}$  showed two principal regions of absorption. At +169 p.p.m. from  $\text{CCl}_3\text{F}$  a singlet of intensity 4 and at approximately +230 p.p.m. a doublet of triplets of intensity 1, ( $J_1 = 490$  Hz;  $J_2 = 140$  Hz.) The spectra were normally run in plastic tubes, if however, glass tubes were used the peak at 169 p.p.m. gradually disappeared and was replaced by others characteristic of  $\text{SiF}_4$  and  $\text{BF}_3$  indicating that the original peak was due to  $\text{HF}_2^-$  or some other species.
- (H) The complex may be recrystallised from dichloro-methane providing this is done rapidly using anhydrous conditions. However, repeated precipitations from methylene chloride, especially if wet, resulted in the elimination of 0.7 mole of triphenyl-phosphine. This product has a similar i.r. spectra to the original material, but shows no n.m.r. absorptions.
- (I) Reaction of the product with boron trifluoride yields  $\left[\text{PtH}(\text{PPh}_3)_3\right]^+ \text{BF}_4^-$ , a known compound identified by its I.R.,  $\text{F}^{19}$ , and  $\text{H}^1$  n.m.r. spectra.
- (J) Reaction with hydrogen chloride yields cis-di-chlorobis(triphenylphosphine)platinum(II).
- (K) An ionic salt can be isolated from the reaction

of the complex with sodium tetraphenylborate for which no  $F^{19}$  resonance could be found.

This data all related to reactions which had been carried out using anhydrous hydrogen fluoride. Some reactions using aqueous hydrogen fluoride were also investigated by Dixon et al. The products obtained from these reactions were similar to those obtained using anhydrous hydrogen fluoride except for an i. r. band at  $2110 \text{ cm}^{-1}$ . The product also exhibited a  $H^1$  n.m.r. absorption typical of a hydride, and was identified as the hydridotris(triphenylphosphine)platinum(II) cation which, by analogy with the work of Ugo<sup>24</sup>, is the expected product.

On the basis of this data Dixon suggested the product to be an ionic platinum hydride complex with a solvated fluoride ion as the counter ion. Following an equilibrium of the type;



similar to that proposed for  $[PPh_3H]^+ F^-$ , and depending on the nature of the solvent, the right hand side being favoured by polar solvents, the left hand side by anhydrous hydrogen fluoride.

This  $F^{19}$  n.m.r. data was unable to justify Dixon's postulated structure although it fitted that of Stocks very well, except for the absence of platinum fluorine satellites; but due to the inability to detect hydrogen, a necessity for the Pt-F model, Dixon rejected

Stocks's formulation.

The central difference between the observations at this time was, on one hand the failure to detect hydrogen and the titration of the salt as a dibasic acid; against the isolation of salts of the cation  $\left[ \text{PtF}(\text{PPh}_3)_3 \right]^+$  and  $\text{F}^{19}$  N.M.R. data.

Later Dixon informed us that they had in fact been able to observe hydrogen gas evolution. The initial failures had been due to the understandable reluctance to connect the reaction system directly to a mass spectrometer and presumably diffusion had occurred from the metal gas transfer apparatus. More complete data were also provided from extended  $\text{F}^{19}$  studies.

Observation of the  $\text{Pt}^{195}$  side bands in the original complex was still not possible due to a poor signal to noise ratio, however a clearly defined doublet of triplets assignable to a Pt-F bond was seen and a weak resonance observed for the ionic salt obtained using sodium tetraphenylborate.

I.3.2.3 In an attempt to elucidate this reaction more fully, we have again reinvestigated the reaction of  $\text{Pt}(\text{PPh}_3)_x$  (  $x= 3,4$  ) with anhydrous hydrogen fluoride.

Very carefully prepared samples of tetra- and tris(triphenylphosphine)platinum(0) have been reacted with redistilled liquid hydrogen fluoride in the absence of moisture and oxygen. The reaction mixture, initially maintained at  $-78^\circ\text{C}$  was allowed to slowly warm to room temperature with stirring and the excess hydrogen

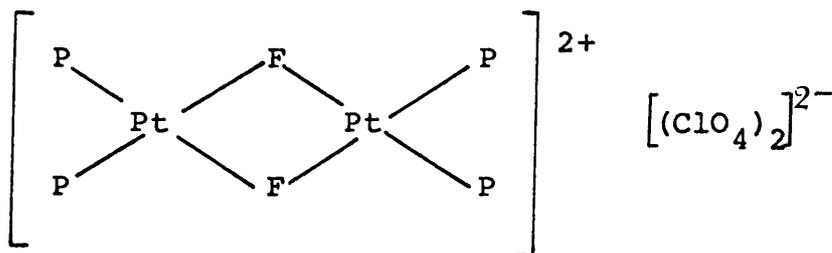
fluoride removed completely in a stream of dry nitrogen, leaving a thick oily liquid or occasionally an off-white solid. Washing with benzene and diethyl ether was followed by recrystallisation by slow precipitation using acetone/ether or nitromethane/ether to yield a white highly crystalline solid.

Samples recrystallised from the same crude reaction product from either of these solvent pairs were found to exhibit identical i.r. spectra, the unusual feature being a very strong broad band at approximately  $1800 \text{ cm}^{-1}$ . This band is occasionally absent in the crude product but is invariably present after recrystallisation.

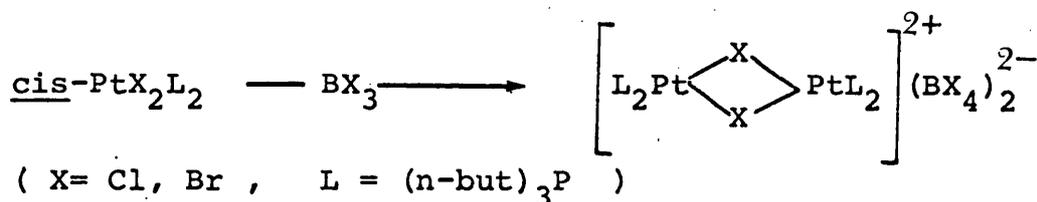
The fluorine analysis for this product is always higher than that required for  $[\text{PtF}(\text{PPh}_3)_3]^+ \text{HF}_2^-$  but the lowest values are found for samples dried under vacuum in the presence of solid potassium hydroxide/sodium fluoride or prepared from tris(triphenylphosphine)platinum(0).

However, reaction with solutions of alkali metal tetraphenylborates or tetrafluoroborates yield very highly crystalline adducts of exact composition  $[\text{PtF}(\text{PPh}_3)_3]^+ \text{X}^-$  (  $\text{X} = \text{BPh}_4^-, \text{BF}_4^-$  ).

Reaction with lithium perchlorate yields a compound analysing as  $\text{PtF}(\text{PPh}_3)_2(\text{ClO}_4)$ . Its i.r. spectra shows bands typical of an uncoordinated perchlorate ion and the conductivity of a univalent electrolyte, hence, a four coordinate structure with a  $\sigma$  bonded perchlorate group may be rejected. Stocks suggested the complex to be an ionic fluorine bridged species.<sup>12</sup>



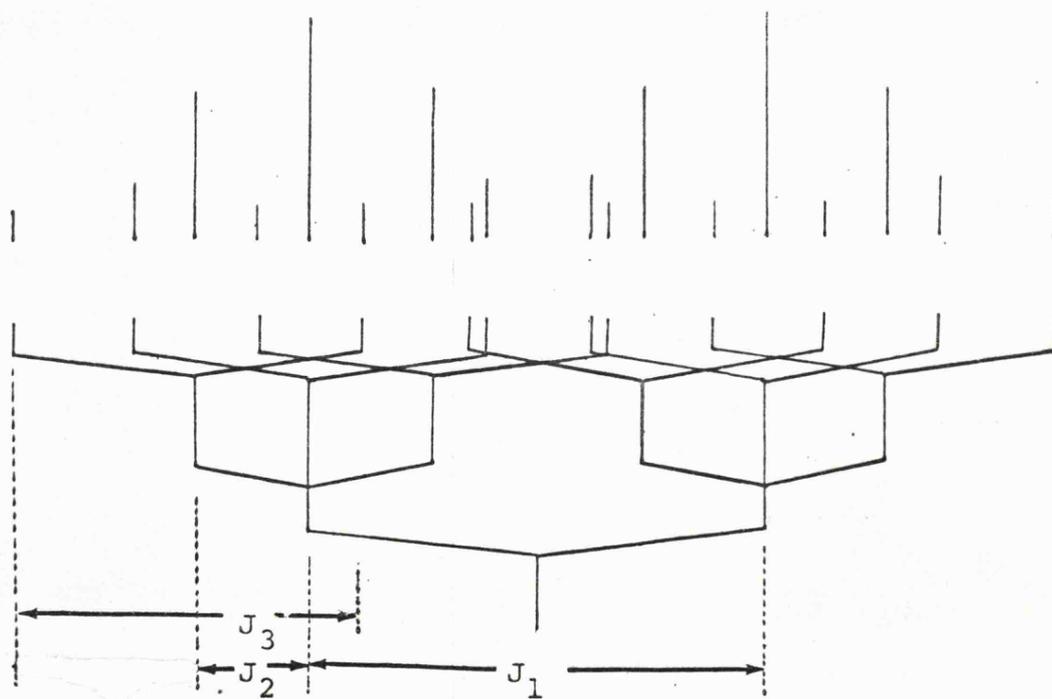
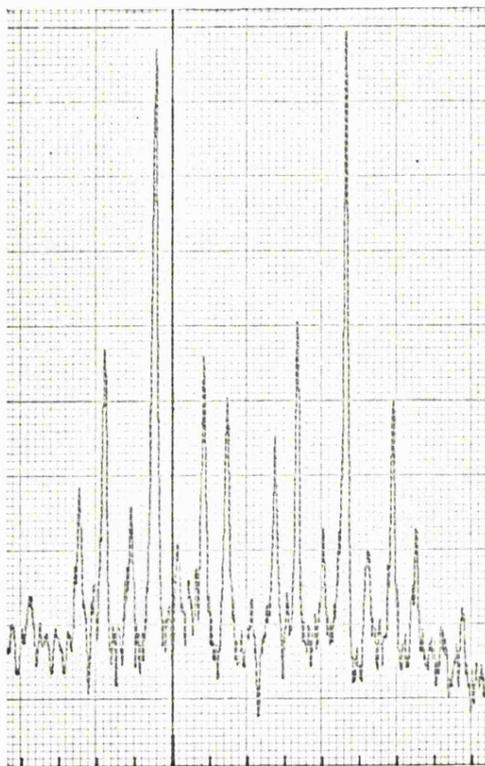
Platinum(II) complexes containing an uncoordinated perchlorate ion have previously been prepared by Church and Mays<sup>26</sup>, and halogen bridged cationic platinum (II) complexes of the type  $[\text{Pt}_2\text{X}_2(\text{PR}_3)_4]^{2+}$  by Druce *et al.*<sup>32</sup>



and Clark<sup>33</sup>



I.3.2.4. The  $\text{F}^{19}$  n.m.r. data obtained by Dixon very strongly inferred the presence of a platinum fluorine bond. However, no  $\text{Pt}^{195}$  satellites were observed. A poor signal to noise ratio together with low solubility of the complex in suitable solvents inhibit observation. Using a spectrometer operating at 56.4 MHz. in solvents such as nitromethane and nitrobenzene Stocks was only able to obtain a single resonance at 4320 Hz. from  $\text{PhCF}_3$  (76.5 p.p.m. upfield  $\text{PhCF}_3$ , 140.2 p.p.m. upfield  $\text{CFCl}_3$ ). However, using an instrument operating at 100 M.Hz. and employing an internal field loop lock system we have been able to obtain very well resolved spectra with very little noise.



$J_1$  (P-F) = 123 Hz.  
 $J_2$  (P-F) = 32.6 Hz.  
 $J_3$  (Pt-F) = 92 Hz.

$\text{F}^{19}$  N.M.R. spectra of the platinum cation  $\text{PtF}(\text{PPh}_3)_3^+$

A solution of the complex in dichloromethane at 30°C shows two regions of absorption, (All shifts are relative to CFC1<sub>3</sub>). A broad peak at +162 p.p.m. and a doublet (of triplets ?) at approximately 224.5 p.p.m. As the solution was cooled the signals sharpened. The solvent was removed from this sample and the solid obtained redissolved in fresh dichloromethane, rapidly cooled to -20°C, and its spectra observed again.

Three signals were now observed; a sharp singlet (123.5 p.p.m - int 22) , a very broad peak (162.5 p.p.m.- int 100) , and a doublet of triplets (221 p.p.m.- int 35) . Cooling of this solution to -40°C again sharpened all signals especially that at approximately 160 p.p.m. , and moved the positions slightly.

Freshly prepared solutions of the complex at -40°C and -60°C showed identical spectra , the ratio of the sharp singlet to the multiplet being approximately I:I. The two platinum fluorine coupling constants ( $J_1 = 128$  Hz,  $J_2 = 38.5$  Hz.) were obtained from the spectra at -60°C.

Using liquid sulphur dioxide as a solvent three signals were again obtained:-

- (A) A broad strong resonance at approximately 130 p.p.m.
- (B) A weaker sharp resonance at 139 p.p.m.
- (C) A very well defined doublet of triplets, each of which has platinum satellites, at approximately 214 p.p.m.

$$J_1 \text{ (P-F)} = 123 \text{ Hz}$$

$$J_2 \text{ (P-F)} = 32.6 \text{ Hz}$$

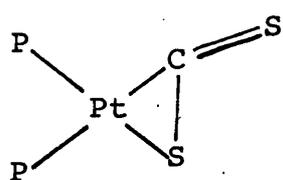
$$J_3 \text{ (Pt-F)} = 92 \text{ Hz.}$$

We assign this multiplet to a platinum fluorine bond coupling with the single trans phosphorus ( $J_1$ ), the two cis phosphorus ( $J_2$ ), and the platinum ( $J_3$ ).

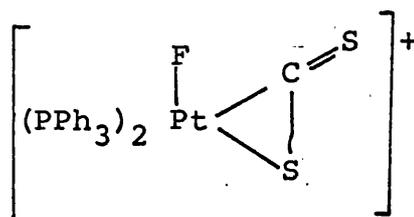
The resonance of the  $\text{HF}_2^-$  ion in salts of the type  $\text{M}^+ (\text{HF}_2)^-$  ( $\text{M} = \text{NH}_3\text{butyl}^+$ ,  $\text{NH}_2(\text{butyl})_2^+$ ,  $\text{NH}(\text{butyl})_3^+$ , and  $\text{N}(\text{butyl})_4^+$ ), have been measured by Soriano et al.<sup>34</sup> and fall in the range 150 - 170 p.p.m. (relative to  $\text{CFCl}_3$ ); the calculated value being 152.1<sup>35</sup>. Several other workers have reported and discussed the  $\text{F}^{19}$  spectra of hydrogen fluoride and the hydrogen bifluoride ion in aqueous solutions of alkali bifluorides<sup>36</sup> and hydrofluoric acid<sup>37,38</sup>. Values for the corresponding fluoride salts  $[\text{ButylNH}_3]^+ \text{F}^-$  and  $[(\text{butyl})_4\text{N}]^+ \text{F}^-$  are found at lower fields; 123.1 and 128.3 p.p.m. respectively.<sup>37</sup>

I.3.3. Reaction of the fluorotris(triphenylphosphine)platinum (II) cation with carbon disulphide.

I.3.3.I As part of a study of the chemistry of the fluoro-complex  $[\text{PtF}(\text{PPh}_3)]^+$  Stocks<sup>12</sup> reported that the reaction with carbon disulphide in ethanol yielded a pale yellow complex (II) which analysed as  $\text{PtF}_3(\text{CS}_2)(\text{PPh}_3)_2$  and assigned it to an ionic bonded structure similar to that found for the complex ( $\pi$ -carbonyl disulphide)bis(triphenylphosphine)platinum(0), (I)



(I)



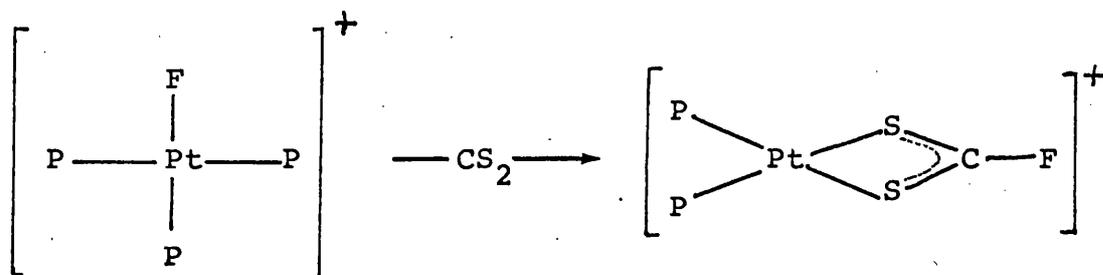
(II)



Both neutral and ionic I:I carbon disulphide

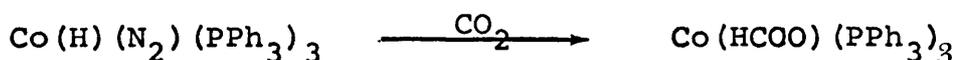
adducts of phosphine containing complexes of Pt<sup>39,40</sup>, Pd<sup>40</sup>, Ni<sup>40</sup>, Ir<sup>40,41,42</sup>, Rh<sup>40,41,42</sup>, and Ru<sup>43</sup> are known and have been assigned similar  $\pi$  bonded structures on the basis of i.r. data, some of which have been confirmed by crystallographic studies<sup>44,45,46</sup>.

We have reinvestigated this reaction and have found that the reaction of carbon disulphide with the fluorotris-(triphenylphosphine) cation in very dry methanol or acetone gives yellow crystals of an ionic adduct which analyses as PtF<sub>3</sub>(CS<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>. A similar reaction in wet solvents yield a highly crystalline white non-ionic product which contains no fluorine. A crystal study of the pale yellow complex has shown it to be a cationic platinum complex of fluoro dithioformic acid, resulting from the insertion of the carbon disulphide into the platinum fluorine bond.



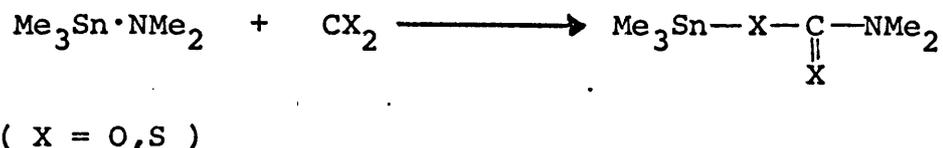
Insertion reactions<sup>47</sup> of carbon disulphide and related molecules are not unknown.

Carbon dioxide readily inserts into the M-H bond of Co(H)(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>3</sub> forming a formate complex Co(HCOO)(PPh<sub>3</sub>)<sub>3</sub>.<sup>48</sup>

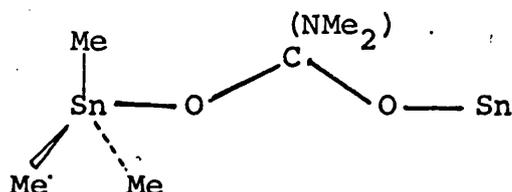


The reaction of dimethylaminotrimethylstannane

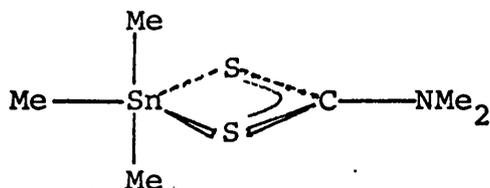
with carbon dioxide and carbon disulphide gives insertion products<sup>49</sup>



For X = O the product is a polymeric carbamate



however for X = S the product is monomeric and a ring structure has been suggested.

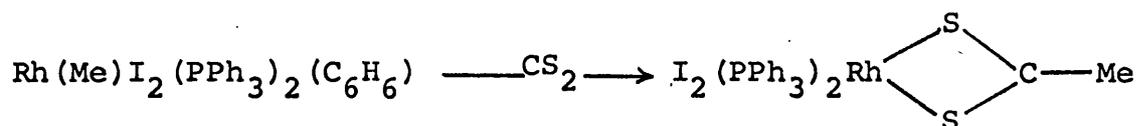


Treatment of aqueous solutions of  $\text{K}_2[\text{Co}(\text{CN})_5]$  with carbon disulphide yields a yellow complex  $\text{K}_6[(\text{CN})_5-\text{Co}-\text{S}-\text{C}(\text{S})-\text{Co}(\text{CN})_5]$  as a result of the insertion of a bridging  $\text{CS}_2$  group into the metal metal bond.<sup>41,44</sup>

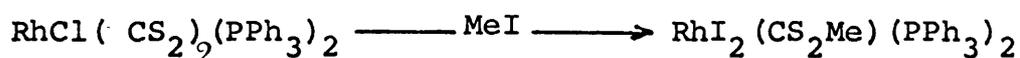
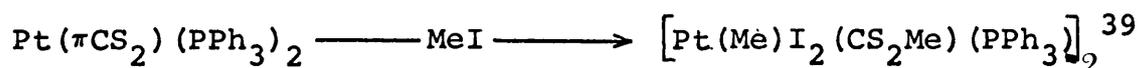
More recently Wilkinson<sup>50</sup> et al. have reported insertion products of carbon disulphide with phosphine complexes of platinum, rhodium and iridium.

The presence of a dithiomethyl group is inferred from n.m.r. and i.r. studies of  $\text{Rh}(\text{Me})\text{I}_2(\text{PPh}_3)_2(\text{C}_6\text{H}_6)$  in neat

carbon disulphide



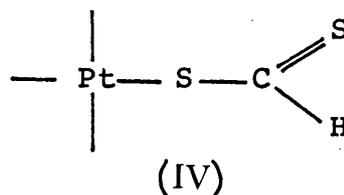
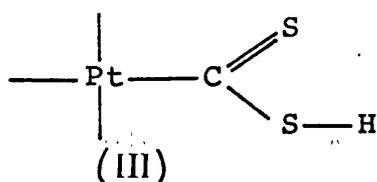
Similar complexes can be prepared by an inverse reaction



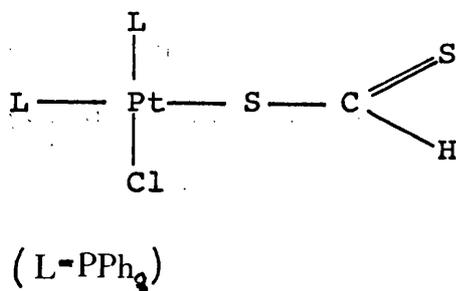
Wilkinson also reported that insertion reactions also occurred into metal hydride bonds but that the immediate products were unstable.

However, the insertion of carbon disulphide into the Pt-H bond of trans-PtHX(PPh<sub>3</sub>)<sub>2</sub>, (X = Cl, Br, I, CN) producing derivatives of the type PtX(S<sub>2</sub>CH)(PPh<sub>3</sub>)<sub>2</sub> has been studied<sup>51</sup>.

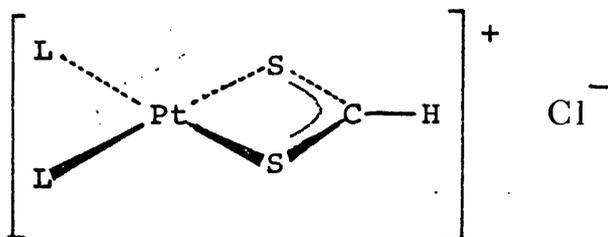
Two structures for the insertion product were postulated, (III, IV)



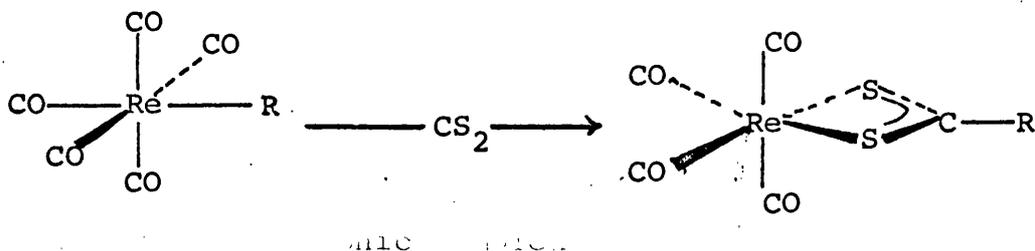
on the basis of n.m.r. and i.r. information. From a study of the chemistry of the complex the structure based on a derivative of dithioformic acid was chosen



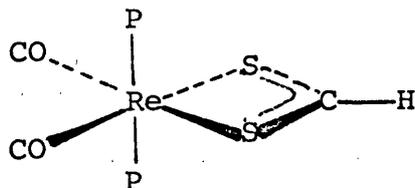
However in the absence of any conductivity data or low frequency i.r. spectral information the complex could equally be formulated as an ionic complex.



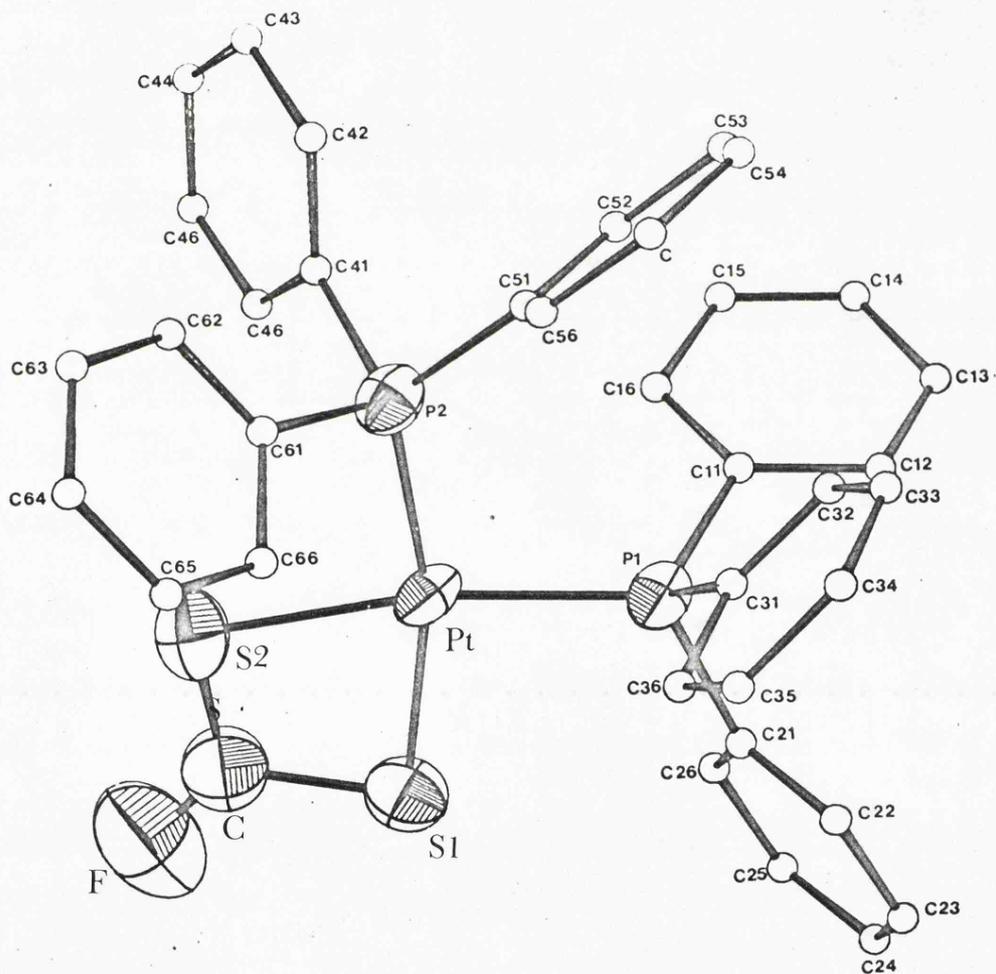
A rhenium complex  $\text{Re}(\text{CO})_4(\text{S}_2\text{CR})^{52}$  (R= Ph, Me ) from the insertion of carbon disulphide into the rhenium carbon bond of  $\text{Re}(\text{CO})_5\text{R}$  has recently been prepared and on the basis of  $\text{H}^1$ , n.m.r. , i.r. , raman, and mass spectra assigned to di-thioalkylformate complexes.



Reaction of carbon disulphide with  $\text{ReH}(\text{CO})_2(\text{PPh}_3)_2$  gives a diamagnetic complex  $\text{Re}(\text{CO})_2(\text{S}_2\text{CH})(\text{PPh}_3)_2$ . A structural determination has shown this to contain a dithioformate group.<sup>53</sup>



I.3.3.2. Detailed geometry of both cation and anion is shown in the enclosed figure. An unexpected feature of the cation geometry is the large departure from ideal  $\text{C}_{2v}$  geometry in



Crystal structure of  $[Pt(S_2CF)(PPh_3)_2]^+ HF_2^-$

Molecular geometry of  $[\text{Pt}(\text{S}_2\text{CF})(\text{PPh}_3)_2]\text{HF}_2$

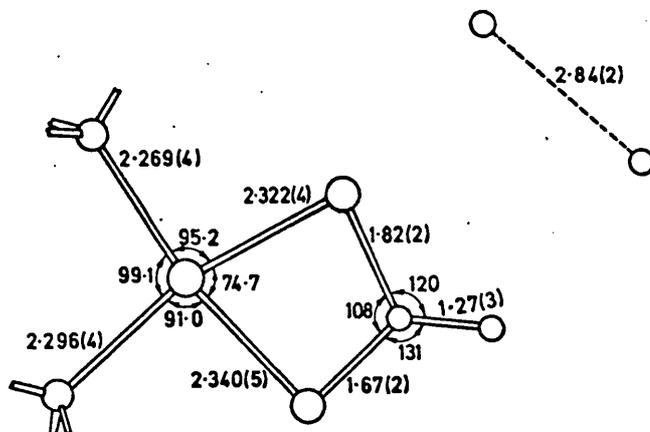


FIGURE. The molecular geometry of  $[\text{Pt}(\text{S}_2\text{CF})(\text{PPh}_3)_2][\text{HF}_2]$ . E.s.d.'s of bond lengths (Å) are in parentheses, e.s.d.'s of angles are  $0.2^\circ$  around Pt,  $1.5^\circ$  about the  $\text{S}_2\text{CF}$  group. Phenyl groups are omitted for clarity.

Bond length (Å)

Pt-P (I)	2.269 (4)
Pt-P (2)	2.296 (4)
Pt-S (I)	2.322 (4)
Pt-S (2)	2.340 (5)
C-S (I)	1.82 (2)
C-S (2)	1.67 (2)
C-F	1.27 (3)

Bond angle

S (I)-C-F	$120^\circ$
S (2)-C-F	$131^\circ$
S (I)-C-S (2)	$108^\circ$
P (I)-Pt-S (I)	$95.2^\circ$
P (2)-Pt-S (2)	$91.0^\circ$
P (I)-Pt-P (2)	$99.1^\circ$
S (I)-Pt-S (2)	$74.7^\circ$

F-F (in  $\text{HF}_2$ ) 2.84(2)

the immediate Pt co-ordination sphere. This is particularly noticeable in the two C-S bond lengths, which differ by 0.15 Å (e.s.d 0.03 Å); this difference approaches that of 0.18 Å found between the co-ordinated and uncoordinated C-S bond lengths in  $\text{Pt}(\pi\text{CS}_2)(\text{PPh}_3)_2$ <sup>45</sup>. One is forced to conclude that there is a marked difference in bond order in these two C-S bonds. This asymmetry is further reflected in the two S-C-F bond angles (the F atom is apparently repelled by the shorter C-S bond), in different Pt-S bond lengths, and in different Pt-P bond lengths (the longer Pt-P bond is trans to the shorter Pt-S).

The source of the asymmetric influence could be steric, involving different arrangements of phenyl groups in the two  $\text{PPh}_3$  ligands; there are some short S-C contacts from 3.2 - 3.5 Å : (cf. the Van der Waals radii sum of 3.55 Å)<sup>54</sup> or crystal packing effects involving the  $(\text{HF}_2)^-$  anion although these must be second order as there are no important (i.e. non-phenyl group) cation-anion contacts less than 4 Å. There is no major departure from planarity in the  $\text{P}_2\text{PtS}_2$  unit, the C-F bond is bent by  $10.5^\circ$  away from this plane.

The F - F distance in the  $\text{HF}_2^-$  anion is unusually long (cf. 2.28 Å in  $\text{KHF}_2$ )<sup>55</sup>; at this distance it is unlikely that the hydrogen atom lies midway between the fluorine atoms. It has proved difficult to observe a band in the i.r. spectrum attributable to the anion; a very broad band at  $1770 \text{ cm}^{-1}$ , which varies in intensity with different samples may be due to the anion. A similar band is observed in the i.r. spectrum of the starting material.

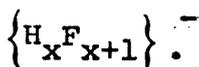
The fluoro-dithioformate ligand is hydrolytically

unstable. Thus if the reaction between  $[\text{PtF}(\text{PPh}_3)_3]^+ (\text{HF}_2)^-$  and carbon disulphide is carried out in damp acetone or methanol a yellow colour, which is initially produced, fades and white crystals of dithiocarbonatobis(triphenylphosphine)platinum(II)  $\text{Pt}(\text{S}_2\text{CO})(\text{PPh}_3)_2$ , separate; identified by analytical and infra-red data<sup>56</sup>.

We have also reacted the fluorotris(triphenylphosphine)platinum(II) cation with sulphur dioxide, tetrafluoroethylene and hexafluorobut-2-yne in an attempt to observe similar insertion reactions of the Pt-F bond. No such reactions have been observed with any of these however.

The ability to isolate analytically pure salts of large anions, comprehensive  $\text{F}^{19}$  n.m.r. spectra and crystallographic data on the adduct with carbon disulphide, indicate that the cation, of the ionic salt obtained from the reaction of tetra- or tris(triphenylphosphine)platinum(0) with liquid hydrogen fluoride, contains a platinum-fluorine bond; and may be formulated as  $[\text{Pt}(\text{F})(\text{PPh}_3)_3]^+$ .

The composition of the anion is a little less well defined. The absence of typical ionic bifluoride absorptions in the solid state infrared spectra, incorrect  $\text{F}^{19}$  integration, high fluorine analysis and long bond length found for the anion in the carbon disulphide adduct indicate that it may not be simply the  $\text{HF}_2^-$  ion. This must be a consequence of the reaction conditions, where the excess of hydrogen fluoride results in the generation of polymeric species of the type



## I.4. EXPERIMENTAL.

- I.4.1. Purification of reagents and preparation of precursors.
  
- I.4.2 Reaction of liquid hydrogen fluoride with :-
  - I.4.2.1. Tetrakis(triphenylphosphine)platinum(0).
  - I.4.2.2. Tris(triphenylphosphine)platinum(0)
  
- I.4.3. Anion exchange on fluorotris(triphenylphosphine)platinum(II) hydrogen difluoride with:-
  - I.4.3.1. Sodium tetraphenylborate.
  - I.4.3.2. Lithium tetrafluoroborate.
  - I.4.3.3. Lithium perchlorate.
  
- I.4.4. Reaction of fluorotris(triphenylphosphine)platinum(II) hydrogen difluoride with :-
  - I.4.4.1. Carbon disulphide
    - I.4.4.1.1. In dry solvents.
    - I.4.4.1.2. In damp solvents.
  - I.4.4.2. Sulphur dioxide.
  - I.4.4.3. Tetrafluoroethylene.
  - I.4.4.4. Hexafluorobut-2-yne.

I.4.I. Unless otherwise stated chemicals were used without further purification.

Potassium chloroplatinite was obtained on loan from Johnson Matthey, aqueous solutions were filtered before use to remove traces of chloroplatinate.

Triphenylphosphine, a gift from Albright & Wilson, was recrystallised twice from ethanol under nitrogen.

Lithium bromide and sodium tetraphenylborate from B.D.H.

Lithium chloride - Fisons.

Lithium perchlorate and lithium bromide - Hopkins & Williams.

Carbon disulphide (May & Baker) was shaken three times with 5% aqueous potassium permanganate, twice with clean mercury, and finally with 10% aqueous mercuric nitrate. After drying over anhydrous calcium chloride, the fraction distilling between 46-47°C was collected and stored in the dark over clean mercury at 0°C.

Sulphur dioxide - B.D.H.

Hexafluorobut-2-yne - Bristol Organics Ltd.

Hydrogen fluoride, from I.C.I., was redistilled in a stream of dry nitrogen at 25°C.

Tetrafluoroethylene was obtained by pyrolysis of polytetrafluoroethylene (I.C.I.) under high vacuum.

Reagent grade benzene and diethyl ether (May & Baker) were dried over sodium wire.

Nitromethane from Fisons was dried over anhydrous sodium sulphate and fractionated, taking the fraction between 100-102°C.

AnalaR acetone was refluxed from anhydrous sodium sulphate taking the fraction 56-57°C

Super dry methanol and ethanol were prepared via the magnesium alkoxide routes.

Tetrakis(triphenylphosphine)platinum(0) and tris(triphenylphosphine)platinum(0) were prepared by literature methods<sup>57</sup>.

Micro-analysis were carried out by Dr.F.Pascher (Mikroanalytisches Laboratorium, 53 Bonn)

Melting points were measured on a Reichert melting point apparatus in air and are uncorrected.

Infrared spectra were recorded using KBr (4000-400  $\text{cm}^{-1}$ ) and polythene (400-200  $\text{cm}^{-1}$ ) windows on a Perkin Elmer 225 diffraction grating spectrometer.

Individual spectra were calibrated using suitable absorption bands of a thin film of polythene (2850, 1603, 906  $\text{cm}^{-1}$ ); and the instrument accuracy and reproducibility periodically checked using atmospheric water absorption bands (3401.9, 1825.2, 1616.7, 506.95 & 376.23  $\text{cm}^{-1}$ )

$\text{F}^{19}$  n.m.r. spectra were obtained by Dr.M.Dove (University of Nottingham), using a Varian spectrometer operating at 100 M.Hz ,fitted with a variable temperature probe and modified to operate on an internal standard phase lock loop system .

All reactions using liquid hydrogen fluoride were carried out in an all polythene apparatus.

I.4.2. Reaction of platinum complexes with liquid hydrogen fluoride.

I.4.2.I. Tetrakis(triphenylphosphine)platinum(0)

Approximately 10 mls of hydrogen fluoride was distilled, in a stream of dry nitrogen at r.t., onto a magnetically stirred sample of tetrakis(triphenylphosphine)platinum(0), (1.23 g. - 1 m.mole), maintained at  $-78^{\circ}\text{C}$  (solid  $\text{CO}_2$ /acetone). The complex readily dissolved producing a deep red solution, which was allowed slowly to warm to room temperature when the excess acid was removed by a stream of warm dry nitrogen. The resultant off-white solid was then stored overnight under high vacuum in the presence of potassium hydroxide and sodium fluoride.

The crude white solid was thoroughly washed with benzene (3 x 20 mls) and diethyl ether (3 x 20 mls), yielding a white crystalline solid which was dissolved in the minimum volume of acetone (or nitromethane) and the resultant yellow solution filtered. Very slow addition of cold diethyl ether to this solution together with very vigorous stirring precipitated a highly crystalline white solid. This was filtered off and after washing with a few mls of diethyl ether was dried under vacuum at  $56^{\circ}\text{C}$ .

The compound was identified as fluorotris(triphenylphosphine)platinum(II) hydrogen difluoride (?), from analytical, infrared, and  $\text{F}^{19}$  n.m.r. data.

I.4.2.2. Tris(triphenylphosphine)platinum(0).

As for I.4.2.I. using tris(triphenylphosphine)platinum(0), (0.98 g. - 1 m.mole).

The compound was identified as fluorotris

-(triphenylphosphine)platinum(II) hydrogen difluoride.

I.4.3. Anion exchange reactions on fluorotris(triphenyl phosphine)platinum(II) hydrogen difluoride.

I.4.3.I. With sodium tetraphenylborate.

A solution of sodium tetraphenylborate, (0.17 g - 0.5 m.mol), in ethanol (5 mls), was added to a solution of the fluoro complex, (0.50 g. - 0.5 m.mole), in ethanol, (30 mls), producing an immediate white precipitate.

The solution was shaken overnight and the solid filtered off. After thorough washing with warm water the white solid was dissolved in warm acetone, filtered and the solid induced to crystallise by careful addition of ethanol/ether, depositing a white highly crystalline solid.

This was identified as fluorotris(triphenyl phosphine)platinum(II) tetraphenylborate,  $[\text{PtF}(\text{PPh}_3)_3]^+$   $(\text{BPh}_4)^-$ , (0.53 g. - 81%), from analytical and infrared data.

I.4.3.2. With lithium tetrafluoroborate.

As for I.4.3.I. using lithium tetrafluoroborate, (0.05 g. - 0.5 m.mole), bright white crystals depositing within a few minutes.

The compound was identified as fluorotris(triphenylphosphine)platinum(II) tetrafluoroborate,  $[\text{PtF}(\text{PPh}_3)_3]^+$   $(\text{BF}_4)^-$ , (0.46 g. - 85%), from analytical and infrared data.

I.4.3.3. With lithium perchlorate.

As for I.4.3.I. using lithium perchlorate, (0.08 g. - 0.5 m.mole).

The compound was identified as di- $\mu$ -fluorotetrakis(triphenylphosphine)diplatinum(II) perchlorate,  $[\text{Pt}_2\text{F}_2(\text{PPh}_3)_4]^{2+} (\text{ClO}_4)_2^{2-}$  (0.34 g. - 80%), from analytical and infrared data.

I.4.4. Reactions of fluorotris(triphenylphosphine)platinum(II) hydrogen difluoride.

I.4.4.I. Reactions with carbon disulphide:-

I.4.4.I.I. Purified carbon disulphide, (1 ml), was added to a solution of freshly prepared fluorotris(triphenylphosphine)platinum(II) hydrogen difluoride, (0.52 g. - 0.5 m.mole), in super dry ethanol (methanol or acetone) (35 mls), producing a pale yellow solution. This solution was shaken at r.t. for eight hours during which time the intensity of the colour increased. The solvent was completely removed leaving a yellow oil which was recrystallised from acetone to yield a pale yellow crystalline solid.

This was filtered off and after washing with a few mls of diethyl ether dried in vacuo at 56°C. The compound was identified as dithioformatobis(triphenylphosphine)platinum(II) hydrogen difluoride,  $[\text{Pt}(\text{S}_2\text{CF})(\text{PPh}_3)_2]^+ (\text{HF}_2)^-$ , from analytical and crystallographic data.

I.4.4.I.2. Purified carbon disulphide, (1 ml), was added to a solution of freshly prepared fluorotris(triphenylphosphine)platinum(II) hydrogen difluoride, (0.52 g. - 0.5 m.mole), in ethanol, (35 mls), and water, (1 ml).

The solution was left to stand for 3 days at r.t. during which the original yellow colour of the solution faded and a crop of white plate like crystals was deposited.

These were filtered off and after washing with ethanol and ether dried in vacuo at 56°C. The compound was identified as dithiocarbonatobis(triphenylphosphine)platinum(II),  $\text{Pt}(\text{S}_2\text{CO})(\text{PPh}_3)_2$ , by melting point, analytical and infrared data<sup>56</sup>.

I.4.4.2. Reaction with sulphur dioxide.

Sulphur dioxide, (1 ml), was distilled into a Carius tube (-196°C) containing a solution of fluorotris(triphenylphosphine)platinum(II) hydrogen difluoride, (0.52 g. - 0.5 m.mole), in dry methanol, (20 mls). The tube was sealed, and after allowing it to warm to r.t., was mechanically shaken for 3 days. No change in the colour of the contents was observed, so it was heated at 45°C for a further 3 days, during which time the solution turned yellow.

The tube was frozen down and opened. Removal of the solvent left a yellow oil which was recrystallised from acetone/ether to yield a white crystalline solid. The i.r. spectra showed no new bands and the compound was identified as the starting material.

I.4.4.3. Reaction with tetrafluoroethylene.

As for I.4.4.2. using tetrafluoroethylene, (1 ml)  
The starting material was isolated in low yield.

I.4.4.4. Reaction with hexafluorbut-2-yne.

As for I.4.4.2. using hexafluorbut-2-yne (1 ml).  
The starting material was isolated in low yield.

I.5. APPENDICES.

I.5.I. Analytical data.

Compound	Colour	M.Pt(°C)	C	H	F	Others
$[\text{PtF}(\text{PPh}_3)_3]^+ (\text{HF}_2)^-$	white	180-185°	60.25	4.37	6.80	
			61.13	4.45	8.84	
			61.87	4.26	5.90	
			62.10	4.35	5.70	
			(62.37)	(4.49)	(5.48)	
$[\text{PtF}(\text{PPh}_3)_3]^+ (\text{BF}_4)^-$	white	199-201°	58.81	4.04	8.94	1.04
			58.27	4.21	9.01	1.16
			(58.60)	(4.09)	(8.58)	(0.98)
						B
$[\text{PtF}(\text{PPh}_3)_3]^+ (\text{BPh}_4)^-$	white	181-182°	70.65	4.91	1.22	0.95
			(70.96)	(4.96)	(1.44)	(0.95)
						B
$[\text{Pt}_2\text{F}_2(\text{PPh}_3)_4]^{2+} (\text{ClO}_4)_2^{2-}$	white	199-200°	52.43	3.89	2.14	4.04
			(51.59)	(3.61)	(2.27)	(4.23)
						Cl
$[\text{Pt}(\text{S}_2\text{CF}(\text{PPh}_3)_2)]^+ (\text{HF}_2)^-$	pale yellow	265-275°	51.09	3.74	2.00	7.68
			(52.11)	(3.66)	(2.23)	(7.52)
						S
$\text{Pt}(\text{S}_2\text{CO})(\text{PPh}_3)_2$	white	175-179°	54.13	3.65		
			(54.74)	(3.72)		

calculated in parenthesis

Infrared data for platinum complexes and reaction products from liquid hydrogen fluoride reactions.

$\text{Pt}(\text{PPh}_4)_4 / \text{HF}$	crude product	1770 m.-br. 810 s. 730 s.
	recrystallised acetone	1775 ms.-v.br. 810 s. 731 s.
$\text{Pt}(\text{PPh}_3)_3 / \text{HF}$	crude product	1775 m.-v.br. 877 ms. 810 m. 788 m.
	recrystallised acetone	1790 vs.-v.br. 877 s. 787 s.
	recrystallised nitromethane	1775 m.-v.br. 1550 ms. 1400 w.-sp. 880 w.-br. 787 w.-br.sh.
$[\text{PtF}(\text{PPh}_3)_3]^+ \text{BF}_4^-$		1095 - 1050 vs.-br.
$[\text{PtF}_2(\text{PPh}_3)_4]^{2+} (\text{ClO}_4)_2^{2-}$		1090 vs.-br.
s m w	strong. medium weak	br sh sp v
	broad shoulder sharp very	

## CHAPTER TWO.

### 2.1. INTRODUCTION.

### 2.2. RESULTS AND DISCUSSION.

2.2.1. Synthesis of fluorocarbonylbis(triphenyl-phosphine)iridium(I).

2.2.2. Reactions of fluorocarbonylbis(triphenyl-phosphine)iridium(I).

2.2.2.1. Halide exchange reactions.

2.2.2.2. Halide displacement reactions.

2.2.3. Oxidative addition reactions of fluoro-carbonylbis(triphenylphosphine)iridium(I)

2.2.3.1. Molecules of the type XY

2.2.3.2. Oxygen.

2.2.3.3. Sulphur dioxide.

2.2.3.4. Fluoro olefins and electronegatively substituted acetylenes.

### 2.3. DISCUSSION.

2.3.1. Bonding of oxygen.

2.3.2. Bonding of sulphur dioxide.

### 2.4. EXPERIMENTAL.

### 2.5. APPENDICES.

2.5.1. Analytical data.

2.5.2. Infrared data.

2.5.3. Thermochemical data.

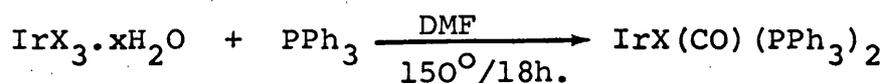
## 2.1. INTRODUCTION.

There is much current interest in the stereochemistry and mechanism of the oxidative addition reactions of complexes of the type  $\text{IrX}(\text{CO})\text{L}_2$ <sup>58,59,60,61</sup>. (X = Cl, Br, I; L = tertiary phosphine or tertiary arsine.)

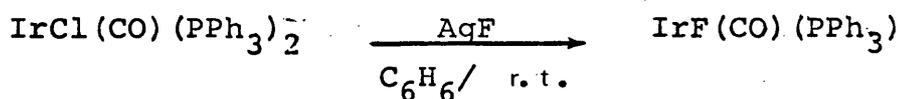
As part of our study of fluorine containing phosphine complexes we have synthesised the fluoro derivative of Vaska's complex and have studied its chemistry and the oxidative additions of unsaturated molecules, such as oxygen, sulphur dioxide and fluoro-olefins and acetylenes.

## 2.2. RESULTS AND DISCUSSION.

2.2.1. The chloro, bromo and iodo complexes  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$  are most easily synthesised from the corresponding hydrated iridium trihalides and triphenylphosphine in boiling dimethyl-<sup>62</sup>formamide .



However, such routes are not available for the fluoride and it has been prepared in high yield by halide exchange on chlorocarbonylbis(triphenylphosphine)iridium(I) using a saturated aqueous solution of silver fluoride.

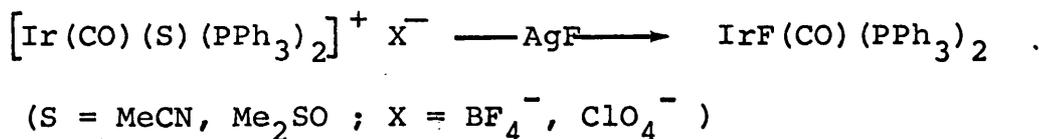


Similar halide exchange reactions have been

used on the chloro complex to provide alternative routes to the bromo and iodo compounds  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ , ( $\text{X} = \text{Br}, \text{I}$ ) using alkali metal halides in various solvents,  $\text{LiBr}/\text{THF}$ <sup>63,64</sup>,  $\text{NaBr}/\text{ethanol-benzene}$ <sup>63</sup>,  $\text{LiI}/\text{ethanol-benzene}$ <sup>64</sup>, and  $\text{NaI}/\text{ethanol-benzene}$ <sup>64</sup>.

During this study Vaska<sup>22</sup> independently reported the synthesis of the compound  $\text{IrF}(\text{CO})(\text{PPh}_3)_2$  by a similar route. Silver fluoride generated in situ, from a saturated methanolic solution of ammonium fluoride and freshly prepared silver carbonate, was refluxed with powdered chlorocarbonyl-bis(triphenylphosphine)iridium(I) yielding fluorocarbonyl-bis(triphenylphosphine)iridium(I) in 46% yield.

Roper et al.<sup>65</sup> also reported the synthesis of the fluoro complex from the reaction of ionic solvent bonded iridium(I) complexes of the type  $[\text{Ir}(\text{CO})(\text{S})(\text{PPh}_3)_2]^+ \text{X}^-$ , which are useful intermediates in the preparation of square planar  $d^8$  complexes of the type  $\text{IrY}(\text{CO})(\text{PPh}_3)_2$ , with silver fluoride.

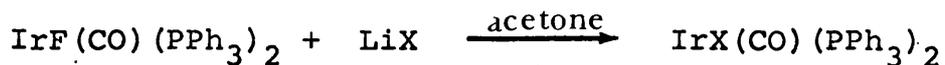


The infrared carbonyl frequencies for the complexes  $\text{MX}(\text{CO})(\text{PPh}_3)_2$ , ( $\text{M} = \text{Ir}, \text{Rh}$  ;  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$  ), show a small but definite trend  $\text{I} > \text{Br} > \text{Cl} > \text{F}$ , which is in direct opposition to that normally found for series of halogen complexes, such as  $\text{MnX}(\text{CO})_5$ , ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$  )<sup>66</sup>.

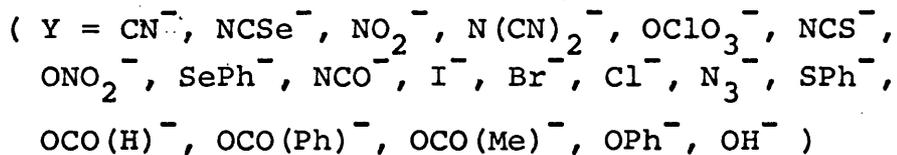
### 2.2.2. Reactions of $\text{IrF}(\text{CO})(\text{PPh}_3)_2$

2.2.2.I. Halide exchange reactions.

Solutions of fluorocarbonylbis(triphenylphosphine)iridium(I) in acetone react quantitatively with lithium halides forming the corresponding halogen derivative  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ , (X = Cl, Br, I) and precipitate lithium fluoride.



Vaska<sup>22</sup> extended this work and using a wide range of alkali metal salts prepared a series of complexes of the type  $\text{IrY}(\text{CO})(\text{PPh}_3)_2$ ,



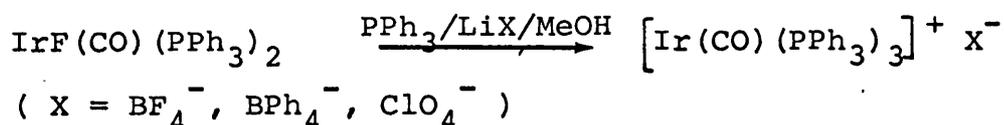
many of which could not be synthesised by similar reactions using the chloride; for example, the reaction of chlorocarbonylbis(triphenylphosphine)iridium(I) with sodium nitrite or nitrate gives complex mixtures including irreversible oxidation products and nitrosyl complexes<sup>67</sup>. From a study of the carbonyl frequencies of these complexes Vaska also suggested a correlation between the observed carbonyl frequency of a complex containing an anionic ligand  $\text{A}^-$  and its electronegativity. The usefulness of this emerges from the fact that for both the hydroxo complexes  $\text{M}(\text{OH})(\text{CO})(\text{PPh}_3)_2$ , (M = Rh, Ir) the predicted value of electronegativity is identical to that calculated by Wilmshurst<sup>68</sup> for the

classical electronegativity of  $\text{OH}^-$ , in accordance with the common notion that this ligand is unable to act as a  $\pi$  acceptor.

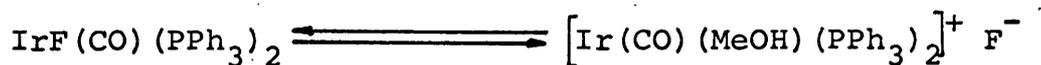
2.2.2.2. Halide displacement reactions.

Suspensions of the complex  $\text{IrF}(\text{CO})(\text{PPh}_3)_2$  in methanol dissolve in the presence of lithium salts of large non-coordinating anions such as tetrafluoroborate, tetraphenylborate and (perchlorate) producing deep orange solutions. These solutions presumably contain the coordinatively unsaturated species  $[\text{Ir}(\text{CO})(\text{PPh}_3)_2]^+ \text{X}^-$  ( $\text{X} = \text{BF}_4^-, \text{BPh}_4^-, \text{ClO}_4^-$ ).

Reaction of such solutions with an excess of neutral donor molecules such as triphenylphosphine yield salts of the type  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]^+ \text{X}^-$ .



Vaska<sup>22</sup> reported that solutions of fluorocarbonyl bis(triphenylphosphine)iridium(I) showed conductivity in methanol and suggested an equilibrium of the type,



A similar reaction in methanol using the chloro complex does not result in halogen bond cleavage. However, using more strongly coordinating solvents such as methyl cyanide and dimethylsulphoxide cleavage does occur and here ionic complexes containing coordinated solvent molecules

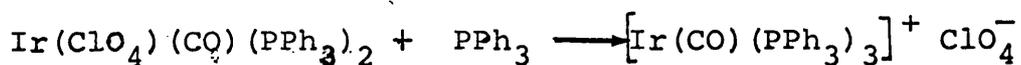
can be isolated<sup>65</sup>.

The solid state spectra of the complexes  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]^+ (\text{X})^-$ , show carbonyl bands at ca.  $2010 \text{ cm}^{-1}$  as would be predicted for Ir(I) cationic complexes.

However, spectroscopic studies of the complex  $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]^+ (\text{ClO}_4)^-$ , in chloroform, have indicated that the complex loses one of the coordinated triphenylphosphine molecules in solution and sigma bonds the perchlorate ion, forming a neutral square planar complex

The neutral square planar complex  $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$  containing a coordinated perchlorate ligand has been synthesised<sup>69</sup> and its chemistry studied<sup>70</sup>. Its reactions fall into one of three patterns:-

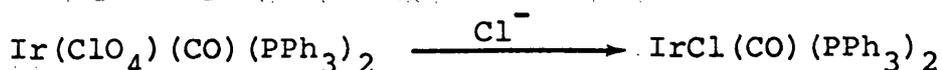
(A) Reaction with neutral donor molecules, L, yielding cationic square planar complex.



(B) Reaction with neutral molecules such as sulphur dioxide or dioxygen yielding 5 (or 6) coordinate species.

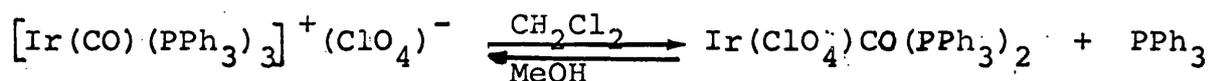


(C) Very fast reaction with anions which displace the weakly coordinating perchlorate producing neutral four coordinate square planar complexes.



Recrystallisation of the ionic complex from dichloromethane/petrol results in a mixture of the ionic and coordinated perchlorate complexes. However, differential

recrystallisation from dichloromethane/methanol results in the recovery of the ionic complex only, presumably due to the reaction of any covalent iridium complex (formed in  $\text{CH}_2\text{Cl}_2$ ) ionising and reacting with displaced triphenylphosphine as the methanol concentration increases.



### 2.2.3. Oxidative addition reactions of $\text{IrF}(\text{CO})(\text{PPh}_3)_2$

Vaska's complex has been shown to undergo oxidative addition reactions with a large number of molecules of the type AB, forming octahedral iridium(III) complexes.

2.2.3.I. Hydrogen chloride<sup>71,72</sup>, methyl iodide<sup>64,73</sup> and mercuric halides<sup>74</sup> all react completely with chlorocarbonyl bis(triphenylphosphine)iridium(I) forming stable I:I adducts  $\text{IrCl}(\text{A})(\text{B})(\text{CO})(\text{PPh}_3)_2$ . (A = H, Me, HgCl, HgBr; B = Cl, Br, I).

However, similar reactions using the fluoro complex  $\text{IrF}(\text{CO})(\text{PPh}_3)_2$ , result in complete or partial halide exchange of the fluorine atom. Complete reaction is indicated by the shift of the Ir(I) carbonyl band at  $1945 \text{ cm}^{-1}$  to approximately  $2000 \text{ cm}^{-1}$ . In all reactions however analytical data, although providing the correct C/H ratios, has a low F/halide ratio and high halogen analysis.

Methyl iodide and mercuric halides react readily yielding white or pale yellow I:I adducts of both fluoro and chloro mixtures of the iridium(I) complexes.

Reaction with an excess of hydrogen chloride results

in complete halogen exchange and isolation of the known compound  $\text{IrCl}_2(\text{H})(\text{CO})(\text{PPh}_3)_2$ <sup>71</sup>; while very careful reaction with exactly one mole of hydrochloric acid results in the same complex and unreacted iridium(I) complex. This can be explained on the basis of competing halide exchange and oxidative addition. Hydrogen fluoride has been shown to react only partially with  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ <sup>17</sup>.

2.2.3.2. There is also much interest in the addition of small neutral molecules such as dioxygen, sulphur dioxide, and unsaturated fluorocarbons to square planar  $d^8$  complexes as a consequence of their relevance to biological and catalytic systems.

The complexes  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$  have all been shown to react with dioxygen in solution forming crystalline I:I adducts  $\text{IrX}(\text{O}_2)\text{CO}(\text{PPh}_3)_2$ , (X = Cl<sup>75</sup>, Br<sup>76</sup>, I<sup>77</sup>) and a kinetic study of these reactions in benzene and dimethylformamide by Chock and Halpern<sup>64</sup> has shown the rates of reaction to be  $\text{I} > \text{Br} > \text{Cl}$ . Vaska<sup>75</sup> reported that the reaction of trans-chlorocarbonylbis(triphenylphosphine)iridium(I) was reversible at higher temperatures and reduced pressures and that a fast stream of an inert gas would remove the coordinated dioxygen molecule.

We have found that a benzene solution of fluorocarbonylbis(triphenylphosphine)iridium(I) reacts very slowly with dioxygen at r.t. and even after six hours the yellow colour of the solution is still present. Removal of the solvent, either under reduced pressure below room temperature with the addition of cold diethyl ether; or at room temperature in a stream of dioxygen yields a mixture of a

pink and yellow solid.

The solid state spectrum has carbonyl bands at 2010, 2004, 2000 and 1945  $\text{cm}^{-1}$  and a medium strong band at 858  $\text{cm}^{-1}$ . By analogy with the oxygen adduct of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ , the carbonyl bands at ca. 2000  $\text{cm}^{-1}$  are assigned to the I:I adduct of fluorocarbonyltris(triphenylphosphine) iridium(I) with dioxygen and at 858  $\text{cm}^{-1}$  to the (O-O) stretch. The presence of some unreacted starting material is shown by the carbonyl band at 1945  $\text{cm}^{-1}$ , but we have not been able, by variation of the reaction conditions, to obtain a pure sample of the dioxygen adduct.

Structural determinations on the two complexes  $\text{IrX}(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$ , ( $\text{X} = \text{Cl}^{77}, \text{I}^{78}$ ) have shown them to adopt the same configuration, based on a trigonal bipyramidal with axial phosphines. The dioxygen molecule is more strongly bound to the metal in the iodo complex as shown by the shorter average Ir-O bond lengths and an increased O-O bond length, than it is in the chloro analogue.

2.2.3.3 The reversibility and reaction of sulphur dioxide with transition metal complexes has been the subject of several investigations and I:I adducts have been isolated for complexes of  $\text{Ru}^{79,80}$ ,  $\text{Fe}^{81}$ ,  $\text{Mn}^{82}$ ,  $\text{Rh}^{21,87}$ ,  $\text{Ir}^{83,84}$ ,  $\text{Pd}^{85,86}$ , and  $\text{Pt}^{85,86}$ .

Sulphur dioxide reacts reversibly with fluorocarbonylbis(triphenylphosphine)iridium(I) in both the solid state and in solution forming a bright green complex. The adduct appears to be thermally much less stable than the corresponding chloro complex and its composition to vary with the reaction conditions.

A spectroscopic study in solution has shown that the passage of a dilute solution of sulphur dioxide in nitrogen through solutions of fluorocarbonylbis(triphenylphosphine)iridium(I) in benzene, acetone or chloroform result in the disappearance of the iridium(I) carbonyl band at  $1955 - 1970 \text{ cm}^{-1}$ , concurrent with the growth of a new band at  $2020 - 2027 \text{ cm}^{-1}$ ; which by comparison with  $\text{IrCl}(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$  is assigned to the carbonyl frequency of a five coordinate adduct with sulphur dioxide.

Saturation of the solutions with sulphur dioxide produces no further shift of these bands or the appearance of any more new bands, indicating that in solution no further molecules of sulphur dioxide are coordinated to the metal by an Ir-S bond. Concentration of these solutions under reduced pressure at slightly above room temperature and under reduced pressure, yielded a yellow-green product whose solid state infrared spectra shows a main carbonyl band at  $2020 \text{ cm}^{-1}$  and a  $\nu(\text{S}=\text{O})$  at  $1172$ , and  $1163 \text{ cm}^{-1}$ . The presence of some starting material is indicated by the carbonyl band at  $1945 \text{ cm}^{-1}$ .

The solid state infrared spectra of samples obtained from similar solutions concentrated at room temperature in a stream of nitrogen containing a few percent of sulphur dioxide show no carbonyl bands due to starting material. The presence of  $\text{IrF}(\text{CO})(\text{SO}_2)(\text{PPh}_3)_2$  is indicated by a very strong carbonyl band at  $2020 \text{ cm}^{-1}$  and (S-O)'s at  $1200$ ,  $1180$ , and  $1173 \text{ cm}^{-1}$ , however, two new weak-medium bands are now also observed at  $2050$  and  $1297 \text{ cm}^{-1}$ .

Reaction of a suspension of  $\text{IrF}(\text{CO})(\text{PPh}_3)_2$  in

benzene/ether produces a powdery green solid whose solid state spectrum is identical to that obtained from solution : except for a very strong band at  $1297 \text{ cm}^{-1}$ .

Reaction of a suspension of  $\text{IrF}(\text{CO})(\text{PPh}_3)_2$  with liquid sulphur dioxide, at  $-10^\circ \text{C}$ , resulted in a deep green crystalline solid whose infrared spectrum showed a very strong band at  $2050 \text{ cm}^{-1}$  and medium strong band at  $2021 \text{ cm}^{-1}$ ; (S-O) bands are also observed at  $1297(\text{s})$ ,  $1174(\text{s})$ , and  $1165(\text{m}) \text{ cm}^{-1}$ .

The stereochemistry and bonding of sulphur dioxide to  $\text{MCl}(\text{CO})(\text{PPh}_3)_2$ , (M = Rh, Ir) has been suggested by Vaska<sup>83</sup> and Grinberg *etal.*<sup>21</sup> on the basis of the observed shifts of the metal carbonyl absorptions of the I:I sulphur dioxide adducts. Detailed structural data on  $\text{IrCl}(\text{CO})(\text{SO}_2)(\text{PPh}_3)_2$ <sup>87</sup> has shown this to be correct; the sulphur dioxide molecule coordinating (based on  $\text{sp}^3$  hybridised S), through its sulphur atom.

A recent<sup>88</sup> investigation of the solid state reactions of complexes of the type  $\text{MX}(\text{CO})(\text{PPh}_3)_2$  and  $[\text{M}(\text{P}-\text{P})_2]^+ \text{X}^-$ , (X = Cl, Br, I; P-P = bis(diphenylphosphino) ethane), with gaseous sulphur dioxide has shown that adducts having an  $\text{SO}_2$ :complex ratio of greater than one are produced. Gas uptake decreases and the rate of sorption increases with increasing temperature. The desorption curves for the compounds show two minima at  $65 \pm 3^\circ \text{C}$  and  $120 \pm 5^\circ \text{C}$  indicating two different bonding modes for the sulphur dioxide molecule. The carbonyl frequencies observed in these complexes show a shift of the same magnitude observed for the I:I adducts crystallised from solution, indicating that only one molecule of sulphur dioxide is sigma bonded in the

solid complex. However in addition to the infrared absorptions due to the coordinated sulphur dioxide molecule, (1180 - 1200  $\text{cm}^{-1}$ ), new bands appear in the region normally associated with the symmetric and asymmetric stretching frequencies of solid sulphur dioxide<sup>89</sup>, ( $\nu_3$  asy 1330, 1308  $\text{cm}^{-1}$ ). These, together with the observed reduction in intensity of these bands when such samples are swept with a warm stream of inert gas; indicate that these extra molecules of sulphur dioxide are in some way 'associated' as opposed to 'bonded' to the complex, but remain more strongly held than by simple physical adsorption since surface area effects have little effect on the rate, yield or exothermicity of the reaction.

On this basis we assign the band at 1297  $\text{cm}^{-1}$  which we have observed in the product from the reaction of the fluoro complex with sulphur dioxide to similar molecules of 'associated' sulphur dioxide; especially since they are observed to be the strongest when the reaction conditions favour combinations of low temperatures, the presence of solid state  $\text{IrF}(\text{CO})(\text{PPh}_3)_2$  (or its I:I.  $\text{SO}_2$  adduct) , and a high concentration of sulphur dioxide.

2.2.3.4. Reaction of Vaska's complex with olefins<sup>62, 90, 91, 92, 93</sup>, and electronegatively substituted acetylenes<sup>62, 92, 93</sup> have been investigated.

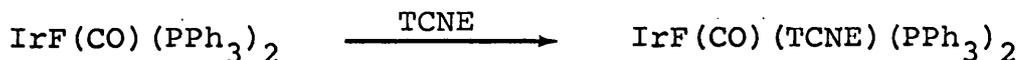
The pale yellow I:I adduct of tetrafluoroethylene<sup>92, 93</sup> prepared by Cramer and Parshall is thermally unstable, readily losing tetrafluoroethylene in solution and hence can only be purified by recrystallisation under an atmosphere of  $\text{C}_2\text{F}_4$ .



The hexafluorobute-2-yne adduct<sup>92,93</sup> prepared at room temperature and under atmospheric pressure, shows greater thermal stability, although pyrolysis of both complexes at temperatures greater than 100°C liberates the unsaturated fluorocarbon and regenerates trans-chlorocarbonylbis(triphenylphosphine)iridium(I); the hexafluorobut-2-yne recombining in the solid state if left in contact with the solid complex.

We have synthesised the corresponding bromo and iodo complexes of tetrafluoroethylene and hexafluorbut-2-yne and found similar instabilities, especially for the C<sub>2</sub>F<sub>4</sub> adducts. However, the I:I adducts of fluorocarbonylbis(triphenylphosphine)iridium(I) are very much more stable and can be easily recrystallised from hot non-chlorinated solvents.

Reaction of fluorocarbonylbis(triphenylphosphine)iridium(I) with tetracyanoethylene yields a I:I adduct containing a π-bonded olefin.

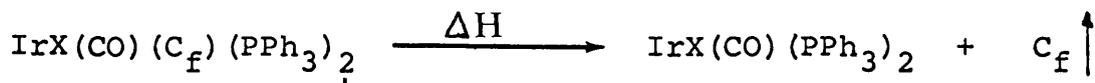


similar to the chloro analogue prepared by Baddley<sup>91</sup>.

Attempts to synthesis the adduct with cis-1,2 dicyanoethylene resulted in only partial reaction as shown by infrared spectra.

In an attempt to provide quantitative information we have made thermochemical measurements of the heat of

reaction for the quantitative loss of hexafluorbut-2-yne and tetrafluoroethylenefrom a series of iridium(II) complexes  $\text{IrX}(\text{CO})(\text{C}_f)(\text{PPh}_3)_2$ , (X = F, Cl, Br, I ;  $\text{C}_f = \text{C}_2\text{F}_4, \text{C}_4\text{F}_6$ ).



using a differential scanning calorimeter. We have found that for adducts of both  $\text{C}_2\text{F}_4$  and  $\text{C}_4\text{F}_6$  the heat of this reaction increases in the order  $\text{F} > \text{Cl} > \text{Br}$ .

### 2.3. DISCUSSION.

Much interest has been shown in factors which affect the tendency of oxidative addition reactions to occur to complexes of the type  $\text{IrX}(\text{CO})\text{L}_2$  and the correlation and prediction of trends from observed reactivity, spectroscopic and structural data.

The reversibility and variation of the bond length observed in the dioxygen adducts of  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ , (X = Cl, I) has been explained in terms of the bonding, electronegativity and polarisability of the halogen atom X. On this basis it would be predicted that the bonding of the dioxygen molecule to fluorocarbonylbis(triphenylphosphine)iridium(I) should be the weakest for the series. The strength of the initial  $\sigma$  bond will be weaker than that of the other halogens due to the high electronegativity of fluorine, and the absence of any form of  $\text{M} \rightarrow \text{X}$  or  $\text{M} \leftarrow \text{X} \pi$  bonding.

For a considerable time there has been much discussion concerning the nature of the bonding of unsaturated molecules to transition metal complexes. Dewar's<sup>94</sup> original model has been modified by Chatt<sup>95</sup> to provide a  $\pi$  bonding scheme to explain the coordination of ethylene to platinum in Zeise's salt<sup>96</sup>.

For the dioxygen molecule (O-O bond length 1.12 Å) early schemes proposed electron transfer to the ligand, which assumed the characteristics of the superoxide ion  $O_2^-$  (bond length 1.28 Å) or the peroxide ion  $O_2^{2-}$  (bond length 1.49 Å) depending on the number of electrons transferred. This type of scheme seems applicable to amine complexes of Co(II), but the diamagnetism of such complexes as  $IrI(CO)(PPh_3)_2(O_2)$  with a bond length of 1.30 Å, which approximates to the superoxide ion, suggests this cannot be applied to such complexes.

In a recent discussion<sup>97</sup> of the bonding of molecular oxygen to transition metal complexes, the coordinated molecule was likened to the excited states of the dioxygen molecule. Similar arguments have been used by Orgel<sup>98</sup>, where the configuration and  $\overset{C-S}{\underset{|}{\text{bond}}}$  lengths in the complex  $Pt(\pi CS_2)(PPh_3)_2$ <sup>44</sup> were found to be very similar to its first excited state in the gas phase. However, Ibers and his co-workers<sup>99</sup> feel that the range of O-O bond lengths observed is too great to allow for a facile allocation of a different excited state to the dioxygen molecule in each complex.

The ligands in complexes of the type  $IrX(CO)L_2$  can exert a significant effect on the reactivity of these complexes towards the addition reactions of covalent or

unsaturated molecules, as a consequence of both steric and electronic effects.

It is well known that n-alkyl tertiary phosphine metal complexes undergo oxidative addition reactions more readily than the corresponding triphenylphosphine complexes<sup>100</sup>. Shaw has also shown that there is a good correlation between the basicity of complexes  $\text{IrX}(\text{CO})\text{L}_2$ , (  $\text{X} = \text{Cl} > \text{Br} > \text{I}$  ;  $\text{L} = \text{PMe}_3 > \text{AsPhMe}_2 > \text{PPhMe}_2 > \text{PPhEt}_2 > \text{PPh}_2\text{Me} > \text{AsPh}_3 > \text{PPh}_3$  ) towards benzoic or acetic acids and the tendency of such complexes to undergo oxidative addition reactions.<sup>101</sup> Crystallographic data has provided more direct evidence of this. A structure determination on the I:I dioxygen adduct of  $\text{IrCl}(\text{CO})(\text{O}_2)(\text{PPh}_2\text{Me})_2$  has shown a much longer bond length ( $1.461_4 \text{ \AA}$ )<sup>102</sup> compared to  $1.303_3 \text{ \AA}$ <sup>77</sup> for the reversible chloro complex and  $1.59_{26} \text{ \AA}$ <sup>78</sup> for the irreversible iodo complex; this complex reacts with oxygen reversibly.

Vaska<sup>103</sup>, in a study of oxygen addition to complexes of the type  $\text{IrCl}(\text{CO})(\text{PR}_3)_2$ , ( $\text{PR}_3 =$  tertiary phosphine), found that the stability constants for the formation of the I:I adduct increased with increasing basicity of the phosphine provided that the substituent R groups have comparable structures, but that the geometry of the groups exerted a profound effect on the dynamics of the reaction, which he attributed to steric effects. Similar arguments have been used by Shaw<sup>101</sup> to explain anomalies in the rates of addition of benzoic acid to complexes of the type  $\text{IrX}(\text{CO})\text{L}_3$ , ( $\text{L} =$  tertiary phosphine or arsine). Steric arguments such as these may also be invoked to explain the inability of the iridium cation  $[\text{IrL}_4]^+$  ( $\text{L} = \text{PPh}_2\text{Et}$ ) to react with dioxygen, while

the carbonyl derivative  $[\text{Ir}(\text{CO})\text{L}_3]^+$  readily forms an adduct.<sup>65</sup>

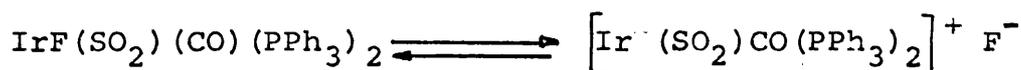
Shaw<sup>104</sup> has more recently shown that steric hindrance can greatly reduce the basicity of complexes of the type  $\text{IrCl}(\text{CO})\text{L}_2$ , eg. with  $\text{L} = \text{P}(\text{But}^t_2\text{R})_3$ , ( $\text{R} = n\text{-alkyl}$ ) there is no tendency to react with benzoic acid and even hydrochloric acid adds with difficulty. The basicity of the complexes falling in the order  $\text{PPhMe}_2 > \text{PBut}^t_2\text{Me}_2 > \text{PBut}^t_2\text{Et}_2 > \text{PBut}^t_2\text{Pr}^n_2 > \text{PBut}^t_2\text{Me} > \text{PBut}^t_2\text{Pr}^n > \text{PBut}^t_2\text{Et}$ .

A large reduction in the electron density at the iridium can be made by the formal replacement of the carbonyl group by the nitrosyl group  $\text{NO}^+$  generating the isoelectronic analogue of Vaska's complex  $[\text{IrCl}(\text{NO})(\text{PPh}_3)_2]^+$ <sup>105</sup>. This undergoes addition reactions with various donor molecules forming 5 coordinate cations such as  $[\text{IrCl}(\text{CO})(\text{NO})(\text{PPh}_3)_2]^+$  and reacts immediately with coordinating anions forming 5 coordinate nitrosyl complexes. This behaviour restricts a study and comparison of many other oxidative additions since many oxidants are potential sources of coordinating anions. However, the reduced electron density on the metal does reduce the complex's reactivity and there is no observed reaction with dioxygen, whereas the uncharged ruthenium analogue  $\text{RuCl}(\text{NO})(\text{O}_2)(\text{PPh}_3)_2$ <sup>107</sup> binds dioxygen irreversibly. The isoelectronic platinum complex  $[\text{PtCl}(\text{CO})(\text{PR}_3)_2]^+$ <sup>108</sup> ( $\text{R} = \text{Me}, \text{Ph}$ ) shows reduced reactivity<sup>109</sup> compared to Vaska's complex.

From the reaction of fluorocarbonylbis(triphenylphosphine)iridium(I) with sulphur dioxide, infrared data has inferred that a 5 coordinate I:I adduct is formed, but that other molecules of sulphur dioxide are 'associated'

with the complex. However in liquid sulphur dioxide a very strong carbonyl band appears at  $2050 \text{ cm}^{-1}$ , higher than that found for the normal adduct  $\text{IrF}(\text{CO})(\text{SO}_2)(\text{PPh}_3)_2$ , ( $2020 \text{ cm}^{-1}$ ). This band is not found in solutions of the fluoro complex saturated with sulphur dioxide and so we do not attribute it to a complex containing two sigma bonded sulphur dioxide molecules, although the small size of the fluoride ion compared to the other halogens could facilitate this.

The iridium fluorine bond has been shown to ionise in polar solvents<sup>22</sup> and this higher carbonyl frequency may be a result of such an ionisation.



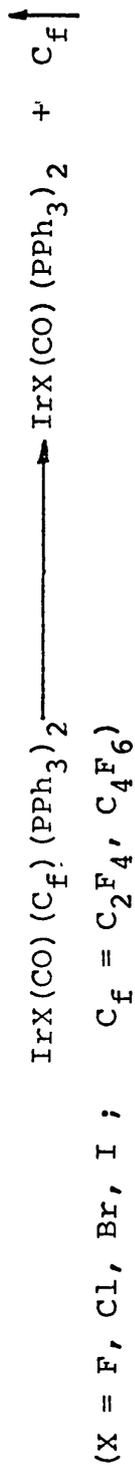
ionisation being facilitated by the 'other' molecules of sulphur dioxide which are presumably associated with the fluoride ion.

Adducts of sulphur dioxide with halide ions have been known since 1916<sup>110</sup> and their spectral and equilibrium properties well characterised<sup>111,112</sup>.

Ibers<sup>113</sup> et al. have recently shown from crystallographic data that a sulphur dioxide molecule is associated with a halide ion. The complex obtained from the reaction of  $\text{PtI}(\text{Me})(\text{PPh}_3)_2$  with  $\text{SO}_2$  does not have a Pt-S bond, but that the sulphur dioxide molecule is associated with the iodine atom. The I-S distance ( $3.39 \text{ \AA}$ ) is significantly shorter than the Van de Waals radii sum ( $3.80 \text{ \AA}$ )<sup>114</sup> but longer than their single bond covalent radii sum ( $2.37 \text{ \AA}$ ).

Ibers has also shown that the reaction of  $\text{IrI}(\text{CO})$

Heats of reaction for the pyrolysis of complexes of the type  $\text{IrX(CO)(C}_f\text{)(PPh}_3\text{)}_2$

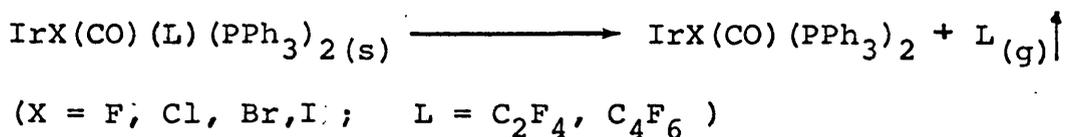


Fluorocarbon	Heat of reaction (k.cal.mole <sup>-1</sup> )			
	F	Cl	Br	I
Tetrafluoroethylene	79.4	67.2	41.0	57.2
Hexafluorobut-2-yne	99.2	95.7	78.6	82.4

$-(PPh_3)_2$  with sulphur dioxide yields a complex containing a  $SO_2$  molecule attached to the iodine as well as the iridium.

Sulphur dioxide uptake of ionic complexes of the type  $[Ir(P-P)_2]^+ X^-$ , ( $X = Cl, Br, I$ ) and other systems  $[R_4N]^+ X^-$ , ( $R = CH_3, C_4H_9, C_7H_{15}$ ), have shown to be related to both the charge and sign of the anion-cation system, i.e. to the dipole moment.<sup>88</sup> The ionic nature of the iridium-fluorine bond may well facilitate such an association.

The enthalpies of the dissociation reactions:-



show an unpredicted trend. Extrapolation of trends in stabilities for the adducts with dioxygen or dimethyl maleate<sup>115</sup>, where stabilities increase in the order  $I > Cl$  suggest that adducts of  $IrF(CO)(PPh_3)_2$  might be expected to be even less stable than those of the chloride.

However, our results indicate that this trend is reversed for the adducts with  $C_2F_4$  and  $C_4F_6$ . The reason for this may involve relative bonding effects of the halide ligands, or simply a closer approach of the coordinating molecule to the metal atom as a result of the smaller size of the fluorine atom.

Either or both of these factors can be used to explain the improved back donation from the iridium to the unsaturated molecule and for the differences in the chemistry of fluorocarbonylbis(triphenylphosphine)iridium(I) compared to its other halogen analogues.

## 2.4. EXPERIMENTAL.

- 2.4.1. Purification of reagents and preparation of precursors.
- 2.4.2. Synthesis of fluorocarbonylbis(triphenylphosphine)iridium(I).
- 2.4.3. Reactions of fluorocarbonylbis(triphenylphosphine)iridium(I).
  - 2.4.3.1. Halide exchange reactions with:-
    - 2.4.3.1.1. Lithium chloride.
    - 2.4.3.1.2. Lithium bromide.
    - 2.4.3.1.3. Lithium iodide.
  - 2.4.3.2. Halide displacement reactions.
  - 2.4.3.3. Oxidative addition reaction with:-
    - 2.4.3.3.1. Methyl iodide.
    - 2.4.3.3.2. Mercuric halides.
    - 2.4.3.3.3. Hydrogen chloride.
    - 2.4.3.3.4. Dioxygen.
    - 2.4.3.3.5. Sulphur dioxide.
    - 2.4.3.3.6. Tetrafluoroethylene.
    - 2.4.3.3.7. Hexafluorobut-2-yne.
    - 2.4.3.3.8. Tetracyanoethylene.
    - 2.4.3.3.9. 1,2 dicyanoethylene.
- 2.4.4. Synthesis of tetrafluoroethylene and hexafluorobut-2-yne adducts of  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$  (X = Br, I)
  - 2.4.4.1. Reaction of bromocarbonylbis(triphenylphosphine)iridium(I) with:
    - 2.4.4.1.1. Tetrafluoroethylene.
    - 2.4.4.1.2. Hexafluorobut-2-yne.

2.4.4.2. Reaction of iodocarbonylbis(triphenyl  
-phosphine)iridium(I) with :-

2.4.4.2.I Tetrafluoroethylene.

2.4.4.2.2. Heaxafluorbut-2-yne.

2.4.I. Unless otherwise stated chemicals were used without purification

Hydrated iridium trichloride was obtained on loan from Johnson Matthey.

Triphenylphosphine, a gift from Albright & Wilson, was recrystallised twice from ethanol under nitrogen.

Lithium bromide, lithium iodide, and sodium tetra-phenylborate from B.D.H.

Sodium iodide - Fisons.

Fumaronitrile - Fluka.

Lithium perchlorate - Hopkin & Williams.

Lithium tetrafluoroborate - Kodak.

Mercuric chloride and mercuric bromide from May & Baker.

Tetracyanoethylene - Ralph Emanuel.

Methyl iodide, from Koch Light, was washed with aqueous thiosulphate to remove traces of iodine, dried over calcium chloride and magnesium sulphate and distilled in a stream of dry nitrogen, taking the fraction boiling  $42-3^{\circ}\text{C}$ .

Sulphur dioxide - B.D.H.

Hexafluorobut-2-yne - Peninsular (Bristol Organics)

Tetrafluoroethylene was obtained by pyrolysis of polytetrafluoroethylene, (I.C.I.), under high vacuum.

AnalaR benzene was dried over sodium wire and distilled in a stream of dry nitrogen.

A standard solution of hydrochloric acid in ethanol was obtained by diluting the calculated volume of constant boiling point aqueous hydrochloric acid with ethanol. The normality was checked by titration with standard NaOH using phenolphthalein.

The silver fluoride solution was prepared by very careful addition of 10% (v/v) aqueous hydrofluoric acid

to a slurry of freshly prepared silver carbonate, (100 g - 363 m.mole.), in water, (25 mls), until nearly all of the solid had dissolved. The solution was then filtered and its volume reduced on a steam bath until signs of crystallisation were observed, approximately 5% of the volume of this solution of 40% aqueous hydrofluoric acid was then added and the solution allowed to cool to r.t. before storing in a polythene bottle. This solution, which is an approximately 14 M. solution of silver fluoride in dilute hydrofluoric acid, will, in contrast to solid silver fluoride, keep indefinitely.

62,116.

Chlorocarbonylbis(triphenylphosphine)iridium(I) and the corresponding iodo- and bromo- derivatives<sup>64</sup> were prepared by literature routes.

Analytical and spectroscopic specifications as for

I.4.I.

2.4.2. Synthesis of fluorocarbonylbis(triphenylphosphine)iridium(I).

A solution of saturated silver fluoride, (2 mls) was added to a solution of trans-chlorocarbonylbis(triphenylphosphine)iridium(I), (3.9 g. - 5 m.mole), in warm benzene, (300 mls), and the solution shaken vigorously for 2 mins. Precipitation of finely divided silver chloride, which rapidly darkens in light, occurs within a few seconds. The solution was filtered and the filtrate concentrated under reduced pressure at 40°C until signs of crystallisation occurred. Addition of 1:1 diethyl ether/ethanol, (100 mls) yielded a crop of fine bright yellow crystals which were filtered off washed with a few mls of EtOH and ether and dried under vacuo at 56°C. The compound was identified as fluorocarbonylbis(triphenylphosphine)iridium(I) from analytical and infrared data, (2.96 g. - 77%).

2.4.3. Reaction of fluorocarbonylbis(triphenylphosphine)iridium(I).

2.4.3.I. Halide exchange reactions.

2.4.3.I.I. Reaction with lithium chloride.

A solution of lithium chloride, (0.025 g. - 0.59 m.mole), in acetone, (10 mls), was added to a solution of fluorocarbonylbis(triphenylphosphine)iridium(I), (0.38 g. - 0.50 m.mole), in warm benzene, (30 mls), and the solution allowed to stand at r.t. for several hours. A white solid was deposited which was removed by centrifuging and identified as lithium fluoride. The filtrate was taken to dryness under reduced pressure and the yellow residue dissolved in

the minimum volume of warm benzene. Slow removal of the solvent from this filtered solution and addition of cold diethyl ether yielded a bright yellow crystalline solid which was identified as chlorocarbonylbis(triphenylphosphine)iridium(I), (0.38 g. - 100%), by comparison of the melting point and infrared spectra to that of an authentic sample.

2.4.3.I.2. Reaction with lithium bromide.

As for 2.4.3.I.I. using lithium bromide, (0.05 g. - 0.56 m.mole). The bright yellow solid was identified as bromocarbonylbis(triphenylphosphine)iridium(I) by comparison of the melting point and infrared spectra to that of an authentic sample, (0.39 g. - 95%).

2.4.3.I.3. Reaction with lithium iodide.

As for 2.4.3.I.I. using lithium iodide, (0.08 g. - 0.58 m.mole). The deep yellow solid was identified as iodocarbonylbis(triphenylphosphine)iridium(I) by comparison of the melting point and infrared spectra to that of an authentic sample, (0.37 g. - 85%).

2.4.3.2. Halide displacement reaction.

Synthesis of the carbonyltris(triphenylphosphine)iridium(I) cation.

Triphenylphosphine, (0.14 g. - 0.53 m.mole), was added to a stirred suspension of fluorocarbonylbis(triphenylphosphine)iridium(I), (0.39 g. - 0.50 m.mole), and lithium perchlorate, (0.056 g. - 0.51 m.mole) in methanol, (30 mls) and water, (2 mls), at room temperature producing a deep orange solution. This solution was stood overnight at 0°C to yield a crop of bright deep yellow-orange crystals.

These were filtered off and after washing with warm water very carefully recrystallised from dichloromethane/methanol in the presence of free triphenylphosphine. The compound was identified as carbonyltris(triphenylphosphine)iridium(I) perchlorate, (0.44 g. - 80%), from analytical and infrared data.

The tetraphenylborate salt, (0.58 g. - 87%), and tetrafluoroborate salt, (0.43 g. - 79%) were also prepared by a similar method using sodium tetraphenylborate, (0.17 g. - 0.51 m.mole) and lithium tetrafluoroborate, (0.05 g. - 0.53 m.mole).

#### 2.4.3.3. Oxidative addition reactions.

##### 2.4.3.3.I. Reaction with mercuric halides $HgX_2$ (X = Cl, Br)

A solution of mercuric chloride, (0.15 g. - 0.55 m.mole), in acetone, (5 mls), was added dropwise to a stirred solution of fluorocarbonylbis(triphenylphosphine)iridium(I), (0.39 g. - 0.50 m.mole), in benzene, (30 mls). The yellow colour faded instantly and a fine white crystalline solid deposited, (0.44 g). This was filtered off washed with a few mls of acetone, benzene and ether and dried under vacuo at 56°C. Analytical and spectral data indicated it to be a mixture of compounds; probably  $IrCl_2(HgCl)CO(PPh_3)_2$  and  $IrClF(HgCl)CO(PPh_3)_2$ .

A similar reaction was observed using mercuric bromide, (0.20 g. - 0.55 m.mole) yielding a white crystalline solid, (0.42 g.), which was also found to be a mixture.

##### 2.4.3.3.2. Reaction with methyl iodide.

A solution of methyl iodide, (1 ml.), in ether, (5 mls), was added dropwise to a stirred solution of fluorocarbonylbis(triphenylphosphine)iridium(I), (0.39 g. - 0.50 m.mole.), in benzene, (30 mls.). The yellow colour slowly faded and a small quantity of a very pale green-yellow solid was precipitated, the solution was concentrated under reduced pressure to yield a green-yellow solid. This was filtered off washed with a few mls of benzene and ether and dried in vacuo at 56°C. Analytical and spectral data indicated it to be a mixture of compounds.

#### 2.4.3.3.3. Reaction with hydrogen chloride.

An excess of a standardised solution of hydrogen chloride in methanol, (5mls. -  $10^{-3}$  M.l) was added dropwise to a stirred solution of fluorocarbonylbis(triphenylphosphine)iridium(I), (0.39 g. - 0.50 m.mole), in benzene, (50 mls.). The yellow colour faded instantly and a white crystalline solid deposited over several minutes. This was filtered off washed with a few mls of warm benzene and dried under vacuo at 56°C. The compound was identified as dichlorohydridocarbonylbis-(triphenylphosphine)iridium(III) by comparison with an authentic sample.

Reaction with the molar quantity of hydrogen chloride produced a solution that was still a pale yellow colour and the infrared spectrum of the product indicated a mixture of I:I adduct with hydrogen chloride and starting material.

#### 2.4.3.3.4. Reaction with dioxygen.

A stream of purified dry dioxygen was bubbled through a solution of fluorocarbonylbis(triphenylphos

-phine)iridium(I), (0.39 g. - 0.50 m.mole), in benzene, (50 mls.), at r.t. for several hours during which time the solution becomes paler and slightly cloudy. The solution was concentrated to a small volume under reduced pressure below room temperature in a stream of oxygen and induced to precipitate by the addition of cold diethyl ether. The resultant pink-yellow solid was filtered off and washed with a few mls of ether. Spectroscopic examination of the product showed it to be a mixture of an iridium(III) adduct with dioxygen and the starting material.

2.4.3.3.5. Reaction with sulphur dioxide.

Sulphur dioxide was bubbled through a solution of fluorocarbonylbis(triphenylphosphine)iridium(I), (0.39 g. - 0.50 m.mole), in benzene, (30 mls,) for 5 minutes at room temperature. The solution immediately changed colour producing a bright emerald green solution. On removing the solvent under reduced pressure the green colour partially faded and addition of diethyl ether to the concentrated solution yielded a yellow-green solid which was shown by infrared spectra to be a mixture of the starting material ( $\nu$  CO  $1945\text{ cm}^{-1}$ ) and the iridium(III) I:I adduct with sulphur dioxide ( $\nu$  CO  $2070\text{ cm}^{-1}$ ).

In an attempt to obtain the adduct pure, sulphur dioxide was bubbled through a stirred concentrated solution of the fluorocomplex for 10 minutes and the solvent removed overnight in a stream of nitrogen containing a few percent of sulphur dioxide. The residue thus obtained was examined by infrared spectroscopy and found to still contain some starting material together with 'associated' sulphur dioxide

molecules.

Finally, liquid sulphur dioxide (10 mls) was condensed onto solid fluorocarbonylbis(triphenylphosphine)iridium(I), (0.39 g - 0.5 m.mole) contained in a 25 ml conical flask fitted with a magnetic stirrer. The green solution was maintained in a carbon tetrachloride/liquid nitrogen slurry bath ( $-28^{\circ}\text{C}$ ) for an hour after which time it was allowed to slowly warm to  $0^{\circ}\text{C}$ ; the sulphur dioxide being removed in a slow stream of dry nitrogen. This left a bright green solid which showed no carbonyl band due to the starting material, but a carbonyl band at higher frequency than found for reactions in solution ( $2050\text{ cm}^{-1}$  as to  $2020\text{ cm}^{-1}$ ) and very strong absorptions due to the presence of associated sulphur dioxide molecules.

#### 2.4.3.3.6. Reaction with tetrafluoroethylene.

Tetrafluoroethylene, (1 ml.), was distilled into a Carius tube ( $-176^{\circ}\text{C}$ ) containing a suspension of fluorocarbonylbis(triphenylphosphine)iridium(I), (0.38 g. - 0.50 m.mole), in degassed benzene, (15 mls) and ether, (5 mls.). The tube was sealed under vacuum, and after allowing to warm to room temperature, shaken mechanically. The yellow colour rapidly faded and within an hour the solution was clear and colourless. Shaking for a further 36 hours yielded a white highly crystalline solid. The tube was opened and the solid after filtering off was washed with a few mls of warm benzene and recrystallised from warm acetone/EtOH. (Recrystallisation is however not necessary since the highly crystalline product obtained from the reaction is analytically and spectroscopically identical to the recrystallised sample)

The complex was identified by analytical, infrared and  $F^{19}$  N.M.R. spectra as fluorocarbonyl(tetra fluoroethylene)-bis(triphenylphosphine)iridium(III), (0.30 g. - 70%).

2.4.3.3.7. Reaction with hexafluorbut-2-yne.

As for 2.4.3.3.6. using hexafluorbut-2-yne, (1 ml.). The complex was identified by analytical, infrared and  $F^{19}$  N.M.R. spectra as fluorocarbonyl(hexafluorbut-2-yne)bis(triphenylphosphine)iridium(III), (0.38 g. - 76%).

2.4.3.3.8. Reaction with tetracyanoethylene.

A solution of tetracyanoethylene, (0.065 g. - 0.51 m.mole), in benzene, (10 mls.), was added to a solution of fluorocarbonylbis(triphenylphosphine)iridium(I), (0.39 g. - 0.50 m.mole), in benzene, (30 mls). The colour of both solutions was very rapidly discharged and after a few minutes a crop of silky very fine white needles was deposited. The solution was allowed to stand overnight and the solid filtered off, after washing several times with warm benzene the product was dried in vacuo at  $56^{\circ}\text{C}$ . The complex was identified as fluorocarbonyl(tetracyanoethylene)bis(triphenylphosphine)iridium(III) from analytical and infrared data, (0.32 g. - 71%).

2.4.3.3.9. Reaction with fumaronitrile.

As for 2.4.3.3.8. using excess fumaronitrile, (0.15 g. - 1.9 m.mole). Even after refluxing the solution for an hour it was still a pale yellow colour. After work up infrared spectra showed the product to be a mixture of a I:I adduct with fumaronitrile and unreacted starting material. Attempts to obtain the pure adduct by further reaction or recrystallisation failed.

2.4.4. Synthesis of tetrafluoroethylene and hexafluorobut-2-yne adducts of IrX(CO)(PPh<sub>3</sub>)<sub>2</sub>; (X = Br, I).

2.4.4.I. Reaction of bromocarbonylbis(triphenylphosphine)iridium(I) with:-

2.4.4.I.I. Tetrafluoroethylene.

Tetrafluoroethylene, (1 ml.), was distilled into a Carius tube (-176°) containing a suspension of bromocarbonylbis-(triphenylphosphine)iridium(I), (0.82 g. - 1 m.mole), in degassed benzene, (15 mls.), and ether, (5 mls.). The tube was sealed under vacuum and after allowing to warm to room temperature, shaken mechanically for 24 h, to yield a very pale yellow crystalline solid which was filtered off and after washing with a few mls of warm benzene and ether dried in air. The complex was identified by analytical and infrared data as bromocarbonyl(tetrafluoroethylene)bis(triphenylphosphine)-iridium(III), (0.60 g. - 65%).

2.4.4.I.2. Hexafluorobut-2-yne.

As for 2.4.4.I.I. using hexafluorobut-2-yne, (1 ml.). The complex was identified as bromocarbonyl(hexafluorobut-2-yne)-bis(triphenylphosphine)iridium(III), (0.70 g. - 72%), from analytical and infrared data.

2.4.4.2. Reactions of iodocarbonylbis(triphenylphosphine)iridium-(I) with:-

2.4.4.2.I Tetrafluoroethylene.

As for 2.4.4.I.I. using iodocarbonylbis(triphenylphosphine)iridium(I), (0.87 g. - 1 m.mole), the complex was identified as iodocarbonyl(tetrafluoroethylene)bis(triphenylphosphine)iridium(III), (0.68 g. - 68%) from analytical and infrared data.

2.4.4.2.2. Hexafluorobut-2-yne.

As for 2.4.4.I.I. using iodocarbonylbis(triphenylphosphine)iridium(I), (0.87 g. - 1 m.mole) and hexafluorobut-2-yne, (1 ml.). The complex was identified as iodocarbonyl(hexafluorobut-2-yne)bis(triphenylphosphine)iridium(III), (0.81 g - 78%), from analytical and infrared data.

2.5. APPENDICES.

Analytical Data.

Compound	Yield	Colour	M.Pt(°C)	C	H	F	Others
$\text{F}(\text{CO})(\text{C}_2\text{F}_4)(\text{PPh}_3)_2\text{Ir}$	83 %	white	dec 150°	53.14 (54.23)	3.85 (3.50)	10.97 (11.00)	
$\text{F}(\text{CO})(\text{C}_4\text{F}_6)(\text{PPh}_3)_2\text{Ir}$	78%	white	dec 140°	52.85 (53.19)	3.28 (3.27)	14.11 (14.37)	
$\text{F}(\text{CO})(\text{C}_6\text{N}_4)(\text{PPh}_3)_2\text{Ir}$	72%	white	300°	57.89 (57.91)	3.38 (3.39)	2.17 (2.13)	6.08 (6.24) N
$[\text{Co}(\text{PPh}_3)_3\text{Ir}]^+\text{BF}_4^-$	73%	deep yellow	210-214°	60.05 (60.39)	4.10 (4.15)	6.64 (6.95)	1.16 (1.0) B
$[\text{Co}(\text{PPh}_3)_3\text{Ir}]^+\text{ClO}_4^-$	68%	deep yellow	181-183°	59.20 (59.70)	4.16 (4.10)		4.02 (4.20) Cl
$[\text{Co}(\text{PPh}_3)_3\text{Ir}]^+\text{B}(\text{Ph})_4^-$	75%	deep yellow	141-142°	70.10 (71.54)	4.78 (4.94)		

(calculated values in parenthesis)

Analytical Data

Compound/reaction	C	H	F	Hal
$\text{Cl}_2(\text{HgCl})\text{CO}(\text{PPh}_3)_2\text{Ir}$	42.25	2.88	-	10.11
$\text{ClF}(\text{HgCl})\text{CO}(\text{PPh}_3)_2\text{Ir}$	42.93	2.92	1.84	6.85
Found for $\text{F}(\text{CO})(\text{PPh}_3)_2\text{Ir}/\text{HgCl}_2$	42.50	2.89	0.91	8.73
$\text{Br}_2(\text{HgBr})\text{CO}(\text{PPh}_3)_2\text{Ir}$	37.30	2.55	-	20.23
$\text{BrF}(\text{HgBr})\text{CO}(\text{PPh}_3)_2\text{Ir}$	39.36	2.69	1.69	14.22
Found for $\text{F}(\text{CO})(\text{PPh}_3)_2\text{Ir}/\text{HgBr}_2$	35.08	2.55	0.74	18.39
$\text{I}_2(\text{CO})\text{Me}(\text{PPh}_3)_2\text{Ir}$	45.03	3.28	-	25.04
$\text{F}(\text{I})\text{CO}(\text{Me})(\text{PPh}_3)_2\text{Ir}$	50.39	3.67	2.10	14.01
Found for $\text{F}(\text{CO})(\text{PPh}_3)_2\text{Ir}/\text{MeI}$	46.72	3.52	1.03	21.20
$\text{Cl}_2\text{H}(\text{CO})(\text{PPh}_3)_2\text{Ir}$	54.41	3.83	-	8.68
Found for $\text{F}(\text{CO})(\text{PPh}_3)_2\text{Ir}/\text{HCl}$	54.03	3.71	0.00	8.07

(calculated values in parenthesis)

Infra-red data.

Compound	$\nu(\text{C}\equiv\text{O}) \text{ cm}^{-1}$	Others ( $\text{cm}^{-1}$ )
$\text{F}(\text{CO})(\text{C}_2\text{F}_4)(\text{PPh}_3)_2\text{Ir}$	2028	1184, 1120, 1052 (C-F)
$\text{F}(\text{CO})(\text{C}_4\text{F}_6)(\text{PPh}_3)_2\text{Ir}$	2005	1800 (C≡C) 1220, 1130 (C-F)
$\text{F}(\text{CO})(\text{C}_6\text{N}_4)(\text{PPh}_3)_2\text{Ir}$	2034	2220 (C≡N)
$[\text{Co}(\text{PPh}_3)_3\text{Ir}]^+ \text{BF}_4^-$	1997 2007	1050 (B-F)
$[\text{Co}(\text{PPh}_3)_3\text{Ir}]^+ \text{ClO}_4^-$	2000 2008	1085 (Cl-O)
$\text{Br}(\text{CO})(\text{C}_2\text{F}_4)(\text{PPh}_3)_2\text{Ir}$	2035	1175, 1118, 1048 (C-F)
$\text{Br}(\text{CO})(\text{C}_4\text{F}_6)(\text{PPh}_3)_2\text{Ir}$	2013	1762 (C≡C) 1250, 1225 (C-F)
$\text{I}(\text{CO})(\text{C}_2\text{F}_4)(\text{PPh}_3)_2\text{Ir}$	2037	1185, 1125, 1115, 1044 (C-F)
$\text{I}(\text{CO})(\text{C}_4\text{F}_6)(\text{PPh}_3)_2\text{Ir}$	1997 2014	1767 (C≡C) 1245, 1235, 1230, (C-F)

	$T_i$	$T_p$	$T_f$	$T_f$ °K	Weight loss Found/(Calc)	$\Delta H$ (kJ.mol <sup>-1</sup> )	$E_a$ (kJ.mol <sup>-1</sup> )	Ln A
F(CO)(C <sub>4</sub> F <sub>6</sub> )(PPh <sub>3</sub> ) <sub>2</sub> Ir	410	480	500	500	17.5±0.147 % (17.5 %)	99.2±0.3	223.8±2.1	25.0
Cl(CO)(C <sub>4</sub> F <sub>6</sub> )(PPh <sub>3</sub> ) <sub>2</sub> Ir	355	430	450	450	18.1±0.7 % (17.19 %)	95.7±1.7	83.8±1.9	10.7
Br(CO)(C <sub>4</sub> F <sub>6</sub> )(PPh <sub>3</sub> ) <sub>2</sub> Ir	405	450	470	470	16.0±0.15 % (16.42 %)	78.6±0.5	131.8±2.9	15.3
I(CO)(C <sub>4</sub> F <sub>6</sub> )(PPh <sub>3</sub> ) <sub>2</sub> Ir	440	480	490	490	16.3±0.20 % (15.67 %)	82.4±1.3	***	*
F(CO)(C <sub>2</sub> F <sub>4</sub> )(PPh <sub>3</sub> ) <sub>2</sub> Ir	420	480	495	495	11.8±0.2 % (11.58 %)	79.4±1.9	142.2±2.5	15.8
Cl(CO)(C <sub>2</sub> F <sub>4</sub> )(PPh <sub>3</sub> ) <sub>2</sub> Ir	385	460	490	490	10.9±0.6 (11.36 %)	67.2±1.9	177.1±6.0	19.5
Br(CO)(C <sub>2</sub> F <sub>4</sub> )(PPh <sub>3</sub> ) <sub>2</sub> Ir	410	455	470	470	11.31±0.04 % (10.81 %)	41.0±0.7	***	*
I(CO)(C <sub>2</sub> F <sub>4</sub> )(PPh <sub>3</sub> ) <sub>2</sub> Ir	420	455	470	470	10.9±0.2	57.2±1.0	***	*

Thermochemical and kinetic data for the reaction:  $\text{IrX(CO)L(PPh}_3)_2\text{(s)} \longrightarrow \text{IrX(CO)(PPh}_3)_2\text{(s)} + \text{L(g)}$

CHAPTER THREE.

3.1. INTRODUCTION.

3.2. RESULTS AND DISCUSSION.

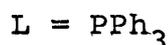
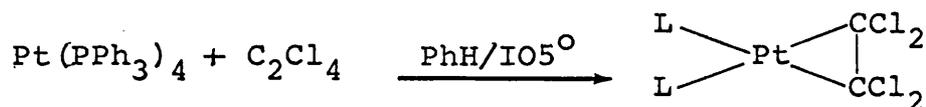
3.3. EXPERIMENTAL.

3.4. APPENDICES.

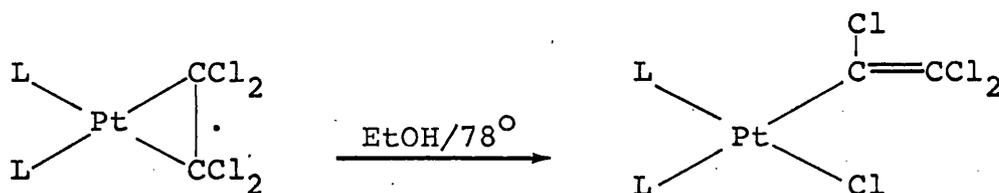
3.1. INTRODUCTION.

Platinum complexes of the type  $Pt(PPh_3)_2L$ , (L = olefin, acetylene)<sup>117-119</sup> are well known and crystal structure determinations for tetracyanoethylene<sup>120</sup> and diphenyl-acetylene<sup>121</sup> have shown the presence of a  $\pi$  bonded moiety.

However, more recent studies have shown that in the presence of hydroxylic solvents chloro and bromo olefin complexes readily isomerise to the corresponding vinyl complexes. Treatment of tetrakis(triphenylphosphine)platinum(0) with tetrachloroethylene in benzene at 105°C yields the olefin complex  $Pt(\pi-C_2Cl_4)(PPh_3)_2$ <sup>122,123</sup>,



however if this olefin complex is refluxed in ethanol rearrangement yields the perchlorovinyl complex  $PtCl(C_2Cl_3)(PPh_3)_2$ <sup>123</sup>



Studies on this isomerisation indicate that the reaction proceeds via an ionic intermediate  $[Pt(C_2Cl_3)(PPh_3)_2]^+$ <sup>124</sup>, the isomerisation of  $Pt(CHCl=CCl_2)(PPh_3)_2$  is more intramolecular however.<sup>125</sup>

This type of rearrangement had previously been observed<sup>126</sup> when the olefin complex  $Pt(CF_2=CFCl)(PPh_3)_2$  was

heated to just below its melting point to give the vinyl complex trans-Pt(Cl)(CF=CF<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>.

In the mechanism proposed for the polymerisation of monosubstituted acetylenes by Ni(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> an analogous rearrangement of the acetylene complex, Ni(π PhC≡CH)(PPh<sub>3</sub>)<sub>2</sub> to an acetylide, Ni(H)(C≡CPh)(PPh<sub>3</sub>)<sub>2</sub> has been suggested<sup>127</sup>.

Stone et al.<sup>128</sup> have reacted tetrakis(triphenylphosphine)platinum(0) with fluoroolefins to yield crystalline complexes of the type Pt(π-fluoroolefin)(PPh<sub>3</sub>)<sub>2</sub> (C<sub>f</sub> = C<sub>2</sub>F<sub>4</sub>, C<sub>2</sub>F<sub>3</sub>Cl, C<sub>2</sub>F<sub>3</sub>(CF<sub>3</sub>), C<sub>2</sub>F<sub>2</sub>CCl<sub>2</sub>, cyclo-C<sub>4</sub>F<sub>6</sub>, cyclo-C<sub>6</sub>F<sub>10</sub>, and CF<sub>2</sub>=CF-CF=CF<sub>2</sub>), similar reactions occurred using tetrakis(methyldiphenylphosphine)platinum(0) and C<sub>2</sub>F<sub>3</sub>X (X = Cl, Br). In refluxing n-butanol the olefin complexes Pt(π-C<sub>2</sub>F<sub>3</sub>X)(PPh<sub>2</sub>R)<sub>2</sub>, (X = Cl, Br; R = Me, Ph) rearrange to yield the trans vinyl complexes trans-Pt(X)(C<sub>2</sub>F<sub>3</sub>)(PPh<sub>2</sub>R)<sub>2</sub>.

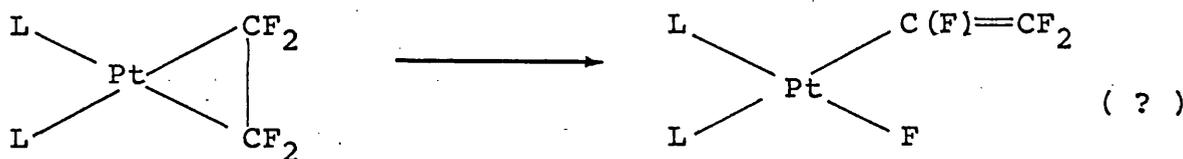
Further studies have shown that:-

(i) The rate of isomerisation has been shown to be enhanced by more basic phosphines; eg Pt(C<sub>2</sub>F<sub>3</sub>X)(PPh<sub>2</sub>Me) will vinylise in ethanol at room temperature (X = Cl, Br)<sup>129,130</sup>.

(ii) Bromoolefins vinylise more readily than the corresponding chloroolefins<sup>129</sup>.

(iii) Palladium(0) and nickel(0) form vinyls more readily than platinum<sup>130,131</sup>.

If such a reaction could be induced for a π bonded tetrafluoroethylene this would provide a route into vinyl complexes containing metal-fluorine bonds.



This reaction is not observed for the triphenylphosphine complex in boiling ethanol or n-butanol.

We thus decided to investigate a similar reaction for the triphenylarsine complex to establish the effect of  $\text{AsPh}_3$  in relation to the other donor ligands in this reaction.

The triphenylarsine olefin complexes can be obtained by the reaction of the olefin with tetrakis(triphenylarsine)platinum(0); but since it has recently been shown<sup>132</sup> that both thermal and photochemical reactions of carbonatobis(triphenylarsine)platinum(II) in alcoholic solvents provides a convenient source of bis(triphenylarsine)platinum(0) we therefore decided to investigate the usefulness of this system for the synthesis of zerovalent platinum halo-olefin complexes. The main advantage being the very 'clean' nature of this source of bis(triphenylarsine)platinum(0).

### 3.2. RESULTS AND DISCUSSION.

Tetrafluoroethylene, hexafluoropropene, trifluoroethylene, tetracyanoethylene and hexafluorobut-2-yne readily react with an ethanolic suspension of carbonatobis(triphenylarsine)platinum(II) at  $40^\circ\text{C}$  to give high yields of the appropriate olefin complexes  $\text{Pt}(\pi\text{-olefin})(\text{AsPh}_3)_2$  and  $\text{Pt}(\text{CF}_3\text{C}\equiv\text{CCF}_3)(\text{AsPh}_3)_2$  which are identical to the complexes previously prepared via tetrakis(triphenylarsine)platinum(0). However, whilst both chlorotrifluoroethylene and bromotrifluoroethylene react with  $\text{Pt}(\text{AsPh}_3)_4$  in benzene at room temperature to produce olefin complexes,  $\text{Pt}(\text{C}_2\text{F}_3\text{X})(\text{AsPh}_3)_2$ , ( $\text{X} = \text{Cl}$ <sup>133</sup>, Br), the reaction of these olefins with  $\text{Pt}(\text{CO}_3)(\text{AsPh}_3)_2$  in ethanol at  $40^\circ\text{C}$  gives vinyl complexes  $\text{PtX}(\text{CF}=\text{CF}_2)(\text{AsPh}_3)_2$  which are readily characterised

by the appearance of the C=C stretching vibration of the tri-fluorovinyl ligand in their infrared spectra as well as a platinum-chlorine stretching vibration in the product when X = Cl.

The reaction of both chlorotrifluoroethylene and bromotrifluoroethylene with the carbonate complex could involve an ionic intermediate,  $(\text{Ph}_3\text{As})_2\text{Pt}^+\text{CF}(\text{X})\text{---CF}_2^-$ , prior to the formation of the vinyl complex as has been suggested for some analogous systems<sup>134</sup>. Alternatively intermediate olefins could be formed which subsequently undergo a vinyl rearrangement in the solvent ethanol<sup>124,128</sup>. Some evidence for this latter scheme is provided by the observation that both  $\text{Pt}(\text{CF}_2=\text{CFCl})(\text{AsPh}_3)_2$  and  $\text{Pt}(\text{CF}_2=\text{CFBr})(\text{AsPh}_3)_2$  give the corresponding vinyl complexes when suspended in ethanol at 40°C. Further since we also find that the reaction of tetrakis(triphenylarsine)platinum(0) with either chloro- or bromotrifluoroethylene in benzene solutions at 40°C gives only vinyl complexes whereas it is known that the corresponding reactions with tetrakis(triphenylphosphine)platinum(0) give olefin complexes<sup>128</sup> it is clear that the triphenylarsine ligands enhance this vinyl rearrangement. In other investigations it has been shown that  $\text{Pt}(\text{CF}_2=\text{CFBr})(\text{PPh}_2\text{Me})$  undergoes rearrangement to the vinyl complex more readily than  $\text{Pt}(\text{CF}_2=\text{CFBr})(\text{PPh}_3)_2$ <sup>129</sup>.

In some previous studies<sup>123</sup> we have shown that tetrachloroethylene reacts with  $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$  to produce the olefin complex,  $\text{Pt}(\text{Cl}_2\text{C}=\text{CCl}_2)(\text{PPh}_3)_2$ . However the analogous reaction with  $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{AsPh}_3)_2$  in benzene at room temperature gives the vinyl  $\text{Pt}(\text{Cl})(\text{CCl}=\text{CCl}_2)(\text{AsPh}_3)_2$ . In view of these findings it is therefore not surprising that the tetrachloroethylene reacts with  $\text{Pt}(\text{CO}_3)(\text{AsPh}_3)_2$  in ethanol at 40°C

to give  $\text{PtCl}(\text{CCl}=\text{CCl}_2)(\text{AsPh}_3)_2$ . The corresponding reactions with tetrabromoethylene and tetraiodoethylene give the dihalo complexes,  $\text{PtX}_2(\text{AsPh}_3)_2$ .

Although triphenylarsine enhances the olefin-vinyl rearrangement it is noteworthy that we have obtained no evidence for the isomerisation of the tetrafluoroethylene complex,  $\text{Pt}(\text{C}_2\text{F}_4)(\text{AsPh}_3)_2$ , to the vinyl complex, even in boiling butanol. The high strength of the carbon-fluorine bond presumably inhibits this rearrangement. Treatment of  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$  with lithium iodide in benzene/ethanol at  $95^\circ\text{C}$  does produce a vinyl complex,  $\text{PtI}(\text{CF}=\text{CF}_2)(\text{PPh}_3)_2$ , ( $\text{C}=\text{C} = 1735 \text{ cm}^{-1}$ ), since the high lattice energy of lithium fluoride formed provides a driving force for the reaction; however, below  $95^\circ\text{C}$  a mixture of  $\text{Pt}(\text{C}_2\text{F}_4)(\text{PPh}_3)_2$  and  $\text{PtI}(\text{CF}=\text{CF}_2)(\text{PPh}_3)_2$  is obtained<sup>135</sup>.

### 3.3. EXPERIMENTAL

- 3.3.1. Synthesis of reagents and preparation of precursors.
- 3.3.2. Synthesis of carbonatobis(triphenylarsine)-platinum(II).
- 3.3.3. Reactions of carbonatobis(triphenylarsine)-platinum(II) with :-
  - 3.3.3.1. Tetrafluoroethylene.
  - 3.3.3.2. Trifluoroethylene.
  - 3.3.3.3. Hexafluoropropene.
  - 3.3.3.4. Tetracyanoethylene.
  - 3.3.3.5. Chlorotrifluoroethylene.
  - 3.3.3.6. Bromotrifluoroethylene.
  - 3.3.3.7. Tetrachloroethylene.
  - 3.3.3.8. Tetrabromoethylene.
  - 3.3.3.9. Tertraiodoethylene.
  - 3.3.3.10. Diphenylacetylene.
  - 3.3.3.11. Hexafluorobut-2-yne.
  - 3.3.3.12. Fumaronitrile.
  - 3.3.3.13. 1,2-difluoroethylene.
- 3.3.4. Reaction of tetrakis(triphenylarsine)platinum(0) with :-
  - 3.3.4.1. Chlorotrifluoroethylene.
  - 3.3.4.2. Bromotrifluoroethylene.

3.3.5. Isomerisation of the olefin complexes  $\text{Pt}(\text{C}_2\text{F}_3\text{X})$   
 $-(\text{AsPh}_3)_2$ :-

3.3.5.1. X = Cl. (Chlorotrifluoroethylene)

3.3.5.2. X = Br (Bromotrifluoroethylene)

3.3.6. Reactions of  $\text{Pt}(\text{AsPh}_3)_2$  (Tolan) with:-

3.3.6.1. Tetrachloroethylene.

3.3.6.2. Tetracyanoethylene.

3.3.7. Attempted vinylisation of tetrafluoroethylene complexes.

3.3.7.1. Tetrafluoroethylenebis (triphenylphosphine)platinum(0).

3.3.7.2. Tetrafluoroethylenebis (triphenylarsine)platinum(0).

3.3.I. Unless otherwise stated chemicals were used without further purification.

Potassium chloroplatinite was obtained on loan from Johnson Matthey; aqueous solutions were filtered to remove traces of chloroplatinate before use.

Triphenylarsine and tetracyanoethylene from Ralph Emanuel.

Fumaronitrile - Fluka.

Diphenylacetylene - Koch Light.

Tetrabromoethylene and tetraiodoethylene from K & K Laboratories.

Tetrachloroethylene - Kodak.

Bromotrifluoroethylene and chlorotrifluoroethylene from Matheson Co.

Hexafluoropropene and hexafluorobut-2-yne from Peninsular Chemicals (Bristol Organics).

1,2-difluoroethylene, trifluoroethylene and tri-fluoroacetonitrile from Pierce Chemical Co.

Tetrafluoroethylene was prepared by the pyrolysis of polytetrafluoroethylene (I.C.I.) under high vacuum

Ethanol was redistilled in a stream of dry nitrogen.

Dichlorobis(triphenylarsine)platinum(II) and tetra-kis(triphenylphosphine)platinum(0) were prepared by literature routes<sup>136</sup>.

Spectroscopic and analytical specifications as for

1.4.1.

### 3.3.2. Preparation of carbonatobis(triphenylarsine)platinum(0).

A solution of cis-dichlorobis(triphenylarsine)platinum(II), (0.88 g. - 1 m.mole), in methylene chloride, (50 mls.), was shaken at room temperature with an excess of freshly prepared silver carbonate, (2.0 g. - 9 m.mole). After 2h. the deep yellow solution had become colourless and the precipitated silver chloride and excess silver carbonate were filtered off. The filtrate was evaporated under reduced pressure until the complex just began to crystallise. Diethyl ether, (100 mls.) was then added slowly to the vigorously shaken solution to give white crystals of carbonatobis(triphenylarsine)-platinum(II), (0.82 g. - 95%), identified by analytical and infrared data.

### 3.3.3. Reactions of carbonatobis(triphenylarsine)platinum(II).

#### 3.3.3.I. Reaction with tetrafluoroethylene.

Tetrafluoroethylene, (1 ml.), was condensed ( $-196^{\circ}$ ) into a Carius tube containing a suspension of carbonatobis(triphenylarsine)platinum(II), (0.89 g. - 1.0 m.mole), in degassed ethanol, (20 ml.). After mechanical shaking of the tube at  $40^{\circ}$  for 2 days the colourless crystals which had been deposited were collected and washed with methanol (3 x 5 ml.). The product was identified as tetrafluoroethylenebis(triphenylarsine)-platinum(0), (0.85 g. - 94%), by comparison of its infrared and  $F^{19}$  spectra with that of an authentic sample.

#### 3.3.3.2. Reaction with trifluoroethylene.

As for 3.3.3.I. using trifluoroethylene, (1 ml.), which gave after 3 h. ; trifluoroethylenebis(triphenylarsine)

-platinum(0),  $\text{Pt}(\text{CF}_2=\text{CFH})(\text{AsPh}_3)_2$ , (70%).

3.3.3.3. Reaction with hexafluoropropene.

As for 3.3.3.I. using hexafluoropropene, (1 ml.) which gave after 2 days; hexafluoropropenebis(triphenylarsine)-platinum(0),  $\text{Pt}(\text{CF}_2=\text{CFCF}_3)(\text{AsPh}_3)_2$ , (95%).

3.3.3.4. Reaction with tetracyanoethylene.

Tetracyanoethylene, (0.13 g. - 1 m.mole), was shaken in a Carius tube at  $40^\circ$  with a suspension of carbonato-bis(triphenylarsine)platinum(II), (0.89 g. - 1 m.ole), in degassed ethanol, (20 mls.), for 2 days. The bright white crystals that were deposited were filtered off and after washing with methanol (3 x 5 ml.) dried in vacuo at  $56^\circ$ . The product was identified as tetracyanoethylenebis(triphenylarsine)platinum(0),  $\text{Pt}\{(\text{CN})_2\text{C}=\text{C}(\text{CN})_2\}(\text{AsPh}_3)_2$ , (0.96 g. - 90%), from infrared and analytical data.

3.3.3.5. Reaction with chlorotrifluoroethylene.

As for 3.3.3.I. using chlorotrifluoroethylene, (1 ml), which gave after 18 h. the vinyl complex  $\text{PtCl}(\text{CF}=\text{CF}_2)(\text{AsPh}_3)_2$ , (74%).

3.3.3.6. Reaction with bromotrifluoroethylene.

As for 3.3.3.I. using bromotrifluoroethylene, (1 ml), which gave after 12 h. the vinyl complex  $\text{PtBr}(\text{CF}=\text{CF}_2)(\text{AsPh}_3)_2$ , (72%).

3.3.3.7. Reaction with tetrachloroethylene.

As for 3.3.3.4. using tetrachloroethylene, (1 ml), which gave after 18 h. sandy yellow crystals of the vinyl complex  $\text{PtCl}(\text{CCl}=\text{CCl}_2)(\text{AsPh}_3)_2$ , (63%).

3.3.3.8. Reaction with tetrabromoethylene.

As for 3.3.3.4. using tetrabromoethylene, (0.35 g. - 1 m.mole), which gave after 2 days dibromobis(triphenylarsine)-platinum(II),  $\text{PtBr}_2(\text{AsPh}_3)_2$ , (100%).

3.3.3.9. Reaction with tetraiodoethylene.

As for 3.3.3.4. using tetrabromoethylene, (0.54 g. - 1 m.mole), which gave after 2 days diiodobis(triphenylarsine)-platinum(II),  $\text{PtI}_2(\text{AsPh}_3)_2$ , (100%).

3.3.3.I0. Reaction with diphenylacetylene.

As for 3.3.3.4. using tolan, (0.18 g. - 1 m.mole) which after 2 days gave diphenylacetylenebis(triphenylarsine)-platinum(0),  $\text{Pt}(\text{tolan})(\text{AsPh}_3)_2$ , (68%).

3.3.3.II. Reaction with hexafluorobut-2-yne.

As for 3.3.3.I. using hexafluorobut-2-yne, (1 ml.), which after 18 h. gave hexafluorobut-2-ynebis(triphenylarsine)-platinum(0),  $\text{Pt} \{ (\text{CF}_3)\text{C}\equiv\text{C}(\text{CF}_3) \} (\text{AsPh}_3)_2$ , (92%).

3.3.3.I2. Reaction with fumaronitrile.

As for 3.3.3.4. using fumaronitrile, (0.1 g. -1.25 m.mole), The contents of the tube became a very dark brown within a few hours and no pure products could be isolated.

3.3.3.I3. Reaction with 1,2-difluoroethylene.

As for 3.3.3.I. using 1,2-difluoroethylene, (1 ml). The contents of the tube became a very dark brown within an hour and no pure product could be isolated; even at r.t. a dark brown solution was produced with 3 hours.

3.3.4. Reactions of tetrakis(triphenylarsine)platinum(0)

3.3.4.I. With chlorotrifluoroethylene.

Synthesis of the olefin complex  $\text{Pt}(\text{C}_2\text{F}_2\text{Cl})(\text{AsPh}_3)_2$

Chlorotrifluoroethylene, (1 ml.), was condensed ( $-196^\circ$ ) into a Carius tube containing a suspension of tetrakis(triphenylarsine)platinum(0), (0.72 g. - 0.5 m.mole) in degassed benzene, (20 mls.). After shaking the tube for 3 hours at room temperature the solution was filtered to remove a small deposit of platinum metal and the filtrate evaporated to dryness under reduced pressure at room temperature. The white residue was dissolved in methylene chloride, (10 mls.), and diethyl ether, (10 mls.) added. Dropwise addition of petrol (b.pt. 60-80) with vigorous shaking yielded a highly crystalline white solid. This was filtered off and afterwashing with diethyl ether dried in vacuo at r.t. The compound was identified as chlorotrifluoroethylenebis(triphenylarsine)platinum(0),  $(\text{C}_2\text{F}_3\text{Cl})(\text{AsPh}_3)_2\text{Pt}$  (0.33 g. - 72%), from infrared and analytical data.

3.3.4.2. With bromotrifluoroethylene.

Synthesis of the olefin complex  $\text{Pt}(\text{C}_2\text{F}_3\text{Br})(\text{AsPh}_3)_2$

As for 3.3.4.I. using bromotrifluoroethylene, (1 ml.) to yield bromotrifluoroethylenebis(triphenylarsine)platinum(0),  $(\text{C}_2\text{F}_3\text{Br})(\text{AsPh}_3)_2\text{Pt}$ , (0.28 g. - 58%) .

3.3.5. Isomerisation of the olefin complexes  $\text{Pt}(\text{C}_2\text{F}_3\text{X})(\text{AsPh}_3)_2$  ( X = Cl, Br).

A suspension of the olefin complex  $\text{Pt}(\text{C}_2\text{F}_3\text{X})(\text{AsPh}_3)_2$ , (0.5 m.mole), (25 mls.) was shaken occasionally and maintained at  $40^\circ$  for several days. During this time the crystal form of the complex was observed to change and very long needle like

crystals were deposited. These were filtered off and after washing with a few mls of ether dried in vacuo at r.t. Infra-red spectra indicated complete conversion to the corresponding vinyl complex by the appearance of a very strong C=C stretching vibration of the trifluorovinyl ligand and, for the chloro-olefin, a platinum-chlorine stretching vibration.

### 3.3.6. Reaction of Pt(tolan)(AsPh<sub>3</sub>)<sub>2</sub>

#### 3.3.6.I. Reaction with tetrachloroethylene.

Tetrachloroethylene, (1 ml.) was added to a solution of diphenylacetylenebis(triphenylarsine)platinum(0), (0.49 g. - 0.5 m.mole), in ether, (35 mls). The pale yellow solution was allowed to stand at r.t. for several hours and the solvent then removed under reduced pressure to leave a yellow oil. This was recrystallised from dichloromethane/ether-petrol to give a white highly crystalline solid, which after washing with a few mls of ether was dried in vacuo at r.t. The complex was identified as the chloro-vinyl complex, Pt(Cl)(C<sub>2</sub>F<sub>3</sub>)(AsPh<sub>3</sub>)<sub>2</sub>, (0.27 g. - 55%) by comparison of the melting point and infra-red spectra with an authentic sample.

#### 3.3.6.2. Reaction with tetracyanoethylene.

Tetracyanoethylene, (0.07 g. - 0.5 m.mole), in benzene, (5 mls.), was added to a solution of diphenylacetylene bis(triphenylarsine)platinum(0), (0.49 g. - 0.5 m.mole), in ether, (35 mls.). The colour of both solutions was very rapidly discharged and within a few minutes a crop of very fine colourless crystals was deposited. These were filtered off, and after washing with a few mls of ether dried in vacuo.

The complex was identified as tetracyanoethylenebis(triphenyl-arsine)platinum(0),  $\{(CN)_2C=C(CN)_2\}(AsPh_3)_2Pt$ , (0.43 g.- 92%), by comparison of melting point and infrared spectra with an authentic sample.

3.3.7. Attempted vinylisation of tetrafluoroethylene complexes.

3.3.7.I. Tetrafluoroethylenebis(triphenylphosphine)platinum(0).

Tetrafluoroethylenebis(triphenylphosphine)platinum(0), (0.20 g. - 0.25 m.mole), was refluxed in ethanol for eight hours. The product was filtered off and examined by infrared spectroscopy, and found to be the starting material. There was no evidence for the presence of any vinyl complex.

The reaction was repeated using n-butanol (b.pt. 117°) but vinylisation was still not observed, and the starting material isolated.

3.3.7.2. Tetrafluoroethylenebis(triphenylarsine)platinum(0)

Tetrafluoroethylenebis(triphenylarsine)platinum(0) (0.23 g. - 0.25 m.mole) was refluxed for 8-10 h. in both ethanol and n-butanol, however, no evidence was found for the presence of the vinyl complex in either reaction; and the starting material was isolated in both cases.

3.4. APPENDICES.

Analytical data.

Compound	Colour	Yield	M.Pt (°C)	C	H	F	Others
(C <sub>2</sub> F <sub>4</sub> ) (AsPh <sub>3</sub> ) <sub>2</sub> Pt	white	95%		50.14 (50.29)	3.35 (3.33)	8.11 (8.39)	
(C <sub>2</sub> HF <sub>3</sub> ) (AsPh <sub>3</sub> ) <sub>2</sub> Pt	white	70%	142 - 143°	51.29 (51.31)	3.62 (3.52)	6.21 (6.41)	
(C <sub>3</sub> F <sub>6</sub> ) (AsPh <sub>3</sub> ) <sub>2</sub> Pt	white	95%	188 - 191°	*			
(TCNE) (AsPh <sub>3</sub> ) <sub>2</sub> Pt	white	90%	300°	52.76 (53.92)	3.61 (3.63)		5.29 (N) (5.99)
Cl (CF:CF <sub>2</sub> ) (AsPh <sub>3</sub> ) <sub>2</sub> Pt	white	74%	217 - 218°	49.87 (49.40)	3.42 (3.27)	6.45 (6.17)	3.90 (Cl) (3.84)
Br (CF:CF <sub>2</sub> ) (AsPh <sub>3</sub> ) <sub>2</sub> Pt	white	72%	229 - 230°	47.00 (47.1)	3.1 (3.1)	8.4 (8.3)	5.8 (Br) (5.9)
Cl (CCl:CCl <sub>2</sub> ) (AsPh <sub>3</sub> ) <sub>2</sub> Pt	sandy yellow	63%	156 - 158°	46.7 (46.9)	3.2 (3.1)		14.4 (Cl) (14.6)
Br <sub>2</sub> (AsPh <sub>3</sub> ) <sub>2</sub> Pt	orange	100%	300°	43.9 (44.7)	3.1 (3.1)		16.9 (Br) (17.8)

\* compared with spectra and melting point of an authentic sample.

(calculated values in parenthesis)

Analytical data.

Compound	Colour	Yield	M. Pt (°C)	C	H	F	Others
$I_2 (AsPh_3)_2 Pt$	sandy orange	100%	300°				
$(C_4F_6) (AsPh_3)_2 Pt$	white	92%		49.56 (49.55)	3.23 (3.12)	11.53 (11.76)	
$(tolan) (AsPh_3)_2 Pt$	sandy yellow	68%	160 - 162°	59.80 (60.92)	4.06 (4.09)		
$(\pi-C_2BrF_3) (AsPh_3)_2 Pt$	white	58%	(160°) 230 dec.	46.9 (47.1)	3.1 (3.1)	5.8 (5.9)	8.3 (8.4)
$(\pi-C_2ClF_3) (AsPh_3)_2 Pt$	white	72%		*			

\* compared with spectra and melting point of an authentic sample.

(calculated values in parenthesis).

## CHAPTER FOUR.

4.1. INTRODUCTION.

4.2. RESULTS AND DISCUSSION.

4.3. EXPERIMENTAL.

4.4 APPENDICES.

#### 4.1. INTRODUCTION.

As part of our study of phosphine complexes of the platinum group metals, containing metal fluorine bonds, we have found that one of the most convenient routes to such complexes is halide exchange on square planar complexes of the type  $MCl(CO)(PPh_3)_2$ , ( $M = Rh, Ir$ ).

We thus decided to investigate new synthetic routes to series of such complexes.

#### 4.2. RESULTS AND DISCUSSION.

We have found that the reaction of hydrogen chloride or bromide with square planar rhodium(I) complexes  $Rh(acac)(CO)L$ , ( $L = PPh_3, AsPh_3$ ) yields halogen bridged dimers  $[RhX(CO)L]_2$ , ( $X = Cl, Br$ ). Similar reactions using hydrogen fluoride are, however, unsuccessful.

These complexes are readily cleaved by donor ligands  $L'$ , to give mixed ligand complexes  $RhX(CO)LL'$  ( $L' = PPh_3, AsPh_3, SbPh_3, P(OPh)_3$ )

The reaction of triphenylphosphine with  $[RhCl(CO)_2]_2$  was thought to initially involve halogen bridge cleavage<sup>137</sup>, further studies<sup>138-9</sup>, have shown that the first step in the reaction involves carbonyl displacement to give the halogen bridged dimer,  $[RhCl(CO)(PPh_3)]_2$ .

The halogen bridged dimers,  $[RhX(CO)L]_2$ , ( $X = Cl, Br$ ;  $L = PPh_3, AsPh_3$ ) exhibit one strong carbonyl stretching frequency, but in the absence of dipole moment data it is not possible to assign either cis- or trans- structures to these complexes. In the region  $400-200\text{ cm}^{-1}$  the chloro complex

shows two strong bands in the range  $260-300\text{ cm}^{-1}$  which are absent from the spectra of the corresponding bromides and hence can be assigned to rhodium - chlorine stretching frequencies.

The dimeric halogen bridged complexes  $[\text{RhCl}(\text{CO})_2]_2$ <sup>140</sup>,  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ <sup>141</sup> and  $(1,5\text{COD})\text{RhCl}_2\text{Rh}\{\text{P}(\text{OPh})_3\}_2$ <sup>142</sup> have been shown by X-ray studies to contain a bent  $\text{RhCl}_2\text{Rh}$  unit  $\text{C}_{2v}$  symmetry whereas in  $[\text{RhCl}(1,5\text{COD})]_2$ <sup>143</sup> a planar  $\text{RhCl}_2\text{Rh}$  unit  $\text{D}_{2h}$  symmetry is present. Infrared studies on these types of complexes have shown that the spectra obtained do not always distinguish a bent  $\text{RhCl}_2\text{Rh}$  unit from a planar arrangement<sup>144</sup>. Consequently although only two rhodium-chlorine stretching frequencies are observed for the complexes  $[\text{RhCl}(\text{CO})\text{L}]_2$ , ( $\text{L} = \text{PPh}_3, \text{AsPh}_3$ ), which would be consistent with a planar arrangement, the present data does not preclude a bent  $\text{RhCl}_2\text{Rh}$  unit.

The precursors for the halogen bridged complexes  $\text{Rh}(\text{acac})(\text{CO})\text{L}$  have previously been prepared by the action of the ligand  $\text{L}$  on  $\text{Rh}(\text{acac})(\text{CO})_2$ <sup>145</sup>. However, during the course of our studies, we have found that the phosphine complex,  $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ , can also be prepared by the action of carbon monoxide upon  $\text{Rh}(\text{acac})(\text{PPh}_3)_2$ <sup>146</sup>.

The mixed ligand complexes are formulated with a trans- configuration since their carbonyl and halogen stretching frequencies are very similar to those found in the adducts trans- $\text{RhX}(\text{CO})(\text{PPh}_3)_2$ <sup>144,147</sup>.

Recently, it has also been independently reported that the chlorine bridge in di- $\mu$ -chlorodicarbonyl-bis(triphenylphosphine)dirhodium(I) is cleaved by donor ligands<sup>139</sup>.

### 4.3. EXPERIMENTAL.

4.3.I. Purification of reagents and preparation of precursors.

4.3.2. Synthesis of the halogen bridged complexes  $[\text{RhX}(\text{CO})\text{L}]_2$

4.3.2.I. Di- $\mu$ -chlorodicarbonylbis(triphenylphosphine)dirhodium(I).

4.3.2.2. Di- $\mu$ -chlorodicarbonylbis(triphenylarsine)dirhodium(I).

4.3.2.3. Di- $\mu$ -bromodicarbonylbis(triphenylphosphine)dirhodium(I).

4.3.2.4. Di- $\mu$ -bromodicarbonylbis(triphenylarsine)dirhodium(I).

4.3.3. Synthesis of the mixed ligand complexes  $\text{RhX}(\text{CO})\text{LL}'$  by cleavage of the halogen bridged dimers  $[\text{RhX}(\text{CO})\text{L}]_2$ .

4.3.3.I. Reactions of di- $\mu$ -chlorodicarbonylbis(triphenylphosphine)dirhodium(I) with:-

4.3.3.I.I. Triphenylphosphine.

4.3.3.I.2. Triphenylarsine.

4.3.3.I.3. Triphenylstibine.

4.3.3.I.4. Triphenylphosphite.

4.3.3.2. Reactions of di- $\mu$ -chlorodicarbonylbis(triphenylarsine)dirhodium(I) with:-

4.3.3.2.I. Triphenylarsine.

4.3.3.2.2. Triphenylstibine.

4.3.3.2.3. Triphenylphosphite.

4.3.3.3. Reaction of di- $\mu$ -bromodicarbonylbis(triphenylphosphine)dirhodium(I) with:-

4.3.3.3.I. Triphenylphosphine.

4.3.3.3.2. Triphenylarsine.

4.3.3.3.3. Triphenylstibine.

4.3.3.3.4. Triphenylphosphite.

4.3.3.4 Reactions of di- $\mu$ -bromodicarbonyl  
bis (triphenylarsine)dirhodium(I)  
with:-

4.3.3.4.I Triphenylarsine.

4.3.3.4.2. Triphenylstibine.

4.3.3.4.3. Triphenylphosphite.

4.3.1. Unless otherwise stated chemicals were used without further purification.

Hydrated rhodium trichloride was obtained on loan from Johnson Matthey.

Triphenylarsine - Ralph Emanuel.

Triphenylantimony and triphenylphosphite from B.D.H.

Triphenylphosphine, a gift from Albright and Wilson was recrystallised from ethanol.

Standard solutions of hydrogen chloride and hydrogen bromide were made by diluting concentrated (or constant boiling point) acid with methanol. The exact molarity was found by titration against standard aqueous sodium hydroxide using phenolphthalein.

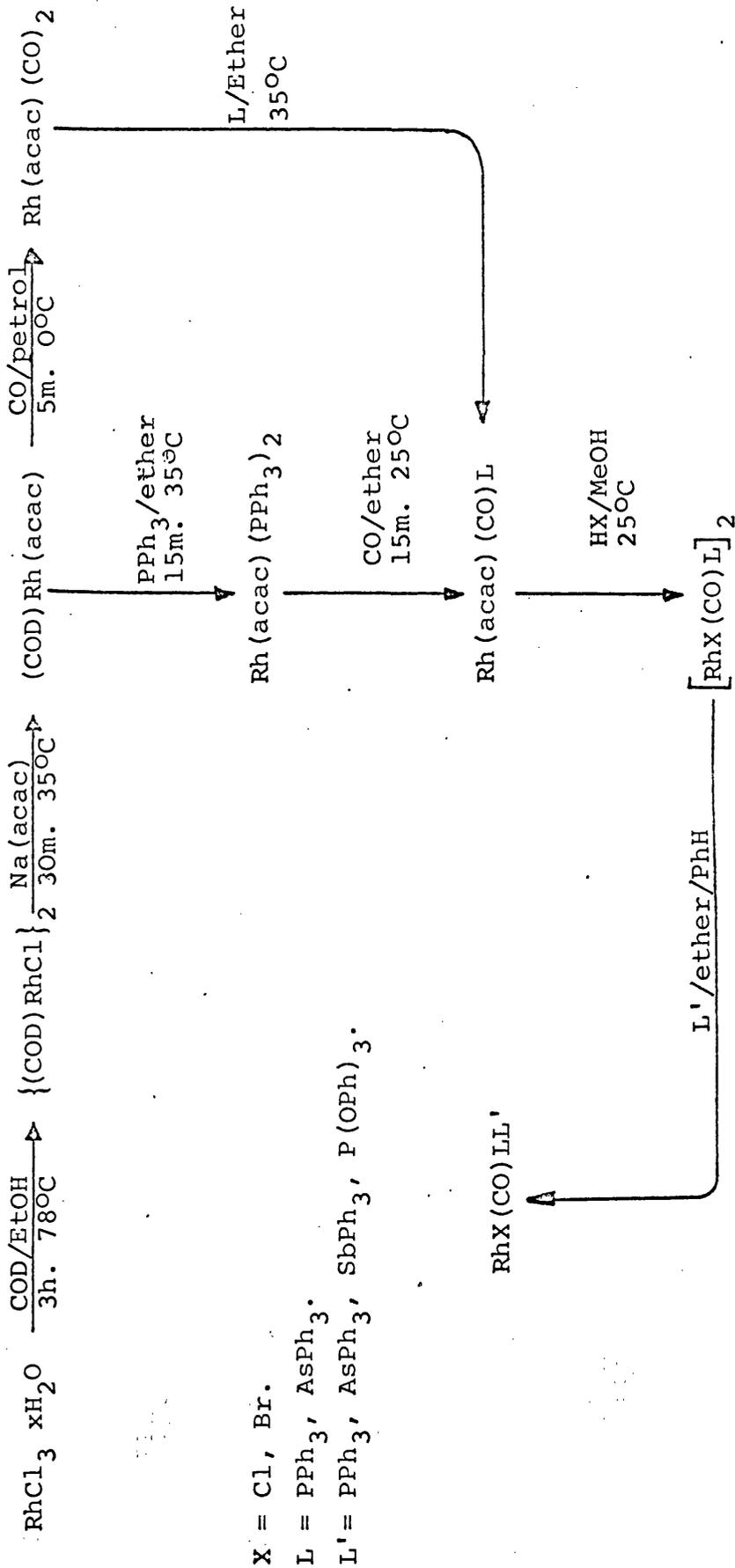
$\{(\text{COD})\text{RhCl}\}_2^{148}$ ,  $(\text{COD})\text{Rh}(\text{acac})^{148}$ ,  $\text{L}(\text{CO})\text{Rh}(\text{acac})^{149}$   
(L =  $\text{AsPh}_3$ ,  $\text{PPh}_3$ ) and  $\text{Na}(\text{Acac})^{150}$  were prepared by literature routes.

$(\text{CO})_2\text{Rh}(\text{Acac})$  was prepared from  $(\text{COD})\text{Rh}(\text{Acac})$  by reaction with carbon monoxide in petrol.

'A slow stream of carbon monoxide was bubbled through a saturated solution of  $(\text{COD})\text{Rh}(\text{acac})$  in petrol (below  $40^\circ\text{C}$  grade) maintained at  $0^\circ\text{C}$  (ice/water). Within a few seconds the solution darkened and almost quantitative precipitation of  $(\text{CO})_2\text{Rh}(\text{acac})$  occurred. This was filtered off, dried in vacuo at R.T. and used without further purification.'

Molecular weights were obtained on a 'Mechrolab' vapour pressure osmometer in benzene at  $38^\circ\text{C}$ .

Reaction scheme for the preparation of mixed ligand rhodium complexes of the type  $\text{RhX}(\text{CO})\text{LL}'$ .

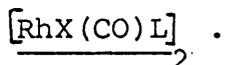


X = Cl, Br.

L = PPh<sub>3</sub>, AsPh<sub>3</sub>.

L' = PPh<sub>3</sub>, AsPh<sub>3</sub>, SbPh<sub>3</sub>, P(OPh)<sub>3</sub>.

4.3.2. Synthesis of the halogen bridged complexes



The calculated volume of a freshly prepared and standardised (ca.  $10^{-2}\text{M}$ ) solution of the acid HX (X = Cl, Br) in dry methanol was added dropwise to a vigorously stirred suspension of the acetylacetonato complex  $\text{Rh}(\text{acac})(\text{CO})\text{L}$ , (1.0 m.mole) (L =  $\text{PPh}_3$ ,  $\text{AsPh}_3$ ) in ether, (35 mls). The original yellow suspension instantly yielded fine orange crystals which were filtered off, washed with ether and dried under vacuo at  $56^\circ\text{C}$ .

Using this method we prepared:-

4.3.2.1 Di- $\mu$ -chlorodicarbonylbis(triphenylphosphine)dirhodium(I), (0.38 g. - 90%), from (acetylacetonato)carbonyl(triphenylphosphine)rhodium(I), (0.50 g. - 1 m.mole), and hydrogen chloride.

4.3.2.2 Di- $\mu$ -chlorodicarbonylbis(triphenylarsine)dirhodium(I), (0.42 g. - 89%), from (acetylacetonato)carbonyl(triphenylarsine)rhodium(I), (0.55 g. - 1 m.mole), and hydrogen chloride.

4.3.2.3 Di- $\mu$ -bromodicarbonylbis(triphenylphosphine)dirhodium(I), (0.34 g. - 87%); from (acetylacetonato)carbonyl(triphenylphosphine)rhodium(I), (0.50 g. - 1 m.mole), and hydrogen bromide.

4.3.2.4. Di- $\mu$ - bromodicarbonylbis(triphenylarsine)di

rhodium(I), (0.46 g. - 89%), from (acetylacetonato)carbonyl (triphenylarsine)rhodium(I), (0.55 g. - 1 m.mole), and hydrogen bromide.

4.3.3. Synthesis of the mixed ligand complex RhX(CO)LL'  
by halogen bridge cleavage of the dimers [RhX(CO)L]<sub>2</sub>

A solution of the donor ligand L', (L' = PPh<sub>3</sub>, AsPh<sub>3</sub>, SbPh<sub>3</sub>, P(OPh)<sub>3</sub>), (1 m.mole), in ether, (10 mls), was added to a solution/ suspension of the dimeric halogen bridged complexes [RhX(CO)L<sub>2</sub>]<sub>2</sub>, (X = Cl, Br L = PPh<sub>3</sub>, AsPh<sub>3</sub>), (0.5 m.mole), in warm benzene, (25 mls).

A clear yellow solution was immediately formed (except in the case of triphenylstibene where a very deep red solution was produced) which was left to stand at 0°C overnight to yield a crop of yellow crystals. These were filtered off washed with a few mls of ethanol and then ether and dried in vacuo at 56°C. A second crop could be obtained by concentration of the filtrate and the addition of ethanol /ether.

4.3.3.I. Reaction of di-μ-chlorodicarbonylbis(triphenyl-phosphine)dirhodium(I).

From Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, (0.43 g. - 0.5 m.mole) we prepared:-

4.3.3.I.I. Chlorocarbonylbis(triphenylphosphine)rhodium(I) (0.66 g. - 100%), using triphenylphosphine, (0.26 g. - 1 m.mole).

4.3.3.I.2. Chlorocarbonyl(triphenylarsine)triphenylphosphine)rhodium(I), (0.69 g. - 92%), using

triphenylarsine, (0.31 g. - 1 m.mole).

- 4.3.3.1.3. Chlorocarbonyl(triphenylantimony)(triphenylphosphine)rhodium(I), (0.63 g. - 80%), using triphenylstibine, (0.35 g. - 1 m.mole).
- 4.3.3.1.4. Chlorocarbonyl(triphenylphosphine)(triphenylphosphite)rhodium(I), (0.57 g. - 77%), using triphenylphosphite, (0.31 g. - 1 m.mole).

4.3.3.2. Reactions of di- $\mu$ -chlorodicarbonylbis(triphenylarsine)dirhodium(I).

From  $\text{Rh}_2\text{Cl}_2(\text{CO})_2(\text{AsPh}_3)_2$ , (0.48 g. - 0.5 m.mole)

we prepared :-

- 4.3.3.2.I. Chlorocarbonylbis(triphenylarsine)rhodium(I), (0.74 g. - 97%), using triphenylarsine, (0.31 g. - 1 m.mole).
- 4.3.3.2.2. Chlorocarbonyl(triphenylarsine)(triphenylantimony)rhodium(I), (0.60 g. - 73%), using triphenylstibine, (0.35 g. - 1 m.mole).
- 4.3.3.2.3. Chlorocarbonyl(triphenylarsine)(triphenylphosphite)rhodium(I), (0.55 g. - 70%), using triphenylphosphite, (0.31 g. - 1 m.mole).

4.3.3.3. Reactions of di- $\mu$ -bromodicarbonylbis(triphenylphosphine)dirhodium(I).

From  $\text{Rh}_2\text{Br}_2(\text{CO})_2(\text{PPh}_3)_2$ , (0.47 g. - 0.5 m.mole)

we prepared:-

- 4.3.3.3.I. Bromocarbonylbis(triphenylphosphine)rhodium(I), (0.67 g. - 95%), using triphenylphosphine (0.26 g. - 1 m.mole).

- 4.3.3.3.2. Bromocarbonyl(triphenylarsine)(triphenylphosphine) rhodium(I), (0.68 g. - 87%), using triphenylarsine, (0.31 g. - 1 m.mole).
- 4.3.3.3.3. Bromocarbonyl(triphenylantimony)(triphenylphosphine)rhodium(I), (0.59 g. - 71%), using triphenylstibine, (0.35 g. - 1 m.mole).
- 4.3.3.3.4. Bromocarbonyl(triphenylphosphine)(triphenylphosphite)rhodium(I), (0.57 g. - 71%), using triphenylphosphite, (0.31 g. - 1 m.mole).

4.3.3.4. Reaction of di- $\mu$ -bromodicarbonylbis(triphenylarsine)dirhodium(I).

From  $\text{Rh}_2\text{Br}_2(\text{CO})_2(\text{AsPh}_3)_2$ , (0.52 g. - 1 m.mole)

was prepared:-

- 4.3.3.4.1. Bromocarbonylbis(triphenylarsine)rhodium(I), (0.72 g. - 91%), using triphenylarsine, (0.31 g. - 1 m.mole).
- 4.3.3.4.2. Bromocarbonyl(triphenylarsine)(triphenylantimony)rhodium(I), (0.59 g. - 68%), using triphenylstibine, (0.35 g. - 1 m.mole).
- 4.3.3.4.3. Bromocarbonyl(triphenylarsine)(triphenylphosphite)rhodium(I), (0.54 g. - 65%), using triphenylphosphite, (0.31 g. - 1 m.mole).

4.4. APPENDICES.

4.4.I. Analytical data.

4.4.2. Infrared data.

4.4.I. Compound	Colour	Yield	M.Pt (°C)	C	H	Hal	Mol.Wt.
$[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$	orange	90	200-204° dec	53.05 (53.24)	3.41 (3.53)	8.40 (8.27)	801±20 (857)
$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	yellow	100					
$\text{RhCl}(\text{CO})(\text{AsPh}_3)(\text{PPh}_3)$	yellow	92	209-212°	60.70 (60.47)	4.28 (4.11)	5.09 (4.82)	716±10 (735)
$\text{RhCl}(\text{CO})(\text{PPh}_3)(\text{SbPh}_3)$	yellow	80	160° dec*	57.88 (56.85)	4.16 (3.87)	4.80 (4.54)	746±12 (782)
$\text{RhCl}(\text{CO})(\text{PPh}_3)\{\text{P}(\text{OPh})_3\}$	yellow	77	176-179	60.77 (60.14)	4.03 (4.09)	4.80 (4.80)	746±11 (739)
$[\text{RhCl}(\text{CO})(\text{AsPh}_3)]_2$	rust orange	89	180 dec*	48.47 (48.29)	3.38 (3.20)	7.40 (7.50)	960±30 (945)
$\text{RhCl}(\text{CO})(\text{AsPh}_3)_2$	yellow						
$\text{RhCl}(\text{CO})(\text{AsPh}_3)(\text{SbPh}_3)$	yellow	73	220° dec*	55.29 (53.82)	3.93 (3.66)	4.50 (4.29)	797±27 (826)
$\text{RhCl}(\text{CO})(\text{AsPh}_3)\{\text{P}(\text{OPh})_3\}$	yellow	70	181-185	55.10 (56.77)	3.71 (3.86)	4.70 (4.53)	756±27 (783)

\* decomposes without melting  
(calculated values in parenthesis)

4.4.I. Compound	Colour	Yield	M.Pt. (°C)	C	H	Hal	Mol. Wt.
$[\text{RhBr}(\text{CO})(\text{PPh}_3)]_2$	rust orange	93	185° dec*	48.30 (48.28)	3.35 (3.20)	16.65 (16.89)	900±40 (946)
$\text{RhBr}(\text{CO})(\text{PPh}_3)_2$	yellow						
$\text{RhBr}(\text{CO})(\text{AsPh}_3)(\text{PPh}_3)$	yellow	87	193-195dec	57.63 (57.02)	4.02 (3.88)	9.61 (10.25)	747±22 (779)
$\text{RhBr}(\text{CO})(\text{PPh}_3)(\text{SbPh}_3)$	deep yellow	71	180° dec*	53.61 (53.79)	3.82 (3.66)	9.18 (9.67)	786±19 (826)
$\text{RhBr}(\text{CO})(\text{PPh}_3)\{\text{P}(\text{OPh})_3\}$	pale yellow	73	162-163°	57.46 (56.73)	3.85 (3.86)	10.20 (10.20)	756±18 (783)
$[\text{RhBr}(\text{CO})(\text{AsPh}_3)]_2$	rust orange	89	160° dec*	46.48 (44.14)	3.08 (2.92)	14.20 (15.45)	1002±35 (1034)
$\text{RhBr}(\text{CO})(\text{AsPh}_3)_2$	yellow	89	228-230°	54.21 (53.98)	3.78 (3.67)	9.33 (9.71)	789±20 (823)
$\text{RhBr}(\text{CO})(\text{AsPh}_3)(\text{SbPh}_3)$	yellow	68	174-175°	51.20 (51.07)	3.37 (3.48)	8.90 (9.18)	850±17 (870)
$\text{RhBr}(\text{CO})(\text{AsPh}_3)\{\text{P}(\text{OPh})_3\}$	yellow	65	175° dec*	52.31 (53.71)	3.47 (3.66)	9.02 (9.66)	790±24 (827)

\* decomposes without melting.  
(calculated values in parenthesis)

4.4.2. Compound	Carbonyl-frequency ( $\text{cm}^{-1}$ )		Low frequency spectra ( $400\text{-}200 \text{ cm}^{-1}$ )	
$[\text{RhCl}(\text{CO})(\text{PPh}_3)]_2$	1975 <sup>a</sup>	1983 <sup>b</sup>	348 <sup>a</sup>	(23) <sup>c</sup>
	1948	(31) <sup>c</sup>	293	(15)
			262	(5)
			250.5	(9)
RhCl(CO)(PPh <sub>3</sub> ) <sub>2</sub>	1960	1977	311.5	(12)
RhCl(CO)(AsPh <sub>3</sub> )(PPh <sub>3</sub> )	1962	1976	330	(15)
			325	(15)
			311.5	(14)
RhCl(CO)(PPh <sub>3</sub> )(SbPh <sub>3</sub> )	1962	1975	308	(13)
			304	(13)
			277.5	(14)
			267.5	(16)
			250	(13)
			225	(13)
RhCl(CO)(PPh <sub>3</sub> ){P(OPh) <sub>3</sub> }	1967	1978	310	(12)
$[\text{RhCl}(\text{CO})(\text{AsPh}_3)]_2$	1977	1980	344.5	(8)
			329	(13)
			295	(14)
			261	(7)
			255	(7)
			255	(8)
			327	(13)
			309.5	(14)
			277	(7)
			268	(7)
RhCl(CO)(AsPh <sub>3</sub> )(SbPh <sub>3</sub> )	1953	1972	327	(25)
			309.5	(15)
			277	(8)
			268	(10)

<u>4.4.2. Compound</u>	<u>Carbonyl frequency (cm<sup>-1</sup>)</u>	<u>Low frequency spectra (400-200 cm<sup>-1</sup>)</u>
RhCl(CO)(AsPh <sub>3</sub> ) <sub>3</sub> {P(OPh) <sub>3</sub> }	1956 <sup>a</sup> 1971 <sup>b</sup> (29) <sup>c</sup>	325 <sup>a</sup> (28) <sup>c</sup> (1.00) <sup>d</sup> 310 (15) (0.71)
RhCl(CO)(AsPh <sub>3</sub> ) <sub>2</sub>	1963 1974 (30)	329 (31) (1.00) 311 (15) (0.87) 305 (0.71)
[RhBr(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	1980 1970 1987 (35)	239.5 (8) (0.24) 225.5 (7) (0.36) 215 (9) (1.00)
RhBr(CO)(PPh <sub>3</sub> ) <sub>2</sub>	1968 1978 (30)	
RhBr(CO)(AsPh <sub>3</sub> )(PPh <sub>3</sub> )	1964 1977 (37)	331 (14) (1.00) 321.5 (10) (0.87)
RhBr(CO)(PPh <sub>3</sub> ) <sub>3</sub> {P(OPh) <sub>3</sub> }	1965 1984 2000 (35)	
RhBr(CO)(PPh <sub>3</sub> )(SbPh <sub>3</sub> )	1957 1984 1976 (34)	277.5 (18) (1.00) 269 (13) (1.00)
[RhBr(CO)(AsPh <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub>	1978 1968 1980 (41)	347 (15) (0.85) 329 (22) (1.00) 236 (0.21) 228.5 (7) (0.62) 215.5 (6) (0.19)
RhBr(CO)(AsPh <sub>3</sub> )(SbPh <sub>3</sub> )	1962 1973 (27)	328 (24) (1.00) 278 (7) (0.38) 268 (11) (0.38)

<u>4.4.2. Compound</u>	<u>Carbonyl frequency (cm<sup>-1</sup>)</u>	<u>Low frequency spectra (400-200 cm<sup>-1</sup>)</u>
RhBr(CO)(AsPh <sub>3</sub> ) <sub>3</sub> {P(OPh) <sub>3</sub> }	1960 <sup>a</sup>	327 <sup>a</sup> (20) <sup>c</sup> d
RhBr(CO)(AsPh <sub>3</sub> ) <sub>2</sub>	1965	353 (12) (0.97) 344.5 (15) (1.00)

- a solid state spectra in nujol mull.
- b solution spectra in chloroform.
- c half band widths in cm<sup>-1</sup>.
- d relative intensity.

## CHAPTER FIVE

5.1. INTRODUCTION.

5.2 RESULTS AND DISCUSSION.

5.3. EXPERIMENTAL.

5.4. APPENDICES.

## 5.I. INTRODUCTION.

The most extensive studies of oxidative addition reactions have been made on square planar iridium(I) complexes of the type  $\text{IrX}(\text{CO})\text{L}_2$  (X = Cl, Br, I; L = tertiary phosphine) and several reviews<sup>58,59,60,61</sup> concerning this or aspects<sup>151-154</sup> of it have appeared.

Attempts have been made to classify the reactivity of metal complexes<sup>155,156</sup> in a similar way to those found for the organic chemistry of carbon; the oxidative addition of  $d^8$  (&  $d^{10}$ ) complexes to that of carbenes, and  $d^7$  complexes to alkyl radicals from their ability to be converted to diamagnetic species by abstraction of radicals. This is however only a superficial comparison since, as Ugo<sup>157</sup> has pointed out, many carbenes act as electrophiles adding preferentially to olefins with electron donating substituents; whereas nucleophilic behaviour is the main characteristic of the reactivity of  $d^8$  and  $d^{10}$  complexes.

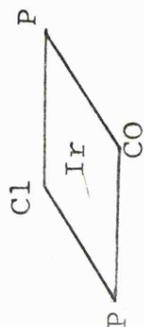
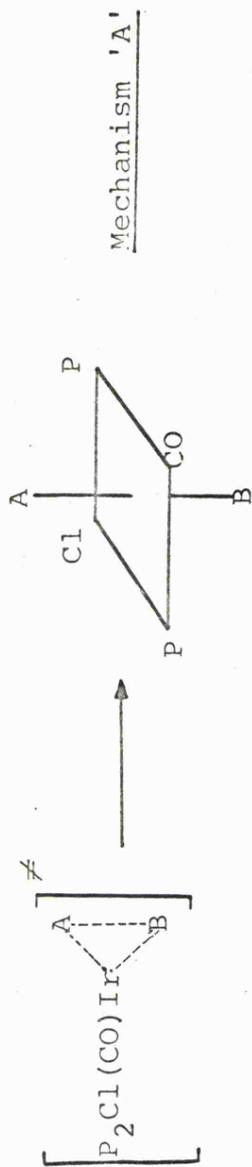
## 5.2. RESULTS AND DISCUSSION.

For Vaska's complex the oxidative addition of molecules of the type  $\text{X}_2$  (or XY) may occur by one of two limiting mechanisms (Fig. I); and result in either cis or trans adducts of the type  $\text{IrCl}(\text{CO})(\text{X})(\text{Y})(\text{PPh}_3)_2$ .

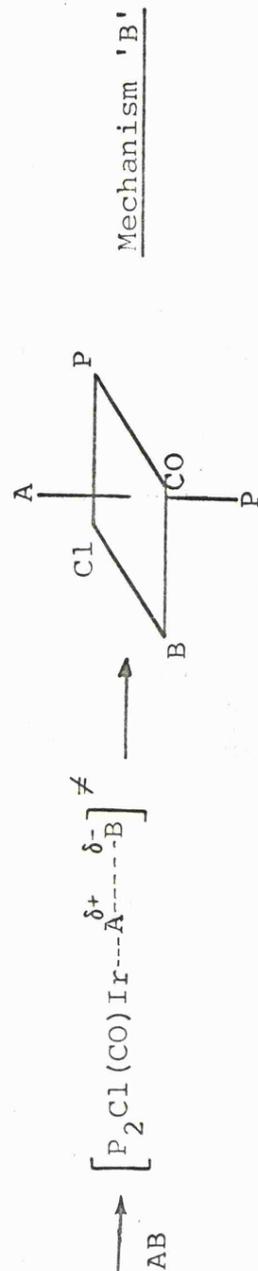
Mechanism (A) is a concerted process involving a three centered transition state of low polarity, in which both coordinating atoms of the addendum molecule interact simultaneously with the metal atom forming M-X and M-Y bonds.

Mechanism (B) involves a dipolar transition state very similar to those accepted for classical  $\text{S}_{\text{N}}2$  reactions of

Mechanisms for the oxidative addition of a molecule AB to a square planar iridium(I) complex.



(P = PPh<sub>3</sub>)



alkyl halides with non-metallic nucleophiles.

There is no reported evidence for free radical mechanisms in the case of two electron oxidations of the metal [Ir(I)→Ir(III)]; however, one electron oxidations of Co(II) complexes with alkyl halides to give Co(III) alkyl compounds have been shown to involve alkyl radicals<sup>158</sup>.

Although these are the only two basic mechanistic types to be considered there are several possible modifications. For example, a transition state of the type (B) may result in complete ionisation with the liberation of free halide ion X<sup>-</sup> in solution, or an ion pair may be formed which rapidly recombines. Alternatively, the complex may react with an alkyl halide which is coordinated to another metal, through the halogen atom, a type of coordination shown to be possible<sup>159</sup>.

Nevertheless, all mechanisms so far proposed are of one of these types, A or B; and the main criteria that have been used in attempts to distinguish them are:-

(i) Type (A) should involve retention of configuration at the carbon atom while for type (B) inversion should be observed.

(ii) The value of activation parameters for type (B) and their solvent dependence should be characteristic of reactions involving molecules of low polarity (for neutral complexes) reacting to give highly polar transition states; as, for example, in the Menschutkin reaction,



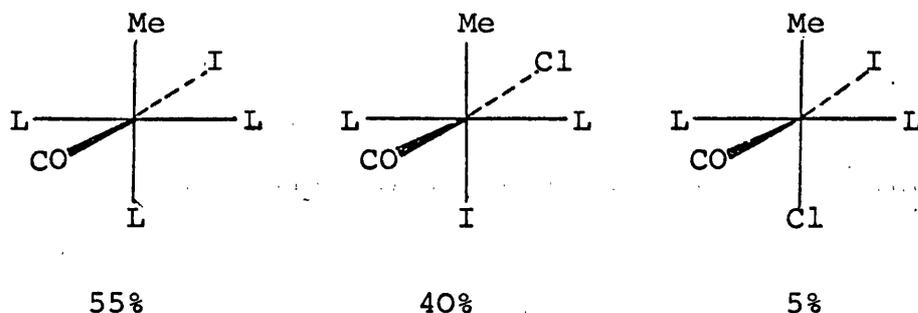
(iii) It may be possible to detect ionic intermediates, for example free halide generated from an alkyl halide

which would support type (B).

It has been shown that the addition of MeX to  $\text{IrY}(\text{CO})\text{L}_2$  to give  $\text{IrMe}(\text{X})(\text{Y})(\text{CO})(\text{PPh}_3)_2$ , both in solution<sup>160,161</sup> and for the reaction of gaseous MeX with crystalline complexes<sup>162</sup> is trans, and these trans additions are kinetically controlled. There is one report<sup>163</sup> of cis addition of MeI to  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  but later work<sup>162</sup> has suggested that this is in fact trans also. Trans addition of acetyl halides to  $\text{IrX}(\text{CO})(\text{PPhMe}_2)_2$  has also been reported<sup>161</sup>.

The additions are however solvent dependent.

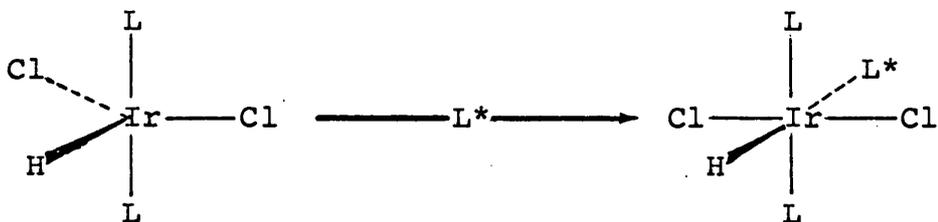
Whereas in benzene the addition of methyl iodide to chlorocarbonylbis(phenyldimethylphosphine)iridium(I) is stereospecifically trans, in the better ionising solvent methanol, a mixture is obtained<sup>161</sup>.



The halide exchange reaction must occur during the oxidative addition process since  $\text{Ir}(\text{Me})\text{I}(\text{Cl})(\text{CO})(\text{PMe}_2\text{Ph})_2$  can be recovered unchanged from refluxing methanol. Hence it has been suggested<sup>161</sup> that the reaction occurs via a transition state of the type (B) to give a five coordinate (or six coordinate solvent containing) cationic alkyl iridium(III) complex and iodide ion, which rapidly substitutes the chloride of the unreacted starting material as would be expected<sup>64,164</sup>.

In benzene either the ions recombine via an ion pair before separation occurs or there is a different mechanism operating.

There is evidence to suggest that such a combination of ions would give the trans product since nucleophilic attack of five coordinate iridium(III) complexes occurs at the most electropositive site of the complex; that is trans to the most strongly sigma bonded ligand , (in this case below, H)<sup>165</sup>



Thus for methyl iodide the solvated halide ion , would attack the iridium trans to the group with the greatest trans influence (in this case the methyl group) to give overall trans addition.

The observation of trans addition itself, however, is not evidence for a two step process since, as Pearson and Muir have pointed out, orbital symmetry considerations allow for either cis or trans addition to occur by one step processes.<sup>162</sup> Indeed the trans addition of gaseous methyl iodide to crystals of  $\text{IrCl}(\text{CO})\text{L}_2$ , (L=PPh<sub>3</sub>, PMePh<sub>2</sub>) is unlikely to go by an ionic mechanism<sup>162</sup>. The addition of MeI to  $\text{IrI}(\text{CO})(\text{PPh}_3)_2$  in the presence of <sup>137</sup>I<sup>-</sup> leads to negligible incorporation of labelled iodine in the adduct<sup>166</sup> (even though rapid equilibrium of free and coordinated iodine might be expected for the iridium(I) complex prior to oxidative addition<sup>164</sup>), suggesting that the halide ion is not liberated in solution.

However, King and Efraty<sup>167</sup> claim evidence for  $[\text{IrMe}(\text{CO})_2(\pi\text{-Cp})]^+ \text{I}^-$  as an intermediate in the reaction of methyl iodide with  $\text{Ir}(\pi\text{-Cp})(\text{CO})_2$ .

The addition of MeI to  $\text{IrI}(\text{CO})(\text{PPh}_3)_2$  in the presence of  $^{137}\text{I}^-$  leads to negligible incorporation of labelled iodine in the adduct, (even though rapid equilibrium of free and coordinated iodine might be expected for the iridium(I) complex prior to oxidative addition), suggesting that the halide is not liberated in solution.

Both retention<sup>162</sup> and inversion<sup>168</sup> of configuration of the alkyl groups have been claimed for the addition of alkyl bromides to complexes of the type  $\text{IrCl}(\text{CO})\text{L}_2$  in dichloromethane.

Optically active  $\text{MeCHBrCOEt}$  has been added to  $\text{IrCl}(\text{CO})(\text{PMePh}_2)_2$  to give an adduct which retained optical activity. Cleavage of the Ir-C bond by bromine regenerated the halide with retained configuration and since it has been shown<sup>169,170</sup> that alkyl-metal bonds are cleaved by bromine with retention, Muir and Pearson<sup>162</sup> argued that the configuration must also be retained during the oxidative addition. However, Dodd and Johnson have shown that there may be a weak link in this argument.<sup>171</sup> Since cleavage of non-transition metal alkyls by electrophiles is generally presumed to take place with retention of configuration at the carbon atom, and this has been verified in a few cases<sup>172</sup>, they expected to obtain (+) 1-methylheptyl bromide from the reaction of optically active (1-methylheptyl)bis(dimethylglyoximinato)pyridenecobalt(III) with bromine in acetic acid. Since the product is substantially (-) 1-methylheptyl bromide one of the assumptions must be incorrect

Rates of reaction and activation parameters for the reaction of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with molecules of the type  $\text{AB}$  and  $\text{A}_2$

Addendum molecule AB or $\text{A}_2$	Solvent	Temp ( $^{\circ}\text{C}$ )	$k_2$ ( $\text{l.m.}^{-1}\text{sec}^{-1}$ )	$\Delta H^{\ddagger}$ (k.cal)	$\Delta S^{\ddagger}$ (eu)	Ref
Methyl iodide	Benzene	25	$3.5 \times 10^{-3}$	5.6	-51	64,166
Hydrogen	Benzene	25	$7.6 \times 10^{-1}$	10.8	-23	64,166
Oxygen	Benzene	25	$3.4 \times 10^{-2}$	13.1	-21	64,166
Methylfluoro -sulphonate	Benzene	25	$8.7 \times 10^{-3}$	17.0	-10.9	this work
Oxygen	Chlorobenzene	30	$6.0 \times 10^{-2}$	9.3	-33	180
Hydrogen	Chlorobenzene	30	1.2	11.5	-20	180

Either the reaction of the cobalt complex with the alkyl halide proceeds with retention of configuration or the cleavage of the M-C bond involves predominant inversion of configuration.

An opposite result has been reported for the reaction of trans-2-fluorocyclohexylbromide with  $\text{IrCl}(\text{CO})(\text{PMe}_3)_2$  for which inversion was demonstrated<sup>168</sup>. Recently an attempt to confirm this observation failed, and it was claimed that there was no reaction between these compounds<sup>173</sup>.

The reaction of silanes with trans- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  seems to involve retention of configuration at silicon.<sup>174</sup>

Chock and Halpern<sup>64</sup> have shown that the addition of methyl iodide to  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ , (X= Cl, Br, I) is a second order process, first order in both iridium complex and methyl iodide; and the dependence of the rate on the halide ion is  $\text{Cl} > \text{Br} > \text{I}$ . Only methyl iodide and not the corresponding bromide or chloride add to the triphenylphosphine complex; with the more basic ligands  $\text{PMe}_2\text{Ph}$ <sup>161</sup> and  $\text{PMePh}_2$ <sup>160</sup> these can however be added. The reaction parameters are in the range  $\Delta H^\ddagger = 5.6 - 8.8 \text{ k.cal.mol}^{-1}$  and  $-\Delta S^\ddagger = 43 - 51 \text{ e.u.}$  in benzene. Such large- $\Delta S$  values are usually associated with a large increase in polarity or in considerable steric confines on forming the transition state.

Large negative  $\Delta S^\ddagger$  values have been obtained in the addition of  $\text{R}_3\text{SiH}$ <sup>174,175</sup>, a reaction unlikely to have an ionic mechanism and, in this case, steric constraints may account for this. The greatest change in  $\Delta S^\ddagger$  was observed in going from benzene, (-51 e.u.) to dimethylformamide, (-10 e.u.); the pattern in various solvents<sup>64,166</sup> being similar to the reaction

of pyridine with ethyl iodide, a reaction known to have a highly polar transition state.

All of this provides strong evidence for a polar transition state. However, care should be taken when interpreting the data in such solvents as DMF since Wilkinson<sup>159</sup> has pointed out that methyl iodide produces conducting solutions in this solvent and a different mechanism may be operative. Equally in benzene a great driving force for this reaction may be the affinity of iodine for the solvent, as shown by the ready formation of charge transfer complexes.

Addition of hydrohalic acids to Vaska's complex are very fast<sup>64</sup> and so far no kinetic study has been reported. The stereochemistry of addition has been established however, and shown to be kinetically controlled in a few cases.

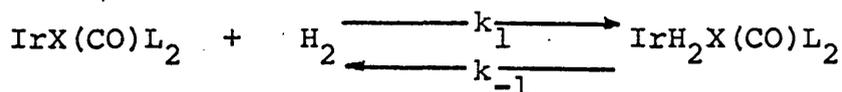
Crystals of  $\text{IrY}(\text{CO})(\text{PPh}_3)_2$  react with gaseous  $\text{HX}$  to give adducts with  $\text{X}$  and  $\text{H}$  in mutually cis positions<sup>72</sup> and since rearrangements are unlikely to occur in the solid state, this probably reflects the mechanism of addition; with a one-step process most favoured.

The addition of  $\text{HBr}$  in ether to a solution of  $\text{IrCl}(\text{CO})\text{L}_2$ , ( $\text{L} = \text{PPh}_3$ <sup>176</sup>,  $\text{PMePh}_2$ <sup>160</sup>) in benzene has been reported to give the same equilibrium mixture of isomers as obtained by the addition of  $\text{HCl}$  to  $\text{IrBr}(\text{CO})\text{L}_2$ ; but it was later shown that in completely anhydrous conditions there is a kinetically controlled cis addition of  $\text{HX}$ <sup>177</sup>. The presence of ionising solvents was shown<sup>177</sup> to enable exchange of halide to occur before, during and after the oxidative addition to give mixtures obtained in the earlier work<sup>160,176</sup>. In ionising solvents the reaction is very likely to involve several stages; probably

the addition of a proton and then a halide ion, but whether in non-ionising solvents a one step process occurs is still to be established.

One of the earliest and most important reported reactions of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  by Vaska was the reversible cis addition of hydrogen.<sup>178</sup> The cis nature of the addition was initially established by infrared studies<sup>178</sup> and later by some n.m.r. studies<sup>161,179</sup>.

Rate and equilibrium constants have been determined for this reaction:



The equilibrium constant for this reaction  $K_{\text{eq}} (k_1/k_{-1})$  showed the following dependence on the ligands:-

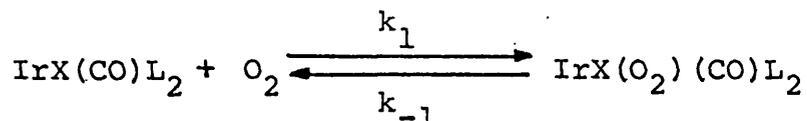
(i) Ligand X :  $\text{I} > \text{Br} > \text{Cl} > \text{SCN} > \text{OCN}$  for the reaction in chlorobenzene at  $40^\circ$ <sup>180</sup>; while in toluene at  $80^\circ$  the order is  $\text{I} \approx \text{Br} > \text{Cl}$ ; the precise order for I and Br depends on the tertiary phosphine used<sup>181</sup>.

(ii) Ligand L : For  $\text{X} = \text{Cl}$  in toluene at  $80^\circ$   $\text{PBuPh}_2 > \text{P}(\text{iPr})_3 > \text{P}(\text{OPh})_3 > \text{P}(\text{p-tolyl})_3 > \text{PPh}_3 > \text{p}(\text{cyclohexyl}) > \text{P}(\text{benzyl})$ . The order is somewhat different when the halide is changed<sup>181</sup>.

Other ligands: Replacement of the carbonyl group by thiocarbonyl to give  $\text{Ir}(\text{CS})\text{Cl}(\text{PPh}_3)_2$  results in no hydrogen uptake, reflecting the greater  $\pi$  acidity of the CS ligand<sup>42</sup>; replacement by  $\text{PPh}_3$ , which is a poorer  $\pi$  acid and better  $\sigma$  base result in irreversible uptake of hydrogen<sup>182</sup>.

Activation parameters and thermochemical data for the overall reaction show that there is a much greater enthalpy than entropy difference on going from the transition state to the final state of the reaction, indicating that the main difference between the transition and final state is in the degree of Ir-H bond formation and the H-H bond cleavage rather than in the polarity or structuring of the molecules.

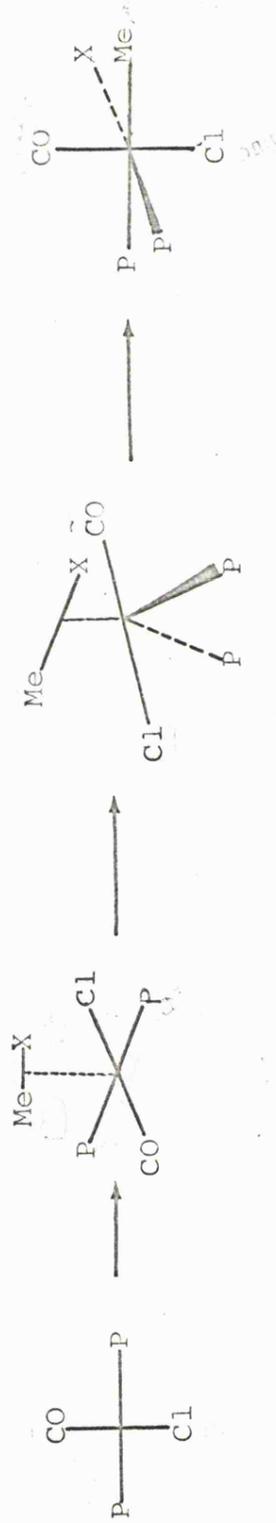
The kinetics of addition of oxygen to the complexes  $\text{IrX}(\text{CO})\text{L}_2$  have been studied by several workers<sup>58,64,176,183,184</sup> who all reported a reaction first order in both iridium complex and gas concentration, with the reverse reaction being first order in adduct concentration.



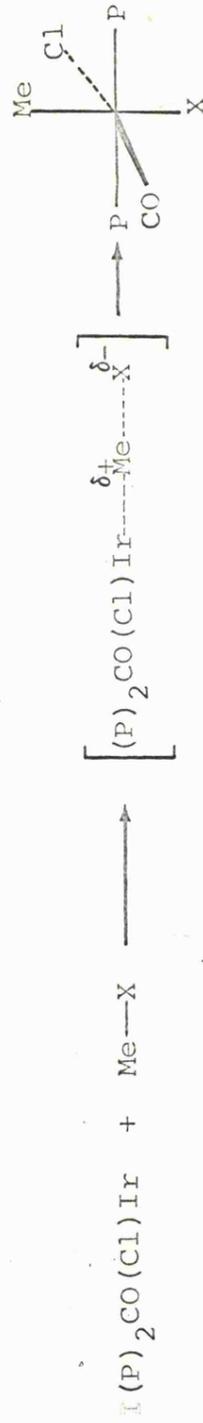
The rate of reaction of  $\text{IrX}(\text{CO})(\text{PPh}_3)_2$  decreases in the order  $\text{I} > \text{Br} > \text{Cl}$  but the dependence on  $k_1$  is not simple.<sup>181</sup> Strohmeier<sup>185</sup> has compared changes in  $k_1$  with apparent electron density changes on the metal as estimated from  $\nu(\text{CO})$ .<sup>186</sup> while Roper *et al.*<sup>65</sup> have examined the steric effects of oxygen uptake for cationic iridium(I) phosphine complexes.

We have found that methyfluorosulphonate reacts with chlorocarbonylbis(triphenylphosphine)iridium(I) in benzene to give a high yield of a white highly crystalline 1:1 adduct. On the basis of infrared and analytical data we have assigned this to an octahedral iridium(III) adduct  $\text{IrCl}(\text{SO}_3\text{F})\text{Me}(\text{CO})(\text{PPh}_3)_2$  containing an O bonded fluorosulphonate group.

Mechanisms for the addition of methylfluorosulphonate to Vaska's complex.



MECHANISM (A)



MECHANISM (B)

(P = PPh<sub>3</sub>, X = O-SO<sub>2</sub>F)

Alkali and alkaline earth fluorosulphonate complexes with both covalent and ionic fluorosulphonate groups are known<sup>187</sup>.

A kinetic study has shown the reaction to be an irreversible bimolecular process exhibiting second order kinetics, the reaction rate being given by;

$$\text{rate} = k_2 [\text{IrCl}(\text{CO})(\text{PPh}_3)_2] [\text{MeSO}_3\text{F}]$$

From a study of the rate at various temperatures we have obtained activation parameters for the reaction.

On the basis of previous data for oxidative addition reactions of Vaska's complex two limiting mechanisms can be envisaged for this reaction.

(i) A concerted reaction involving sideways nucleophilic attack of the iridium(I) complex with simultaneous formation of an Ir-C and Ir-O bonds as the rate determining step with very little charge dispersion in the transition state. (MECHANISM A)

(ii) An  $S_N2$  reaction involving nucleophilic attack at the carbon atom involving significant charge dispersion, both carbon and iridium going through a five coordinate configuration in the transition state. (MECHANISM B)

A cursory examination of the activation parameters obtained for  $\text{MeSO}_3\text{F}$  ( $\Delta H^\ddagger = 17 \text{ K.cal.}$ ,  $\Delta S^\ddagger = -10.9 \text{ e.u.}$ ) compared to those obtained for the addition of other molecules such as hydrogen, oxygen or methyl iodide under identical conditions, show that the activation enthalpy is significantly higher than any of these; but that on the basis of the entropy term alone exhibits behaviour closer to hydrogen and oxygen than to methyl

iodide. (see table (I) )

However, we feel intuitively that since the methyl -fluorosulphonate molecule is polarised  $\text{Me}^{\delta+}-\text{SO}_3\text{F}^{\delta-}$ , in a similar way to and probably to a greater extent than methyl iodide, an  $\text{S}_{\text{N}}2$  mechanism is more likely. Methyl fluorosulphonate is infact a very powerful methylating agent readily quaternising amines (some  $10^2$  times faster than other related molecules) and will even methylate amides (eg DMF) . All of these reactions necessitating the formation of  $\text{Me}^+$  .

If the reaction does occur via. an  $\text{S}_{\text{N}}2$  type of reaction a comparison could be made with methyl iodide which has been interpreted by Chock and Halpern <sup>64,166</sup>. in terms of such a pathway. Such a comparison, however, shows a great disparity in both their entropy (  $\text{MeI} = -51 \text{ eu}$  ;  $\text{MeSO}_3\text{F} = -10.9 \text{ eu}$ .) and their enthalpy (  $\text{MeI} = 5.6 \text{ k.cal}$  ;  $\text{MeSO}_3\text{F} = 17 \text{ k.cal}$ ) of activation Ignoring , for the moment, solvation effects, the activation energy for these reactions can be related to, the strength of the Ir-C bond being formed  $\{H_f(\text{Ir-C})\}$  and that of the C-X (X= I, O ) bond being broken  $\{H_d(\text{C-X})\}$ .

$$\Delta H^\ddagger \approx -\{H_f(\text{Ir-C})\} + \{H_d(\text{C-X})\}$$

There is however significant charge dispersion in the transition state and , assuming solvation of the iridium moiety remains essentially the same an enthalpy term is also present for the solvation of the  $\text{Y}^-$  species which is being generated  $\{H_{\text{sol}}(\text{Y})\}$ . The equation is thus modified;

$$\Delta H^\ddagger \approx -\{H_f(\text{Ir-C})\} + \{H_d(\text{C-X})\} - \{H_{\text{sol}}(\text{Y})\}$$

( $\text{Y} = \text{I}; \text{SO}_3\text{F}$ )

The assumption concerning the solvation of the iridium moiety is not very valid, particularly for solvents which have donor properties, since such molecules may become associated with the planar face opposite to that of the attaching group and will be displaced (with a concurrent change in enthalpy and entropy) as the configuration of the iridium molecule changes from square planar through an approximate square pyramidal (or trigonal bipyramid) to octahedral; equally solvation effects of the rest of the system which have been ignored will also effect the reaction enthalpy.

However, if we compare the contribution of the effects mentioned on the activation enthalpy for the addition of methyl iodide and methyl fluorosulphonate, the term involving the formation of the Ir-C bond will be essentially the same. In fact, for  $\text{MeSO}_3\text{F}$  it may be a little greater as a consequence of the more electropositive nature of the  $\alpha$  carbon atom in this molecule compared to  $\text{MeI}$ . This is not significantly reflected in the difference in rates for the two compounds under identical conditions in their reaction with Vaska's complex, ( $\text{MeI} = 3.5 \times 10^{-3} \text{ l.M.}^{-1} \text{ sec}^{-1}$ ;  $\text{MeSO}_3\text{F} = 8.7 \times 10^{-3} \text{ l.M.}^{-1} \text{ sec}^{-1}$ ).

The activation enthalpy difference ( $\text{MeI} = 5.6 \text{ K.cal}$ ;  $\text{MeSO}_3\text{F} = 17 \text{ K.cal}$ ) is thus a consequence of the differences between the strength of the C-X bond that must be broken  $\{H_d(\text{C-X})\}$  and the solvation enthalpy  $\{H_{\text{sol}}(\text{Y})\}$ .

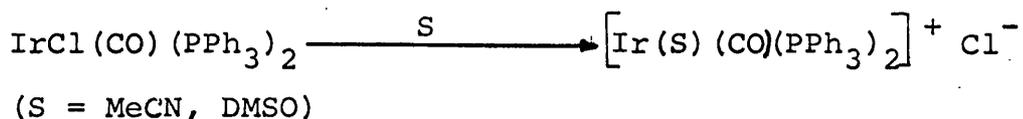
In poor solvents such as benzene the enthalpy contribution for the solvation of  $\text{SO}_3\text{F}^-$  cannot be very large hence the activation enthalpy for the reaction must be dominated by the strength of the carbon-oxygen bond in  $\text{MeSO}_3\text{F}$ .

The entropies of activation also reflect the difference in solvation (assuming that both reactions go by the

same mechanistic route ?) ; (MeI = -51 eu. ; MeSO<sub>3</sub>F = -10 eu.)

The data for methyl iodide in benzene, however, may be atypical, this is further exemplified by the unpredicted behaviour in dimethylformamide. A much better comparison would be to compare the reactions of MeBr, or MeCl; however, these do not add to the triphenylphosphine complex, which may be an important observation in itself, and hence no such comparisons are possible.

The data obtained by Chock and Halpern<sup>64</sup> is suspect since various factors indicate that the reactants may be significantly modified such that the kinetic pattern is different. Wilkinson has showed the ionisation of methyl iodide occurs in dimethylformamide<sup>159</sup>. Roper et al. have shown that in polar solvents such as DMSO and methyl cyanide the iridium-carbon bond can become ionised and species containing bonded solvent molecules<sup>65</sup> produced.



A similar reaction may occur using DMF, even if ionisation does not occur 'association' of solvent molecules may modify both the reactivity pattern and activation parameters. There is an extensively documented literature for analogous d<sup>8</sup> Pt(II) complexes with much evidence for the modifying effects of 'associated' solvent molecules along the z axis. Some semi-empirical evidence of solvent coordination by Vaska's complex has been provided by Strohmeier who has equated changes in the carbonyl frequency of the complex, and hence electron density on the

TABLE (II).

Rates of reaction and activation parameters for the reaction of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with methyl iodide in various solvents at 25°C.\*

Solvent	$k_2$ ( $\text{M}^{-1}\text{sec}^{-1}$ )	$\Delta H^\ddagger$ (k.cal)	$\Delta S^\ddagger$ (eu.)
Benzene	$3.5 \times 10^{-3}$	5.6	-51
Chlorobenzene	$8.5 \times 10^{-3}$	8.0	-41
Bromobenzene	$1.1 \times 10^{-2}$	7.9	-41
Iodobenzene	$1.6 \times 10^{-2}$	6.6	-45
Acetone	$1.8 \times 10^{-2}$	7.1	-42
Dimethylformamide	$1.6 \times 10^{-2}$	16.4	-10

(\*) P.Chock & J.Halpern.

Proceedings of the International Conference on Coordination Chemistry  
(10 th) 1967 135.

metal, in various solvents to the formation of complexes with the solvent itself.

We have also studied the reaction of Vaska's complex with methylfluorosulphonate in various solvents in an attempt to provide further evidence to elucidate the mechanism. The range of solvents which can be used is limited because of solubility, solvent reactivity or solvent absorption in the region where spectroscopic observations are made. Solvent such as alcohols do not dissolve the iridium complex, methyl cyanide, dimethylsulphoxide, pyridine or dimethylformamide react with either the iridium complex or methylfluorosulphonate; while solvent like nitromethane or nitrobenzene absorb in the region studied.

The rates of reaction in benzene, chlorobenzene, bromobenzene and toluene at 25° are shown below;-

	$k_2 (\text{LM}^{-1} \cdot \text{sec}^{-1})$
Benzene	$8.77 \times 10^{-3}$
Chlorobenzene	$2.08 \times 10^{-2}$
Bromobenzene	$2.84 \times 10^{-2}$
Toluene	$1.17 \times 10^{-2}$

Relation of these rates to solvent parameters such as  $Z$  (derived from electronic transition - 'solvatochromic' - shifts of certain organic dyes), Bronstein  $R$  values for weakly ionising solvents or dielectric (or derivative) constants showed zero correlation; probably due to the very small range of solvents and hence parameters and rates available for comparison. Chock and Halpern also found very little change in rates or activation parameters for the reaction of MeI with Vaska's complex in a similar series of substituted benzenes <sup>166</sup>.

An attempt was also made to observe the kinetic pattern in mixed solvents such as MeCN/benzene,  $\text{CHCl}_3$ /benzene EtOH/benzene; however unusual results were obtained. An initial very fast reaction ( $t_{1/2} \approx 2-3$  seconds) was followed by a much slower reaction typical of that observed in benzene alone. This may be due to partial ionisation of either or both of the reactants in these solvent mixtures resulting in a different kinetic pattern and was not investigated further.

The rate of reaction of the corresponding bromo iridium complex, bromocarbonylbis(triphenylphosphine)iridium(I) with methylfluorosulphonate in benzene at  $25^\circ$  was measured, and found to be slower than that of the chloro complex (as Chock and Halpern found for the reaction of methyl iodide); however similar attempts to obtain data with the iodo iridium complex failed to provide meaningful results, since an unusual pattern very similar to that observed for the chloro complex in mixed solvents was observed.

5.3. EXPERIMENTAL.

5.3.1. Spectrophotometric measurements were made by sequential observation of the absorbance of series of four separate cells, each with a different concentration of methylfluorosulphonate, at fixed time intervals using an SP25(C) spectrometer fitted with a (water) thermostated copper cell compartment, at a fixed wavelength.

The temperature of the solutions was measured using a Varian copper-constantan thermocouple.

All solvents, which were of AnalaR or spectroscopic grade, were redistilled in a stream of dry nitrogen and stored under nitrogen until required.

'Stock' solutions of the iridium complexes and of methylfluorosulphonate were contained in an apparatus specifically designed for easy measurement, mixing and storage of air sensitive compounds to minimise reaction of such dilute iridium(I) solutions with oxygen.

$\text{IrX}(\text{CO})(\text{PPh}_3)_2$ , ( $\text{X} = \text{Cl}^{116}, \text{Br}^{64}, \text{I}^{64}$ ) were prepared by literature routes.

5.3.2. Solutions of chlorocarbonylbis(triphenylphosphine) iridium(I), (ca.  $1.0 \text{ g.l}^{-1} \approx 1.3 \times 10^{-3} \text{ M.l}^{-1}$  in benzene, methylfluorosulphonate (ca.  $1.3 \text{ M.l}^{-1}$  at  $19.2^\circ\text{C}$  to  $0.25 \text{ M.l}^{-1}$  at  $40.6^\circ\text{C}$ ) solution and solvent were mixed such that:-

(a) The initial absorbance of the solution was in the region of two.

(b) The half life of the fastest cell was not less than approximately 10 mins.

(c) The concentration of the methylfluorosulphonate was always very much greater than that of the iridium(I)

complex; consistent with (b).

(d) And as wide a range as possible of methylfluoro-sulphonate concentration was achieved; consistent with (b) & (c).

The rate of reaction was followed by monitoring the concentration of the iridium(I) complex from its absorption band at a fixed wavelength (488 millimicrons), where the product has no appreciable absorbance.

The same procedure was adopted for the reaction in different solvents, solvent mixtures and for the bromo and iodo derivatives in benzene.

The resultant concentration of the iridium(I) complex and methylfluorosulphonate are tabulated in the appendices together with all relevant spectral, kinetic and arithmetical data.

All kinetic data involving linear regression of the form  $y = mx + c$  was processed by means of a least mean squares linear regression analysis written in ALGOL 68 for an I.C.L. 4130 computer.

In data tables:-

"R" is the correlation coefficient

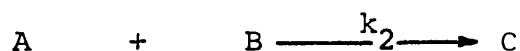
"T" is the 'Student T value' (A probability function)\*

%inc - %data in regression

\* See:- K.J.Laidler. 'Reaction Kinetics' 1966  
Pergamon Press Ltd. Appendix I.Pg 216 - 221.

5.4. APPENDICES.

For a second order reaction:



the rate of reaction is given by;

$$\text{rate} = k_2 [A] [B]$$

Hence;

$$\frac{d[C]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2 [A] [B]$$

ie:

$$dt = \frac{-d[A]}{k_2 [A] [B]}$$

But if one reactant is present in a high concentration relative to the other the change in its concentration is insignificant

thus:

$$dt = \frac{-1}{k_2 [B]} \times \frac{d[A]}{[A]}$$

ie;

$$t = \frac{-1}{k_2 [B]} \ln([A]) + \text{constant}$$

At  $t=0$   $A=A_0$  ; hence:

$$\text{constant} = \frac{-\ln([A_0])}{k_2 [B]}$$

thus:

$$t = \frac{-\ln([A_0])}{k_2 [B]} - \frac{\ln([A])}{k_2 [B]}$$

ie:

$$\underline{[B]k_2 t = -\ln([A_0]) - \ln([A])}$$

Thus plots of  $\log_e([A]) \vee t$  will give a straight line of gradient  $k_{\text{obs}} (= -k_2 \times [B])$

and since the optical density is proportional to the concentration plots of  $\ln(A_t - A_\infty)$  against time will give a straight line of gradient  $-k_2[B]$ . Thus plots of  $k_{obs}$  against  $[B]$  will give a straight line passing through the origin of gradient  $-k_2$ .

The variation of the rate of the reaction with temperature is given by the Arrhenius equation;

$$k = A e^{-(E_a/RT)}$$

A plot of  $\log_e(k_2)$  against  $(1/T)$  affords, from the slope, the value for  $E_a$ .

The value for the activation enthalpy  $\Delta H^\ddagger$  was calculated from:-

$$\Delta H^\ddagger = E_a - RT$$

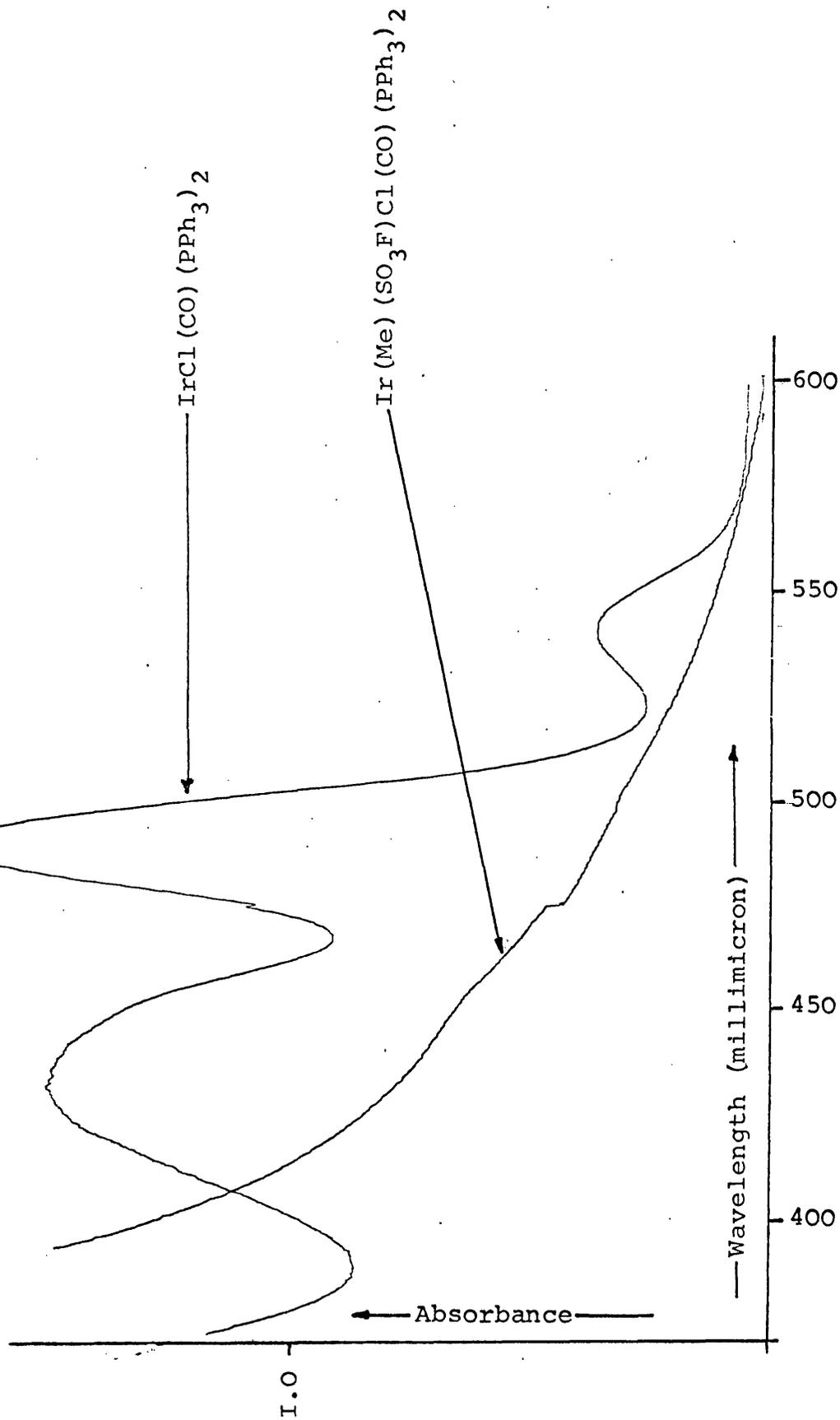
the activation free energy from:-

$$k_2 = \frac{KT}{h} e^{-(\Delta G^\ddagger/RT)}$$

and the entropy of activation  $\Delta S^\ddagger$  using:-

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

Solution absorption spectra of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  and the adduct with methylfluorosulphonate

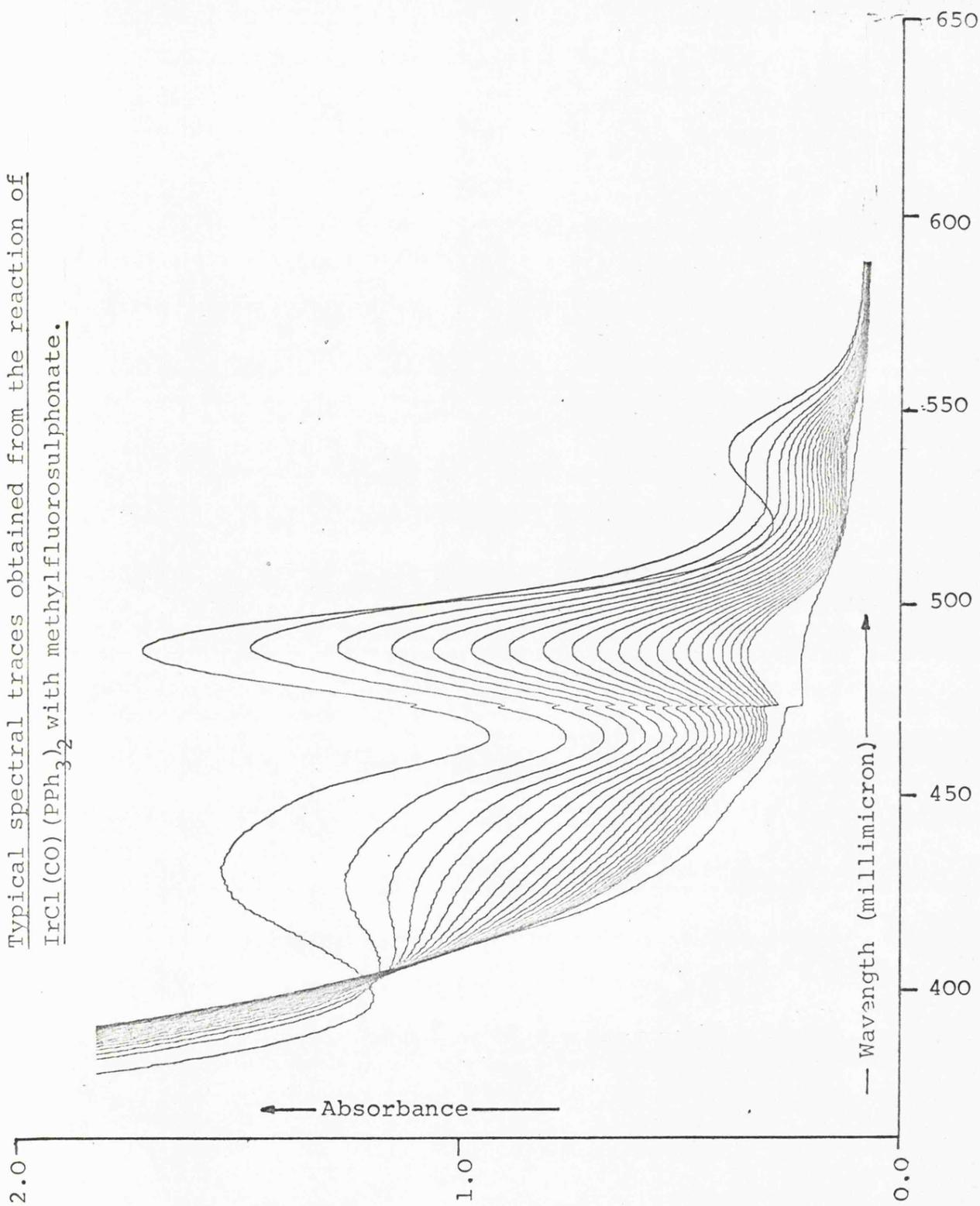


Typical spectral traces obtained from the reaction of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  with methylfluorosulphonate.

Temp =  $25^\circ\text{C}$

Solvent - benzene

Scans at 90 sec intervals



Concentrations of iridium(I) complexes and methylfluorosulphonate used in kinetic studies.

(A) Reaction of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> in benzene.

Range of concentration of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> = (4.27 - 5.10) × 10<sup>-4</sup> M.l<sup>-1</sup>

Temp (°C)	Range of MeSO <sub>3</sub> F conc (M.l <sup>-1</sup> )
19.2	0.2378 - 0.0490
24.85	0.2838 - 0.0762
29.27	0.1752 - 0.0470
34.7	0.1968 - 0.0528
38.35	0.0679 - 0.0182
40.6	0.0679 - 0.0182

(B) Reaction of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> in various solvents at 25°C.

Range of concentration of IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub> = (4.27 - 5.10) × 10<sup>-4</sup> M.l<sup>-1</sup>

Solvent	Range of MeSO <sub>3</sub> F conc (M.l <sup>-1</sup> )
Chlorobenzene	0.1359 - 0.0226
Bromobenzene	0.1562 - 0.0229
Toluene	0.1229 - 0.0294

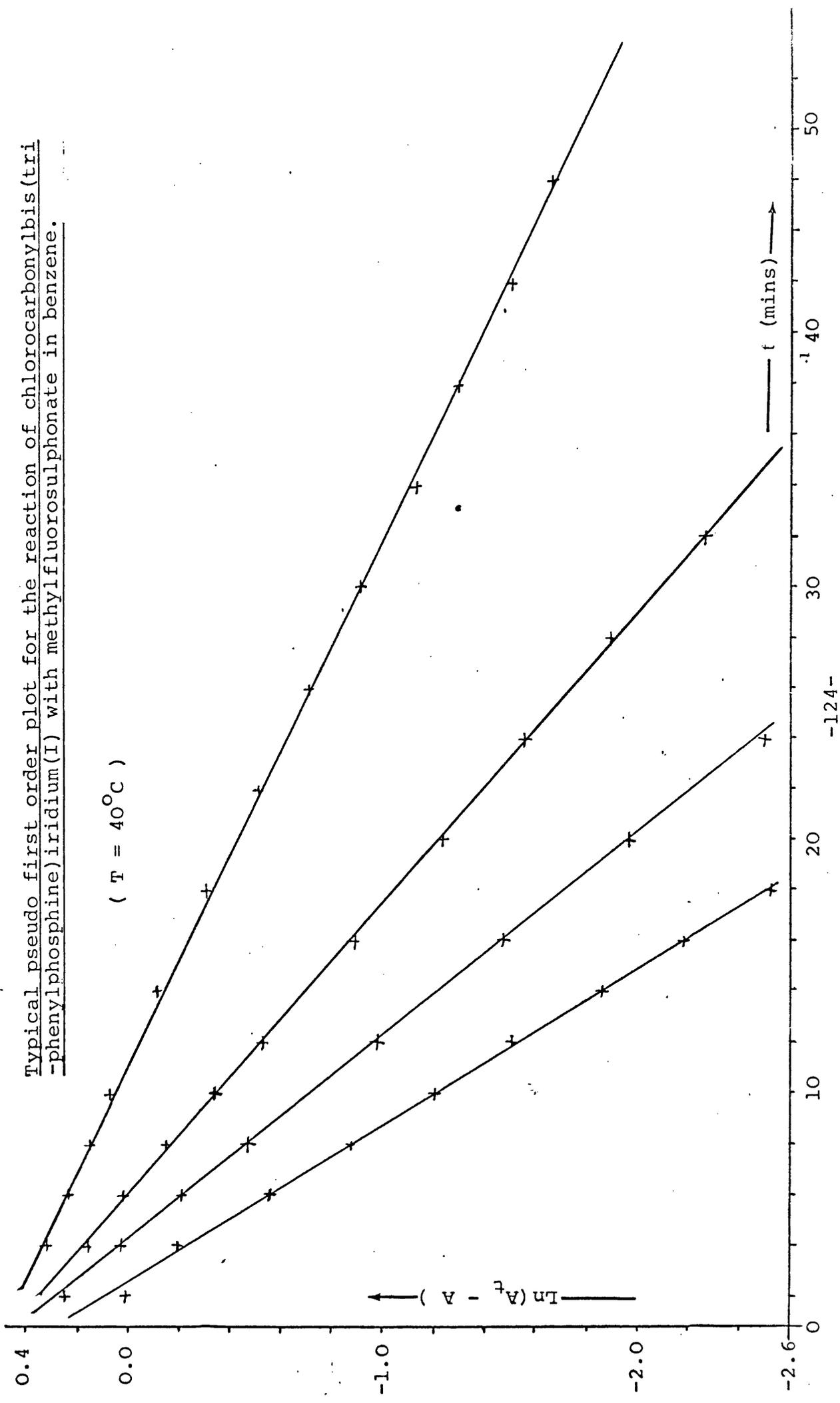
Kinetic data for the reaction of chlorocarbonylbis(triphenylphosphine)iridium(I) with methyl fluorosulphonate in benzene.

(A) Observed pseudo first order rate constants

Temp (°C)	% incl.	'R'	T	Gradient (sec <sup>-1</sup> )	error	%
19.20	86.5	-0.995409	45.3	-0.001305	0.0000288	(2.2%)
19.20	89.1	-0.999860	353.0	-0.001161	0.0000033	(0.2%)
19.20	79.6	-0.999482	265.3	-0.000393	0.0000015	(0.4%)
24.85	84.8	-0.999605	128.2	-0.002868	0.0000224	(0.8%)
24.85	82.6	-0.998213	204.9	-0.002425	0.0000118	(0.5%)
24.85	74.9	-0.996294	155.6	-0.001841	0.0000118	(0.6%)
24.85	87.8	-0.999865	359.6	-0.001039	0.0000029	(0.2%)
29.27	82.5	-0.999738	163.4	-0.002601	0.0000159	(0.8%)
29.27	79.6	-0.999797	192.2	-0.002160	0.0000112	(0.5%)
29.27	88.2	-0.999727	234.6	-0.001475	0.0000063	(0.4%)
29.27	79.7	-0.999479	216.7	-0.000740	0.0000034	(0.5%)
34.70	83.8	-0.999470	81.2	-0.004482	0.0000525	(1.2%)
34.70	83.1	-0.999858	187.6	-0.003326	0.0000177	(0.6%)
34.70	78.9	-0.999188	92.8	-0.002336	0.0000252	(1.1%)
34.70	89.1	-0.999595	213.7	-0.001067	0.0000050	(0.5%)
38.35	79.1	-0.999590	135.2	-0.002176	0.0000161	(0.7%)
38.35	79.7	-0.999574	157.0	-0.001601	0.0000102	(0.6%)
38.35	80.9	-0.999737	240.2	-0.001147	0.0000048	(0.4%)
38.35	92.0	-0.999562	236.2	-0.000628	0.0000027	(0.4%)
40.60	94.7	-0.999885	294.7	-0.002720	0.0000092	(0.3%)
40.60	84.3	-0.999737	190.0	-0.002052	0.0000108	(0.5%)
40.60	83.9	-0.999698	211.4	-0.001434	0.0000069	(0.5%)
40.60	83.7	-0.999347	168.2	-0.000798	0.0000047	(0.6%)

Typical pseudo first order plot for the reaction of chlorocarbonylbis(tri-phenylphosphine)iridium(I) with methylfluorosulphonate in benzene.

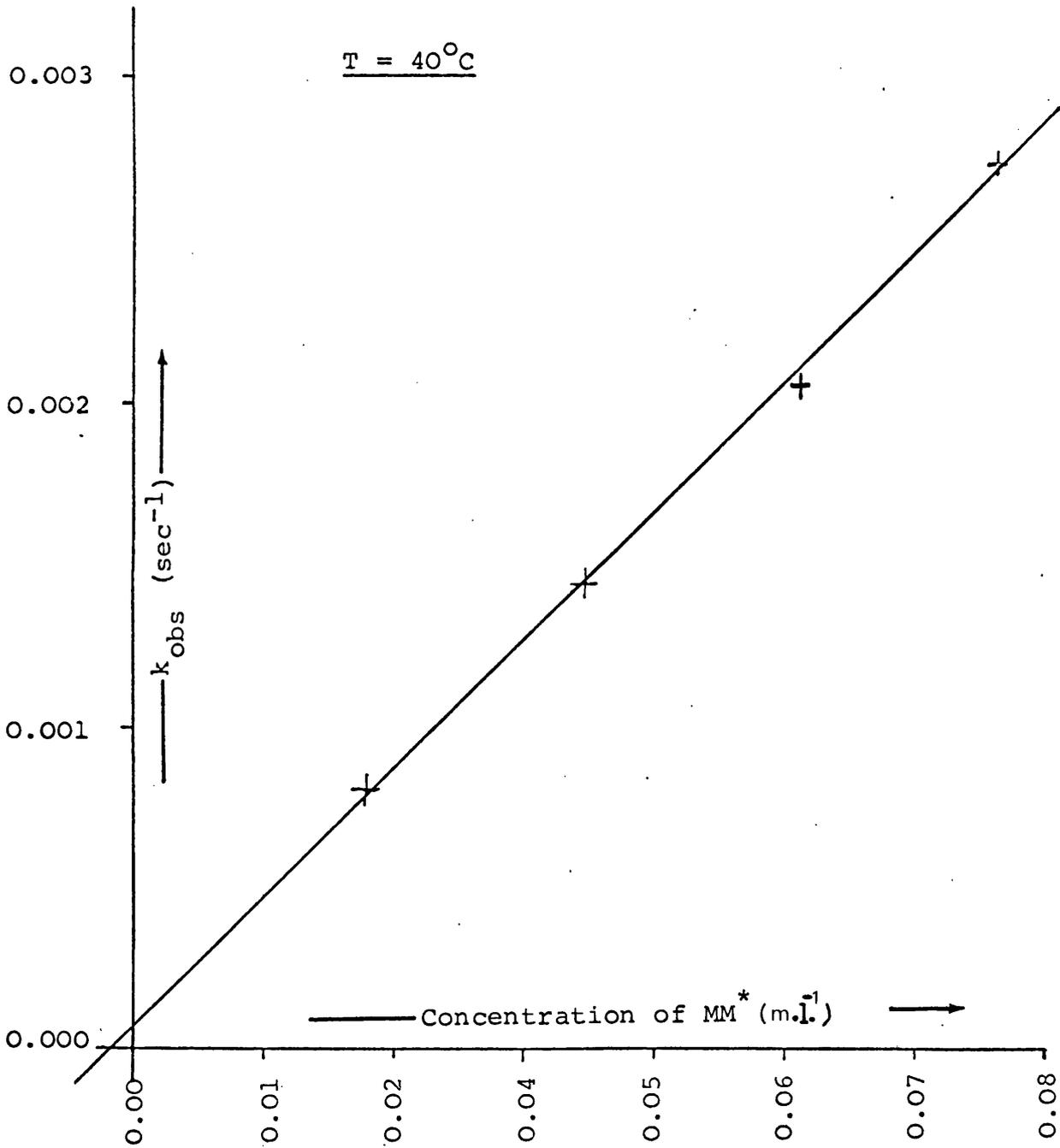
( T = 40°C )



Kinetic data for the reaction of chlorocarbonylbis(triphenylphosphine)iridium(I) with methyl fluorosulphonate in benzene.

(B) Calculated second order rate constants.

Temp (°C)	$k_{obs}$ (sec <sup>-1</sup> )	Conc. MM (m <sup>-1</sup> .)	R	T	Gradient (l.sec <sup>-1</sup> mole. <sup>-1</sup> )	error	Intercept
19.2	0.001305	0.23782	0.999744	42.2	0.004786	0.000108	0.000157
	0.001160	0.21225					
	0.000392	0.04898					
24.5	0.002868	0.28284	0.991367	10.7	0.008766	0.000320	0.000466
	0.002425	0.21461					
	0.001841	0.14538					
	0.001039	0.07615					
29.27	0.002601	0.17521	0.994065	12.9	0.014663	0.000413	0.000115
	0.002160	0.13248					
	0.001475	0.08974					
	0.000746	0.04701					
34.70	0.004482	0.19685	0.998965	31.1	0.023400	0.000756	0.000118
	0.003326	0.14884					
	0.002336	0.10082					
	0.001067	0.05281					
38.35	0.002176	0.06794	0.999044	32.2	0.030770	0.000952	0.000062
	0.001601	0.05137					
	0.001147	0.03480					
	0.000626	0.01823					
40.60	0.002720	0.06749	0.999879	90.7	0.038331	0.000425	0.000091
	0.002052	0.05137					
	0.001434	0.03480					
	0.000798	0.01823					



Typical plot of  $k_{\text{obs}}$  v concentration of  $\text{M.M.}^*$  to obtain the second order rate constant  $k_2$

\* methylfluorosulphonate.

Kinetic data for the reaction of chlorocarbonylbis(triphenylphosphine)iridium(I) with methyl fluorosulphonate in benzene.

(C) Arrhenius regression.

Temp °C	Temp °K	1/T (deg <sup>-1</sup> )	k (l.sec. <sup>-1</sup> mole. <sup>-1</sup> )	Ln k <sub>2</sub>
19.2	292.20	0.0034223	0.004786	5.34199
24.85	297.85	0.0033574	0.008766	4.73687
29.27	302.27	0.0033083	0.014663	4.22244
34.70	307.70	0.0032499	0.023400	3.75499
38.35	311.35	0.0032118	0.030770	3.48121
40.60	313.60	0.0031888	0.038331	3.25630

R = -0.998540

T' = -36.9

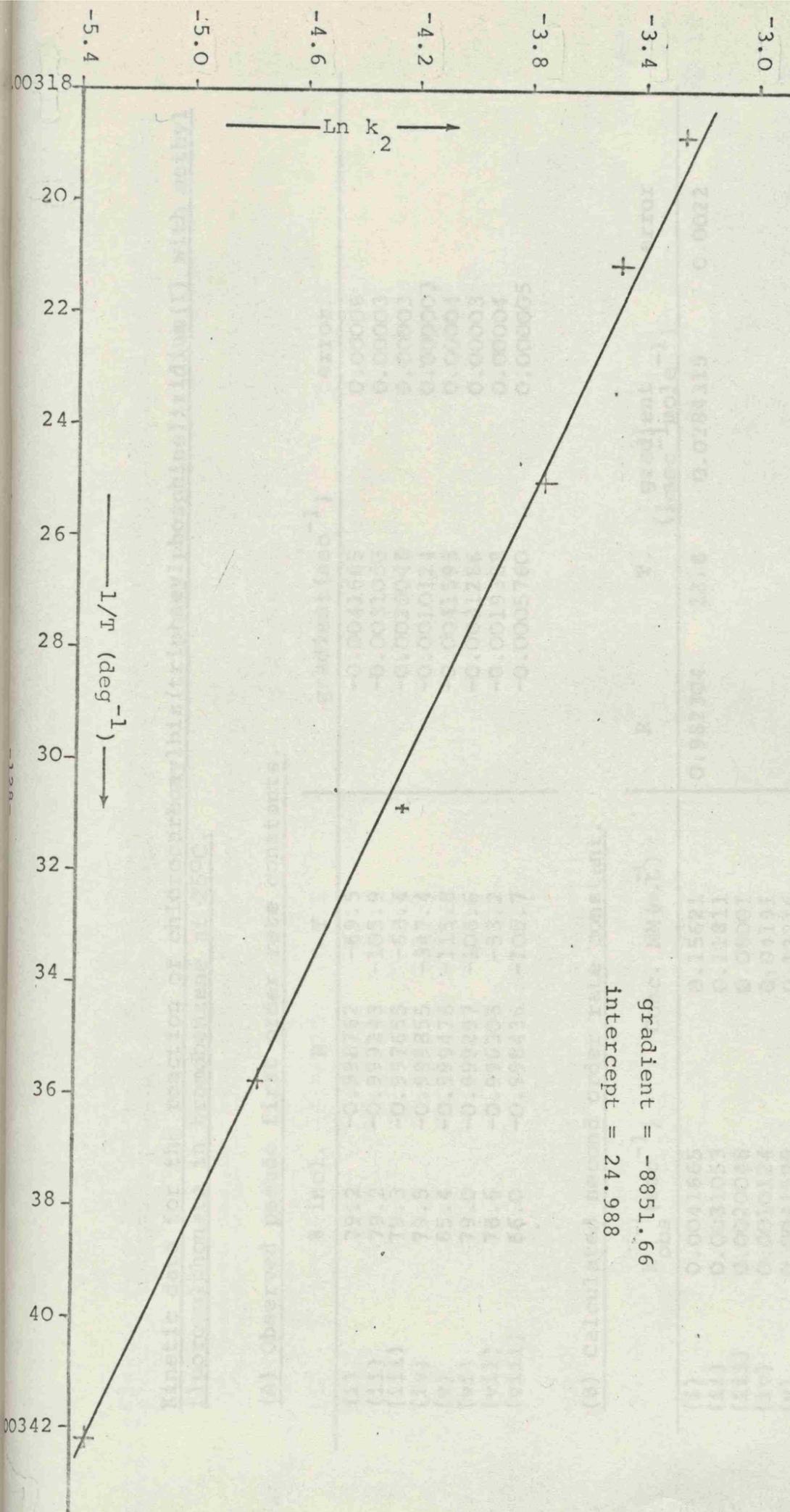
Gradient = -8851.66

Intercept = 24.988

error = 239.6

error = 0.788

Arrhenius plot for the reaction of chlorocarbonylbis(triphenylphosphine) iridium (I) with methyl fluorosulphonate in benzene.



Kinetic data for the reaction of chlorocarbonylbis(triphenylphosphine)iridium(I) with methyl fluorosulphonate in bromobenzene at 25°C.

(A) Observed pseudo first order rate constants.

	% incl.	R	T	gradient (sec <sup>-1</sup> )	error
(i)	79.2	-0.998762	-69.5	-0.0041665	0.00006
(ii)	79.2	-0.999243	-105.9	-0.0031053	0.00003
(iii)	79.3	-0.997655	-68.4	-0.0020048	0.00003
(iv)	79.5	-0.999855	-347.4	-0.0010124	0.000003
(v)	85.4	-0.999478	-115.8	-0.0041598	0.00004
(vi)	79.0	-0.999297	-106.6	-0.0031286	0.00003
(vii)	78.6	-0.996308	-53.2	-0.0019388	0.00004
(viii)	66.0	-0.998436	-105.7	-0.0005760	0.000005

(B) Calculated second order rate constant.

	k <sub>obs</sub> (sec <sup>-1</sup> )	Conc. MM (m.l.)	R	T	gradient (l.sec <sup>-1</sup> mole <sup>-1</sup> )	error
(i)	0.0041665	0.15621	0.982304	12.8	0.0284315	0.0022
(ii)	0.0031053	0.11811				
(iii)	0.0020048	0.08001				
(iv)	0.0010124	0.04191				
(v)	0.0041598	0.13716				
(vi)	0.0031286	0.09906				
(vii)	0.0019388	0.06096				
(viii)	0.0005760	0.02286				

Kinetic data for the reaction of chlorocarbonylbis(triphenylphosphine)iridium(I) with methyl fluorosulphonate in chlorobenzene at 25°C.

(A) Observed pseudo first order rate constants.

	% incl.	R	T	gradient (sec <sup>-1</sup> )	error
(i)	79.7	-0.999230	-101.8	-0.0028441	0.000053
(ii)	79.7	-0.995716	-51.6	-0.0021038	0.000041
(iii)	79.9	-0.998053	-93.3	-0.0011950	0.000012
(iv)	75.5	-0.999979	-339.6	-0.0004400	0.000001
(v)	89.8	-0.997619	-61.4	-0.0032737	0.000053
(vi)	76.4	-0.998993	-86.2	-0.0029376	0.000034
(vii)	79.8	-0.999247	-115.2	-0.0021856	0.000019
(viii)	79.6	-0.994067	-49.2	-0.0012377	0.000025

(B) Calculated second order rate constants

	k <sub>obs</sub> (sec <sup>-1</sup> )	Conc. MM (m.l <sup>-1</sup> )	R	T	Gradient (l.sec <sup>-1</sup> mole <sup>-1</sup> )	error	Intercept
(i)	0.0028441	0.13586	0.968525	9.5	0.0208282	0.0022	-0.000180
(ii)	0.0021038	0.09812					
(iii)	0.0011950	0.06038					
(iv)	0.0004400	0.02264					
(v)	0.0032737	0.15473					
(vi)	0.0029376	0.11699					
(vii)	0.0021856	0.07925					
(viii)	0.0012377	0.04151					

Kinetic data for the reaction of chlorocarbonylbis(triphenylphosphine)iridium(I) with methyl  
-fluorosulphonate in toluene at 25°C.

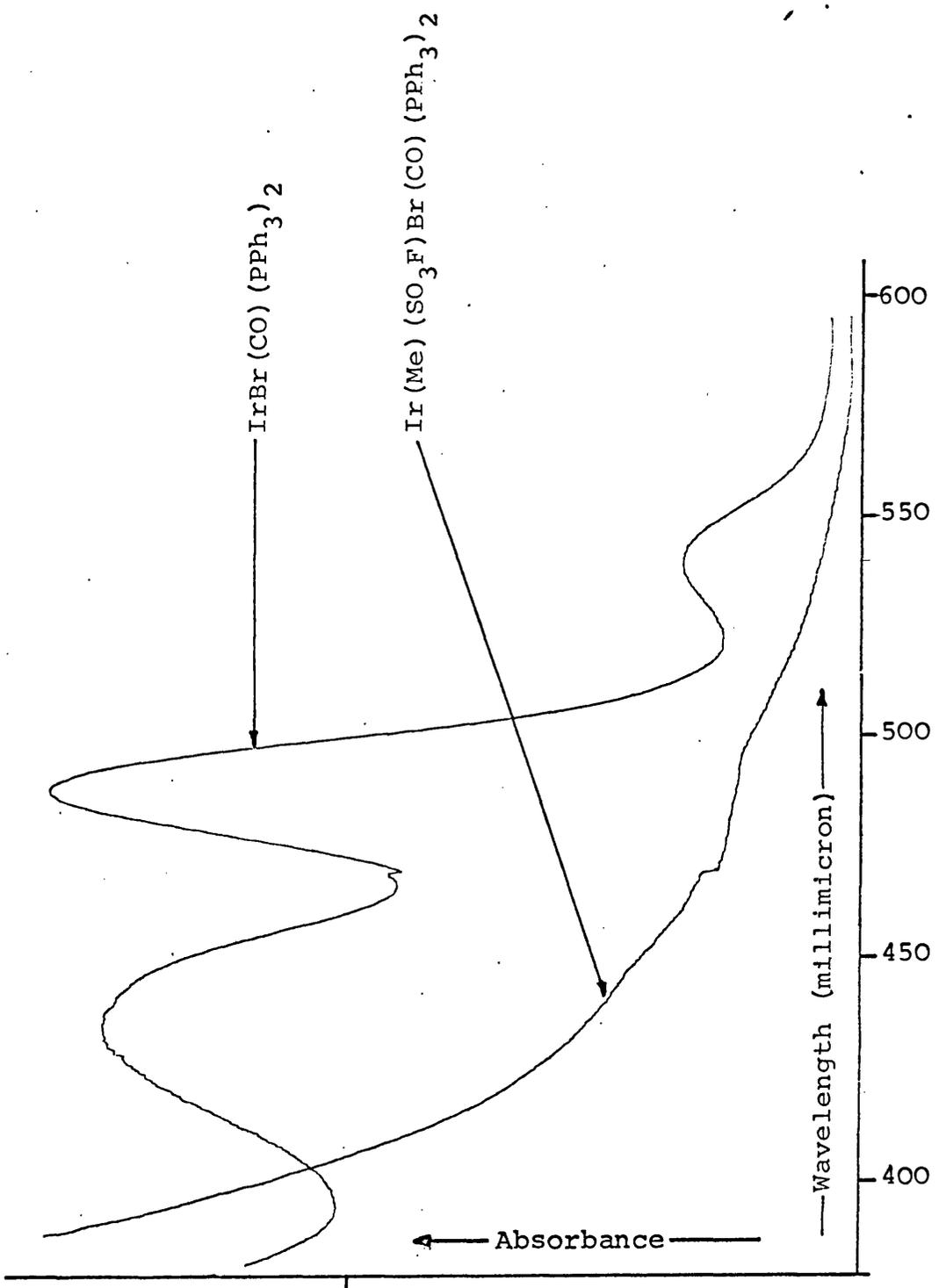
(A) Observed psuedo first order rate constants.

	grad & incl	R	T	gradient(sec <sup>-1</sup> )	error
(i)	679.0	-0.999891	-325.5	-0.0011450	0.000004
(ii)	694.3	-0.998711	-122.9	-0.0007586	0.000006
(iii)	690.5	-0.999458	-196.7	-0.0004920	0.000003
(iv)	70.5	-0.998739	-110.8	-0.0002571	0.000002
(v)	84.1	-0.999126	-121.9	-0.0013660	0.000011
(vi)	79.8	-0.999045	-127.3	-0.0010667	0.000008
(vii)	79.5	-0.998498	-106.3	-0.0007391	0.000007
(viii)	81.5	-0.999654	-258.7	-0.0004298	0.000002

(B) Calculated second order rate constants.

	k <sub>obs</sub> (sec <sup>-1</sup> )	Con. MM(m.l.)	R	T	Gradient (l.sec <sup>-1</sup> mole <sup>-1</sup> )	error	intercept
(i)	0.0011450	0.10958	0.98941	17.1	0.0116712	0.00068	0.000107
(ii)	0.0007586	0.08285					
(iii)	0.0004920	0.05612					
(iv)	0.0002571	0.02940					
(v)	0.0013660	0.12294					
(vi)	0.0010667	0.09621					
(vii)	0.0007391	0.06949					
(viii)	0.0004298	0.04276.					

Solution absorption spectra of  $\text{IrBr}(\text{CO})(\text{PPh}_3)_2$  and the adduct with methylfluorosulphonate in benzene.



Kinetic data for the reaction of bromocarbonylbis(triphenylphosphine)iridium(I) with methyl  
-fluorosulphonate in benzene at 25°C.

(A) Observed psuedo first order rate constants.

	% incl.	R	T	gradient (sec <sup>-1</sup> )	error
(i)	83.7	-0.999100	-166.6	-0.0002519	0.000002
(ii)	79.3	-0.997749	-99.8	-0.0004363	0.000004
(iii)	88.7	-0.999239	-177.5	-0.0006054	0.000003
(iv)	79.5	-0.997308	-70.7	-0.0008669	0.000012
(v)	79.4	-0.999668	-212.6	-0.0010091	0.000005
(vi)	83.3	-0.999642	-175.2	-0.0012605	0.000007
(vii)	79.8	-0.999229	-119.4	-0.0013469	0.000011
(viii)	85.0	-0.999369	-119.5	-0.0017083	0.000014

(B) Calculated second order rate constants.

	K <sub>obs</sub> (sec <sup>-1</sup> )	Con. MM (m.l <sup>-1</sup> )	R	T	Gradient (1.sec <sup>-1</sup> mole <sup>-1</sup> )	error	intercept
(i)	0.002519	0.02654	0.9942765	22.8	0.0076867	0.00033	0.000016
(ii)	0.0004363	0.05554					
(iii)	0.0006054	0.07961					
(iv)	0.0008669	0.10958					
(v)	0.0010091	0.13269					
(vi)	0.0012605	0.15603					
(vii)	0.0013469	0.18576					
(viii)	0.0017083	0.21035					

" The brevity of our life, the dullness of our senses, the torpor of our indifference, the futility of our occupation, suffer us to know but little: and that little is soon shaken and then torn from the mind by that traitor to learning, that hostile and faithless stepmother to memory, oblivion. "

John of Salisbury (d.1180)  
Prologue to the Policraticus.

BIBLIOGRAPHY.

- ( 1) A.Cahours & H.Gal.  
Ann. Chem. Liebig. 1870, 155, 223.  
Compt. Rend 1870, 70, 897.  
Ann. Chem. Liebig. 1870, 155, 355.  
Compt. Rend 1870, 70, 1380.  
Ann. Chem. Liebig 1870, 156, 302.  
Compt. Rend. 1870, 71, 208.
- ( 2) S.Ahrland, J.Chatt, & N.R.Davies.  
Quat.Rev.(London) 1958, 12, 265.
- ( 3) S.Ahrland, J.Chatt, N.R.Davies & A.A.Williams  
J.Chem.Soc. 1958, 276.
- ( 4) J.Chatt & A.A.Williams  
J.Chem.Soc 1951, 3061.
- ( 5) H.Moissan.  
Bull.Soc.Chim. 1891, 5, 454.
- (6) M.Schutzenberger.  
Bull.Soc.Chim. 1872, 17, 482
- ( 7) E.L.Muetterties.  
'Advances in the Chemistry of Co-ordination  
Compounds'.  
International Symposium.(New York 1971)
- ( 8) K.C.Moss.  
Ph.D. Thesis. Imperial College 1962
- ( 9) J.A.Chopoorian, J.Lewis, & R.S.Nyholm.  
Nature. 1961, 190, 528.
- (10) L.Malatesta & R.Ugo.  
J.Chem.Soc. 1963, 2080.
- (11) A.D.Allen & C.D.Cook.  
Proc.Chem.Soc. 1962, 218.
- (12) J.Stocks.  
Ph.D. Thesis. Leicester University  
1969.
- (13) J.Mc Avoy.  
Ph.D. Thesis. University of  
Strathclyde 1965.

- (14) J. Mc Avoy, K.C. Moss & D.W.A. Sharp.  
J. Chem. Soc. 1965, 1376.
- (15) H.C. Clark & W.S. Tsang.  
J. Amer. Chem. Soc. 1967, 89, 529.
- (16) W.J. Bland & R.D.W. Kemmitt.  
J. Chem. Soc (A) 1969, 2062.
- (17) L. Vaska.  
J. Amer. Chem. Soc. 1966, 88, 5324.
- (18) L. Vaska.  
Chem. Comm. 1966, 614,
- (19) F.H. Jardine, L. Rule & A.G. Vohra.  
J. Chem. Soc (A) 1970, 238.
- (20) R.D.W. Kemmitt, R.D. Peacock & I.L. Wilson.  
Chem. Comm. 1968, 772.
- (21) A.A. Grinberg, M.M. Singh & Yu.S. Yarshavskii.  
Russ. J. Inorg. Chem. 1968, 13, 1399.
- (22) L. Vaska & J. Peone (jnr.).  
Chem. Comm. 1971, 418,
- (23) J. Chatt & B.L. Shaw.  
J. Chem. Soc. 1962, 5075.
- (24) F. Cariati, R. Ugo & F. Bonati.  
Inorg. Chem. 1966, 5, 1128.
- (25) S.O. Grim, R.L. Keiter & W. Mc Farlane.  
Inorg. Chem. 1967 6, 1133.
- (26) M.J. Church & M.J. Mays.  
J. Chem. Soc (A) 1968, 3074.
- (27) H.C. Clark & K.R. Dixon.  
J. Amer. Chem. Soc. 1969, 91, 596.
- (28) H.C. Clark, K.R. Dixon & W.J. Jacobs  
J. Amer. Chem. Soc. 1969, 91, 1346.
- (29) K.R. Dixon.  
Private communication to R.D.W. Kemmitt.

- (30) M. Van den Akker & F. Jellinek.  
Rec. Trav. Chim. 1967, 86, 275
- (31) R Newman and R M Badger.  
J. Chem. Phy. 1951, 19, 1207.
- (32) P.M. Druce, M.F. Lappert & P.N.K. Riley.  
Chem. Comm. 1967, 486.
- (33) H.C. Clark, K.R. Dixon & W.J. Jacobs.  
J. Amer. Chem. Soc. 1968, 90, 2259.
- (34) J. Soriano, J. Shamir, A. Netzer & Y. Marcus.  
Inorg. Nuc. Chem. Let. 1969, 5, 209,
- (35) K. Schauburg & C. Deverell.  
J. Amer. Chem. Soc. 1968, 90, 2495.
- (36) R. Haque & L.W. Reeves.  
J. Amer. Chem. Soc. 1967, 89, 250.
- (37) I.T. Vang. & F.I. Skripov..  
Dolk. Akad. Nauk. S.S.S.R.  
1961, 136, 58,
- (38) P.M. Boradin & E.N. Sventitskii.  
Yadern. Magn. Rezonans. (Leningrad. Gos. Univ)  
1965, 1, 76.
- (39) M.C. Baird & G. Wilkinson.  
Chem. Comm. 1966, 514.
- (40) M.C. Baird & G. Wilkinson.  
J. Chem. Soc. (A). 1967, 865.
- (41) M.C. Baird, G. Hartwell (jnr.), & G. Wilkinson.  
J. Chem. Soc. (A). 1967, 2037.
- (42) M.P. Yagupsky & G. Wilkinson.  
J. Chem. Soc. (A). 1968, 2813.
- (43) J.D. Gilbert, M.C. Baird & G. Wilkinson.  
J. Chem. Soc. (A). 1968, 2198.
- (44) M. Baird, G. Hartwell (jnr.), R. Mason, A.I.M. Rae,  
& G. Wilkinson.  
Chem. Comm. 1967, 92.

- (45) R.Mason & A.I.M.Rae.  
J.Chem.Soc(A). 1970, 1767.
- (46) T.Kashiwagi, N.Yasuoka, T.Ueki, N.Kasai, M.Kakudo  
S.Takahashi & N.Hagihara.  
Bull.Chem.Soc.Japan. 1968, 41, 296.
- (47) M.F.Lappert & B.Prokai.  
'Advances in Organometallic Chemistry'  
ed. F.G.A.Stone & R.West.  
Academic Press - New York - London.  
1967, Vol 5, p.225.
- (48) L.S.Pu, A.Yamamoto & S.Ikeda.  
J.Amer.Chem.Soc. 1968, 90, 3896.
- (49) T.A.George, K.Jones & M.F.Lappert.  
J.Chem.Soc. 1965, 2157.
- (50) D.Commereuc, I.Douek & G.Wilkinson.  
J.Chem.Soc(A). 1970, 1771.
- (51) A.Palazzi, L.Busetto & M. Graziani.  
J.Organomet.Chem. 1971, 30, 273.
- (52) E.Lindner, R.Grimmer & H.Weber.  
J.Organomet.Chem. 1970, 23, 209.
- (53) V.G.Albano, P.L.Bellon & G.Ciani.  
J.Organomet.Chem. 1971, 31, 75.
- (54) L.Pauling.  
'The Nature of the Chemical Bond'  
Cornell University Press - New York (1960)
- (55) J.A.Ibers.  
J.Chem.Phys. 1964, 40, 402.
- (56) J.P.Fackler & W.C.Seidel.  
Inorg.Chem. 1969, 8, 1631.
- (57) Inorganic Synthesis  
Vol (XI) Pg. IO5.
- (58) L.Vaska.  
Accounts.Chem.Res. 1968, 1, 335.
- (59) J.P.Collman.  
Accounts.Chem.Res. 1968, 1, 136.

- (60) J. Halpern.  
Accounts.Chem.Res. 1970, 3, 386.
- (61) S. Cárra & R. Ugo.  
Inorganica.Chimica.Acta.Revs.  
1967, 49.
- (62) J.P. Collman & J.W. Kang.  
J.Amer.Chem.Soc. 1967, 89, 844.
- (63) J.A. Mc Ginnety, R.J. Doedens & J.A. Ibers.  
Inorg.Chem. 1967, 6, 2243.
- (64) P.B. Chock & J. Halpern.  
J.Amer.Chem.Soc. 1966, 88, 3511.
- (65) G.R. Clark, C.A. Reed, W.R. Roper, B.W. Skelton & T.N. Walters.  
Chem.Comm. 1971, 758.
- (66) E.W. Abel & F.G.A. Stone.  
Quat.Rev. 1969, 23, 325.
- (67) P. Carty, A. Walker M. Mathew & G.J. Palenik.  
Chem.Comm. 1969, 1374.
- (68) J.K. Wilmshurst  
J.Chem.Phys. 1958, 28, 733.
- (69) J. Peone (jnr.) & L. Vaska.  
Angew.Chem. 1971, 10, 511
- (70) L. Vaska & J. Peone (jnr.).  
Suomen Kemiskilehli(English).  
1971, 44, 317.
- (71) L. Vaska & J.W. DiLuzio.  
J.Amer.Chem.Soc. 1962, 84, 679.
- (72) L. Vaska.  
J.Amer.Chem.Soc. 1966, 88, 5325.
- (73) R.F. Heck.  
J.Amer.Chem.Soc. 1964, 86, 2796.
- (74) R.S. Nyholm & K. Vrieze.  
Chem.Ind. (London). 1964, 318.
- (75) L. Vaska.  
Science. 1963, 140, 809.

- (76) F.Carziani, U.Sartorelli & F.Zingales.  
Chimica et Industria. (Milan).  
1967, 49, 469.
- (77) J.A.Ibers & S.J.LaPlaca.  
Science. 1964, 145, 920  
J.Amer.Chem.Soc. 1965, 87, 2581.
- (78) J.A.McGinnety, R.J.Doedens & J.A.Ibers.  
Science. 1967, 155, 709.  
Inorg.Chem. 1967, 6, 2243.
- (79) V.K.Gleu & K.Rehm  
Z.Anorg.Allgem.Chem. 1936, 227, 237.  
Z.Anorg.Allgem.Chem. 1938, 235, 201.
- (80) D.F.Christian & W.R.Roper.  
Chem.Comm. 1971, 1271.
- (81) E.H.Brave & W.Hubel.  
Angew.Chem. 1963, 75, 345.
- (82) W.Strohmeier & J.F.G.Guttenberger.  
Chem.Ber. 1964, 97, 1871.
- (83) L.Vaska & S.S.Bath.  
J.Amer.Chem.Soc. 1966, 88, 1333.
- (84) L.Vaska & D.L.Catone.  
J.Amer.Chem.Soc. 1966, 88, 5324.
- (85) J.L. Levison & S.Robinson.  
Chem.Comm. 1967, 198.
- (86) T.Kashiwagi N.Yasuoka T.Ueki, N.Kasai & M.Kakudo  
Bull.Chim.Soc.Japan. 1968, 41, 296.
- (87) S.J.LaPlaca & J.A.Ibers.  
Inorg.Chem. 1966, 5, 405.
- (88) E.C.Moroni, R.A.Friedel & I.Wender.  
J.Organomet.Chem. 197 , 21, P-23.
- (89) R.N.Wiener & E.R.Nixon.  
J.Chem.Phys. 1956 , 25, 175.
- (90) L.Vaska & R.E.Rhodes.  
J.Amer.Chem.Soc. 1965, 87, 4970.

- ( 91) W.H.Baddley.  
J.Amer.Chem.Soc. 1966, 88, 4545.
- ( 92) R.Cramer & G.W.Parshall.  
J.Amer.Chem.Soc. 1965, 87, 1392.
- ( 93) G.W.Parshall & F.N.Jones.  
J.Amer.Chem.Soc. 1965, 87, 5356.
- ( 94) M.J.S.Dewar.  
Bull.Soc.Chim.France. 1951, 18, C-71.
- ( 95) J.Chatt & L.A.Duncanson.  
J.Chem.Soc. 1953, 2939.
- ( 96) W.C.Zeise.  
Pogg.Ann. 1827, 9, 632.
- ( 97) R.Mason.  
Nature. 1968, 217, 543.
- ( 98) L.E.Orgel.  
'An Introduction to Transition Metal Chemistry'  
Methuen & Co.Ltd. London 1960  
"Ligand field theory" pg. 137.
- ( 99) J.A.Mc Ginney, N.C.Payne & J.A.Ibers.  
J.Amer.Chem.Soc. 1969, 91, 6301
- (100) A.J.Deeming & B.L.Shaw.  
J.Chem.Soc.(A) 1969, 1128.
- (101) A.J.Deeming & B.L.Shaw.  
J.Chem.Soc.(A). 1969, 1802.
- (102) M.S.Weininger, I.F.Taylor & E.L.Amma.  
Chem.Comm. 1971, 1172.
- (103) L.S.Chen & L.Vaska.  
Chem.Comm. 1971, 1080.
- (104) B.L.Shaw & R.E.Stainbank.  
J.Chem.Soc. 1972, 223.
- (105) C.A.Reed & W.Roper.  
Chem.Comm. 1969, 1459.
- (106) C.A.Reed. & W.R.Roper.  
Chem.Comm. 1969, 155.

- (107) K.R.Laing & W.R.Roper.  
Chem.Comm. 1968, 1556.
- (108) H.C.Clark & K.R.Dixon.  
J.Amer.Chem.Soc. 1967, 89, 3360.
- (109) H.C.Clark , K.R.Dixon & W.J.Jacobs.  
J.Amer.Chem.Soc. 1968, 90, 2259.
- (110) T.C.Waddington  
'Non aqueous solvent systems'  
Academic Press London - New York. 1965 p.256.
- (111) E.J.Woodhouse & T.N.Norris.  
Inorg.Chem. 1971, 10, 614.
- (112) E.R.Lippincott & F.E.Welsh.  
Spectrochim.Acta. 1961, 17, 123.
- (113) M.R.Snow, J.Mc Donald, F.Basolo & J.A.Ibers.  
J.Amer.Chem.Soc. 1972, 94, 2526
- (114) A.Bondi.  
J.Phys.Chem. 1964, 68, 441.
- (115) W.Strohmeier & R.Fleischmann.  
Z.Naturforsch. 1969, 24B, 1217.
- (116) Inorganic Synthesis  
Vol (XI), pg. IO3 Method (B).
- (117) J.Chatt, B.L.Shaw & A.A.Williams.  
J.Chem.Soc. 1962, 3269.
- (118) J.Chatt, G.A.Rowe & A.A.Williams.  
Proc.Chem.Soc. 1957, 208.
- (119) W.H.Baddley & L.M.Venanzi.  
Inorg.Chem. 1966, 5, 33.
- (120) C.Panattoni, G.Bombieri & U.Belluco.  
J.Amer.Chem.Soc. 1968, 90, 798.
- (121) J.O.Glanville, J.M.Stewart & S.O.Grim.  
J.Organometallic.Chem. 1967, 7, P9.
- (122) W.J.Bland & R.D.W.Kemmitt.  
Nature. 1966, 211, 963.

- (123) W.J.Bland & R.D.W.Kemmitt.  
J.Chem.Soc. 1968, 1278.
- (124) W.J.Bland, J.Burgess & R.D.W.Kemmitt.  
J.Organometallic.Chem. 1968, 14, 201.
- (125) W.J.Bland, J.Burgess & R.D.W.Kemmitt.  
J.Organometallic.Chem. 1969, 18, 199.
- (126) M.Green, R.B.L.Osborn, A.J.Rest & F.G.A.Stone.  
Chem.Comm. 1966, 502.
- (127) L.S.Meriwether, E.C.Colthup & G.W.Kennerly.  
J.Org.Chem. 1961, 26, 5163.
- (128) M.Green, R.B.L.Osborn, A.J.Rest & F.G.A.Stone.  
J.Chem.Soc. 1968, 2525.
- (129) A.J.Mukhedkar, M.Green & F.G.A.Stone.  
J.Chem.Soc(A). 1970, 947.
- (130) A.J.Mukhedkar, M.Green & F.G.A.Stone.  
J.Chem.Soc(A). 1969, 3023.
- (131) P.Fitton & McKeon.  
Chem.Comm. 1968, 4.
- (132) D.M.Blake & R.Mersecchi.  
Chem.Comm. 1971, 1045.
- (133) B.Y.Kimura, R.D.W.Kemmitt, G.W.Littlecott & R.D.Moore.  
J.Organometallic.Chem. In press.
- (134) J.Ashley-Smith, M.Green & D.C.Wood.  
J.Chem.Soc.(A). 1970, 1847.
- (135) G.W.Littlecott.  
Ph.D. Thesis. University of Leicester  
1971.
- (136) L.Malatesta & G.Cariello.  
J.Chem.Soc. 1958, 2323.
- (137) P.Uguagliati, G.Deganello, L.Busetto & U.Belluco.  
Inorg.Chem. 1969, 8, 1625.
- (138) R.Poilblanc & J.Gallay.  
J.Organometallic.Chem. 1971, 27, C53.
- (139) D.F.Steele & T.A.Stephenson.  
Inorg.Nucl.Chem.Lett 1971, 7, 877.

- (140) L.F.Dahl, C.Martell & D.L.Wampler.  
J.Amèr.Chem.Soc. 1961, 83, 1761.
- (141) K.Klanderma & L.F.Dahl  
quoted by W.E.Oberhansli & L.F.Dahl.  
J.Organometallic.Chem 1965, 8, 43.
- (142) J.Coetzer & G.Gafner.  
Acta.Cryst 1970, B26, 985.
- (143) J.A.Ibers & R.G.Snyder.  
Acta.Cryst. 1962, 15, 923.
- (144) M.A.Bennett, R.J.H.Clark & D.L.Milner.  
Inorg.Chem. 1967, 6, 1647.
- (145) F.Bonati & G.Wilkinson.  
J.Chem.Soc. 1964, 3156.
- (146) D.Barlex.  
Ph.D. Thesis. University of Leicester.  
1970
- (147) J.Chatt & B.L.Shaw.  
J.Chem.Soc. (A) 1966, 1437.
- (148) J.Chatt & L.M.Venanzi.  
J.Chem.Soc. 1957, 4735,
- (149) F.Bonati & G.Wilkinson.  
J.Chem.Soc. 1964, 3156.
- (150) Organic Syntheses. (Collective Volume IV)  
Published JohnWiley and Sons Ltd. - LONDON.  
1963 pg.869.
- (151) R.Cramer  
Accounts.Chem.Res. 1968, 1, 186.
- (152) G.W.Parshall.  
Accounts.Chem.Res. 1970, 3, 139.
- (153) D.F.Shriver.  
Accounts.Chem.Res. 1970, 3, 231.
- (154) R.Ugo.  
Coord.Chem.Revs. 1968, 3, 319.
- (155) J.Halpern  
Adv.Chem.Series. 1968, 70, 1.

- (156) G.L. McClure & W.H. Baddley.  
J. Organometallic Chem. 1970, 25, 261.
- (157) R. Ugo, G. La Monica, F. Cariati, S. Cenini & F. Conti.  
Inorg. Chim. Acta 1970, 4, 390
- (158) MTP International Review  
Series I, Vol 9. Pg. 123.  
Butterworths
- (159) I.C. Douek & G. Wilkinson  
J. Chem. Soc. (A) 1969, 2604.
- (160) J.P. Collman & C.T. Sears.  
Inorg. Chem 1968, 7, 27.
- (161) A.J. Deeming and B.L. Shaw.  
J. Chem. Soc. (A) 1969, 1128.
- (162) R.G. Pearson & W.R. Muir.  
J. Amer. Chem. Soc 1970, 92, 5519  
160 th Amer. Chem. Soc. Nat. Meeting (Chicago)  
1970, Inorg 56.
- (163) M.A. Bennett, R.J.H. Clark & D.L. Milner.  
Inorg. Chem. 1967, 6, 1647.
- (164) H.B. Gray & A. Wojcicki.  
Proc. Chem Soc. 1960, 358.
- (165) D.M. Blake & M. Kubota.  
J. Amer. Chem. Soc. 1970, 92, 2578.
- (166) J. Halpern & P.B. Chock.  
Proc. 10th. Int. Conf. Coord. Chem. (Tokyo)  
1967, 135.
- (167) R.B. King & A. Efraty.  
J. Organometallic Chem. 1971, 27, 409.
- (168) J.A. Labinger, R.J. Braus, D. Dolphin & J.A. Osborn  
J. Chem. Soc. (D) 1970, 612.
- (169) F.R. Jensen & L.H. Gale.  
J. Amer. Chem. Soc. 1960, 82, 148.
- (170) F.R. Jensen L.D. Whipple, D.K. Wedegaertner & J.A. Landgrebe.  
J. Amer. Chem. Soc. 1960, 82, 2466.
- (171) D. Dodd & M.D. Johnson.  
J. Chem. Soc. (D) 1971, 571.

- (172) C.K. Ingold.  
Structure and Mechanism in Organic Chemistry  
2nd edition. Cornell University Press  
1971, chapter VII.
- (173) F.R. Jensen & B. Knickel,  
J. Amer. Chem. Soc. 1971, 93, 6339.
- (174) A. J. Chalk.  
J. Chem. Soc. (D) 1969, 1207.
- (175) F. DeCharentenay J.A. Osborn and G. Wilkinson.  
J. Chem. Soc. (A). 1968, 787.
- (176) K. Vrieze.  
Reference given by M.C. Baird J.T. Maque J.A. Osborn  
and G. Wilkinson.  
J. Chem. Soc. (A) 1967, 1347.
- (177) D.M. Blake & M. Kubota.  
Inorg. Chem. 1970, 9, 989.
- (178) L. Vaska.  
J. Amer. Chem. Soc. 1966, 88, 4100.
- (179) R. Craig-Taylor, J.F. Young & G. Wilkinson.  
Inorg. Chem. 1966, 5, 20.
- (180) L. Vaska.  
155th Amer. Chem. Soc. Nat. Meeting (San. Francisco)  
1968, M51.
- (181) W. Strohmeier & F.J. Muller.  
Z. Naturforsch. 1969, 24B, 931.
- (182) M.A. Bennett & D.L. Milner.  
J. Amer. Chem. Soc. 1969, 91, 6983.
- (183) L. Vaska.  
Inorg. Chim. Acta. 1971, 5, 295.
- (184) L. Vaska & L. Chen.  
J. Chem. Soc. (D) 1971, 1080.
- (185) W. Strohmeier & T. Onoda.  
Z. Naturforsch 1969, 24B, 515
- (186) W. Strohmeier & T. Onoda.  
Z. Naturforsch 1968, 23B, 1377
- (187) D.W.A. Sharp.  
J. Chem. Soc. 1957, 3716.