

SOME REACTIONS OF TRANSITION METAL HYDRIDE
COMPLEXES CONTAINING TERTIARY PHOSPHORUS LIGANDS

A Thesis submitted by

DENIS GEORGIU, B.Sc.

for the Degree of

DOCTOR OF PHILOSOPHY

of the

UNIVERSITY OF LONDON

Department of Chemistry
Royal College of Science
Imperial College of Science and Technology
London SW7 2AY

September 1973

ABSTRACT

Direct interaction of the complexes $\text{IrH}(\text{CO})(\text{PPh}_3)_3$, $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ with various alk-1-ynes has yielded the new complexes $\text{M}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$ and $\text{M}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_3$ [$\text{M} = \text{Ir}, \text{Rh}$; $\text{R} = \text{alkyl}$ or substituted alkyl] and a mechanism for the formation of these complexes is suggested. The complexes exist as bis- and tris(triphenylphosphine) species which are in equilibrium with each other in solution. The infra-red and n.m.r. spectral properties of the complexes are described.

The complexes reacted with a variety of unsaturated fluorocarbons to give adducts in which the alkynyl group remains intact. These adducts have been characterised and compared to similar fluorocarbon adducts by the use of ^{19}F n.m.r. Oxidative-addition reactions of the new complexes with other substrates are described and the alkynyl complexes have been shown to behave similarly to trans- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ in this connection. Reactions in which the alkynyl group is displaced are described and the mechanism for this displacement is suggested as being similar to that involved in the formation of the complexes.

The complexes $\text{MH}(\text{CO})(\text{PPh}_3)_3$ [$\text{M} = \text{Ir}, \text{Rh}$] have also been reacted with a variety of organic acids such as p-nitrophenol, pyridine-2-thiol, trifluoroacetic and trifluoromethylsulphonic acids and the new complexes $\text{Ir}(\text{OC}_6\text{H}_4\text{NO}_2)(\text{CO})(\text{PPh}_3)_2$, $\text{IrH}(\text{C}_6\text{H}_4\text{NS})_2(\text{PPh}_3)_X$ [$X = 1$ or 2], $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ and $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3$ have been characterised. The $\text{IrH}(\text{C}_6\text{H}_4\text{NS})(\text{PPh}_3)_X$ complex has been shown, by ^1H n.m.r. spectroscopy, to insert ethylene to quantitatively form the alkyl complex $\text{Ir}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_4\text{NS})(\text{PPh}_3)_X$. More convenient routes to the known complexes $\text{Rh}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$, $\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$ and the cationic complex $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]^+$ are given. The factors which determine whether a particular acid will react with the complexes $\text{MH}(\text{CO})(\text{PPh}_3)_3$ are discussed.

To my Parents

and

my Wife

ACKNOWLEDGEMENTS

I would like to express gratitude to Professor G. Wilkinson, F.R.S., for continual discussions during his supervision of this work; and to all my colleagues, past and present, for their friendship, advice and good (and bad) humour. My special thanks to Dr C.K. Brown for initiating me into research methods during my first year and to Messrs R. Shadwick, J. Walton, and the late H.J. Smith for technical assistance. Thanks are also due to Mrs U.O. Fowler for the efficient typing of this thesis.

I acknowledge financial support from S.R.C. during the past three years.

CONTENTS

	Page
ABSTRACT	2
ABBREVIATIONS	6
INTRODUCTION	7
A. Oxidative Addition Reactions	16
B. Reductive Elimination Reactions	18
C. Hydride Complexes of Transition Metals	18
CHAPTER I	
The Interaction of Hydridocarbonyl(tris- triphenylphosphine) Complexes of Iridium and Rhodium with Alk-1-ynes.	
A. Introduction	26
B. Preparation and Description of the Complexes	27
C. Infra-red and ^1H n.m.r. Spectra	28
D. Reactions with Unsaturated Fluorocarbons	29
E. ^1H and ^{19}F n.m.r. of the Fluorocarbon Adducts	37
F. Other Reactions	39
G. Discussion	48
CHAPTER II	
The Interaction of Hydridocarbonyl(tris- triphenylphosphine) Complexes of Iridium and Rhodium with Organic Acids.	
A. Introduction	59
B. Preparation and Description of the Complexes	62
C. Discussion	67
EXPERIMENTAL	77
REFERENCES	87

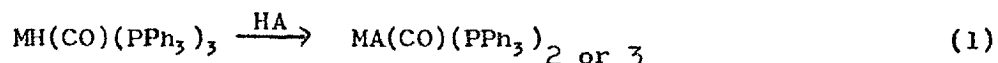
ABBREVIATIONS

acac	acetylacetonato
BIPE	1,2-bis(diphenylphosphino)ethane
Bu ⁱ	isobutyl
Bu ⁿ	<u>n</u> -butyl
Bu ^t	<u>t</u> -butyl
Cp	cyclopentadienyl
Et	ethyl
Me	methyl
Ph	phenyl
Pr ⁱ	isopropyl
g.l.c.	gas-liquid chromatography
n.m.r.	nuclear magnetic resonance
i.r.	infra-red

INTRODUCTION

This thesis is a detailed report of the experiments carried out during the period October, 1970 to May, 1973 and the conclusions of the results obtained.

The experiments are of the general type represented by the following equation (1);

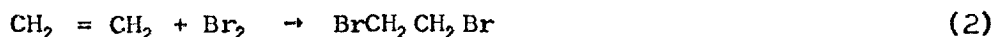


where M = Ir, Rh and HA = organic substrate with a labile hydrogen atom. The contents of this thesis can therefore be considered as being a study of how low-spin d^8 transition metal hydride complexes will react with various substrates. One particular type of reaction that low-spin d^8 complexes (whether they be hydrides, or not) will undergo is called an "oxidative addition", and this term will be continually used throughout this thesis. It is as well, therefore, to spend a little space here on a general discussion and definition of this term.

A. Oxidative Addition Reactions

Taken literally the term oxidative addition is almost self-explanatory. In very general and ideal terms if an atom [A] reacts with another atom [B] to produce a molecule [AB] then, providing that [A] is different from [B], the asymmetrical nature of this molecule will result in one atom taking a lesser share of the total electron density and, by definition, will have undergone some sort of oxidation. Supposing [A] is less electronegative than [B], then [A] will have undergone an oxidation. A possible example is the reaction of a hydrogen atom, $\text{H}^\bullet$, with a fluorine atom, $\text{F}^\bullet$, to give HF in which the hydrogen has been oxidised (and, of course, the fluorine reduced). From the point of view of the hydrogen atom the reaction it has undergone can be described as an oxidative addition. Of course, in this particular example it is of little practical use to classify the reaction in this way and bears little relationship to the present work but it serves as a starting point for the discussion. In developing the discussion a little further let us give different assignments to [A] and [B]. Let [A] and [B] represent, instead of free atoms which can have no independent existence, molecules which

are stable species in their own right and can exist independently of each other. Again, suppose reaction proceeded to give a single molecule [AB], the different electronegativities of the constituent atoms of [A] and [B] will give rise to a rearrangement of the electron density and if the drift of electrons is from [A] to [B] then [A] will have undergone an oxidative addition. A simple example of this is, for example, the reaction of ethylene (= [A]) with bromine (= [B]) to produce 1,2-dibromoethane:



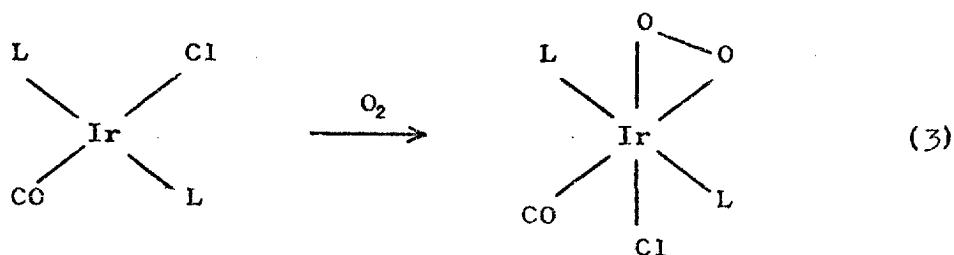
Here the ethylene has undergone an oxidative addition of ~~bromine~~. This latter example brings us nearer to the type of oxidative addition reaction which is relevant to the present work, but before we specifically discuss these types, let us consider the factors involved for the more general case.

- (i) As mentioned above the electronegativity of [A] must be less than that of [B], and when [A] and [B] represent groups of atoms the atoms involved in reaction must have a lower electronegativity in [A] than in [B]. The smaller the difference the less favourable will be this type of reaction. For example, in the above case represented by equation (2), if the adding molecule (i.e. [B]) was hydrogen then a catalyst would be required to make the reaction proceed at a respectable rate; one of the reasons being that hydrogen (atom) is less electronegative than iodine*.
- (ii) [A] must have free coordination sites which can be made available to [B] so that a stable complex, [AB], may be formed. In the example in equation (2) the carbon atoms in the olefin have a coordination number of 3 which can be expanded to 4 to accommodate the iodine atoms.

* In the hydrogenation of olefins, the electronegativity difference mentioned above is so unfavourable that an oxidative addition type of mechanism does not operate at all. Thus a metal catalyst (Ni, Pd, Pt) is required and reaction proceeds via a different mechanism giving cis addition of hydrogen, as opposed to the trans addition observed for bromination.

- (iii) [A] must have "available" electron density which can easily be removed to form a bond with [B] which will result in an effective oxidation of [A]. In equation (2) it is the weakly held π -bonding electrons in the carbon-carbon double bond which are utilised for bonding to the bromine.
- (iv) As a necessary consequence of (iii), [B] must have orbitals which are of the correct symmetry and energy to accept electron density from [A].

The type of oxidative addition reactions which are particularly relevant to the present work are those in which [A] is a transition metal complex. The central metal atom is the "active" part of the molecule as it is to this that the addendum [B] attaches itself. [B] in this case can be a wide variety of molecules but is usually fairly simple and quite often diatomic. An example of this type of oxidative addition reaction follows.



As will be noted all the elements discussed for the general case are present:

- (i) the iridium atom in the complex is considerably less electronegative than is oxygen;
- (ii) the iridium is four-coordinate initially and expands its coordination number to six (the most common coordination for transition metal complexes);
- (iii) the complex $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ has electron density lying in the metal d-orbitals which is available for bonding; and
- (iv) the oxygen molecule has low-lying, semi-filled orbitals (viz. $\pi(2p_y, z)^*$) which can accept this electron density.

Halpern⁽¹⁾ has reviewed oxidative addition reactions of low-spin d^7 , d^8 and d^{10} complexes but most studies have been carried out with

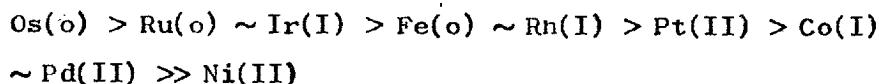
low-spin d^8 four- or five- coordinate complexes and as it is this type of complex which is directly relevant to the present work, only this type will be discussed. Of all the metals, iridium is the most widely studied in this connection, in particular the complex $\text{IrCl}(\text{CO})\text{L}_2$ ($\text{L} = \text{tertiary phosphine}$).^(2,3,4,5,6,7,8) The second most widely studied metal has been rhodium and in particular the analogue of the above iridium complex for $\text{L} = \text{PPh}_3$, i.e. $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ ^(1,9) and $\text{RhCl}(\text{PPh}_3)_3$.^(3,10,11) Other low-spin d^8 complexes studied are $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$,⁽¹²⁾ $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ ⁽¹³⁾ and some platinum(II) complexes.⁽¹⁴⁾ Below is given a short list of some of the types of addenda used in these studies on oxidative addition reactions.

Hydrogen,^(15,16,17,18) oxygen,^(16,17,19) olefins,⁽⁶⁾ acetylenes,⁽²⁰⁾ halogens,^(5,9,13,14) carbon disulphide,⁽²¹⁾ hydrogen halides,^(5,10,18) alkyl halides,^(2,5,16,18) acyl halides and aroyl halides,⁽¹⁰⁾ hydrogen cyanide,⁽²²⁾ hydrogen sulphide,⁽³⁾ fluorocarboxylic acids,⁽³⁾ carboxylic acids,⁽⁸⁾ trichlorosilane,^(11,23,24) thioketones,⁽²¹⁾ mercuric halides, acetate, cyanide and isothiocyanate.⁽⁷⁾

This list is by no means exhaustive but gives some idea of the type of molecules which have been used to oxidatively add to d^8 complexes, and of the vast volume of literature published on this type of work. As can be seen from the above list the addenda in these oxidative addition reactions can in most cases be represented by XY , where X and Y are atoms or groups of atoms which after reaction become bonded to the metal. In most of the examples a single bond joins X to Y and after reaction the groups will become completely dissociated from each other, e.g. as in the addition of hydrogen. In other examples X and Y are joined by a multiple bond and only a single bond is broken during the addition, leaving X and Y still attached to each other; this is the case for the addition of oxygen, olefins and acetylenes. Both cases are essentially the same though. The factors which determine the ease of oxidative addition have been discussed for the general case, below is given a brief outline of the factors which will effect the ease of oxidative addition reactions to low-spin d^8 complexes.

Firstly, the tendency for d^8 complexes of the GpVIII, platinum metals has been found to increase from right to left in the group and,

also, from the first to the third transition series; thus Collman and Roper⁽¹³⁾ have compiled the following series for the tendency of the metal complexes to undergo oxidative addition.*



Another factor which influences the *ability* of the complex to oxidatively add is the nature of the ligands attached to the metal atom in the complex. As oxidative addition involves the transfer of d-electron density from metal to the addendum XY, the electron-accepting powers of the ligands will obviously effect the reaction. For example, for the reaction of carboxylic acids with IrX(CO)L_2 (X = halide, L = tertiary phosphine or arsine) Deeming and Shaw⁽⁸⁾ have established the following patterns. Reaction is more complete in the series $\text{X} = \text{Cl} < \text{Br} < \text{I}$ and $\text{L} = \text{PPh}_3 < \text{AsPh}_3 < \text{PMePh}_2 < \text{PEt}_2\text{Ph} < \text{PMe}_2\text{Ph} < \text{PMe}_3$. These trends can be explained by the fact that the ligands to the left of the series can accept more metal d-electron density than can the ligands to the right of the series, thus making this d-electron density less easily available for bonding to XY. In effect the central metal atom is rendered more electropositive in proceeding from left to right in the series.

The other factor which influences addition is the nature of XY, and Vaska⁽²⁵⁾ has reviewed this. He used the value of $\nu(\text{CO})$ in the i.r. of the complex $\text{IrXYCl(CO)(PPh}_3)_2$ as the measure of the "extent" of addition, the point being that during addition the iridium has undergone a loss of d-electron density which alters the value of $\nu(\text{CO})$ as there will be less π -electron density available for back-bonding into π^* molecular orbitals of carbon monoxide. This approach of using the $\nu(\text{CO})$ value to determine the extent of reaction proves to be a very useful, convenient and valid method and has been previously used by Heck⁽²⁾ and Vaska and Diluzo⁽¹⁵⁾ for monitoring reactions. In his review Vaska has arbitrarily taken $\text{IrCl(CO)(PPh}_3)_2$ to represent iridium in its +1 oxidation state and

* It is interesting to note that this series also represents the general trend for the decrease in electronegativity, a factor already discussed.

$\nu(\text{CO})$ has a value 1967 cm^{-1} for this complex. At the other end of the scale he has taken $\text{IrCl}_3(\text{CO})(\text{PPh}_3)_2$ (i.e., oxidative addition of Cl_2) to represent iridium in its +3 oxidation state, that is, representing complete oxidative addition. $\nu(\text{CO})$ for $\text{IrCl}_3(\text{CO})(\text{PPh}_3)_2 = 2075 \text{ cm}^{-1}$. Thus for oxidative addition products having $\nu(\text{CO})$ lying between these two values a relative oxidation state can be calculated, assuming that $\nu(\text{CO})$ is a linear function of the electron density on the iridium. A summary of his results is presented in Table 1.

The first column of the table carries a comment about the stability of the adducts and it will be noted that the more stable adducts have higher $\nu(\text{CO})$ frequencies and relative oxidation state values. Another point is that $\nu(\text{CO})$ will increase with the electronegativity, oxidising power and acidity (Lewis) of XY. (All these quantities measure approximately the same thing, i.e. the ability of XY to accept electron density).

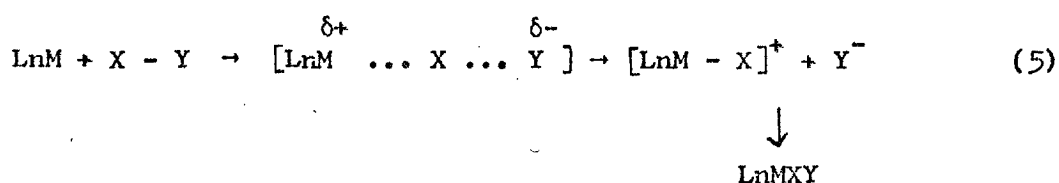
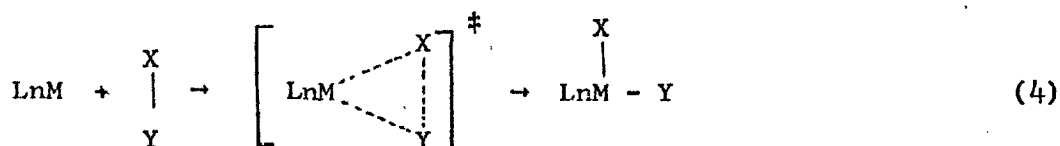
When there is a single bond between X and Y the groups X and Y are completely detached from each other in the final, six-coordinate complex. The geometrical relationship of these groups in the adduct can either be trans or cis and there have been many studies on the stereochemistry of addition. (Of course, when there is a multiple bond between X and Y addition can only be cis). Stereochemical studies are useful because they can complement the results obtained from kinetic studies on the oxidative addition reactions in elucidating the mechanism of these reactions. The kinetic and purely mechanistic studies will therefore be discussed here with the stereochemical studies, as they are complementary. Before we commence this discussion, one point has to be made. That is, when one of the groups X or Y is a hydrogen atom then the resulting adduct will be a hydride complex and XY may be described as an acid. In many ways these acids may behave differently, with reference to mechanism, owing to the special nature of the hydrogen atom. Therefore oxidative addition reactions of acids will be discussed specifically in the relevant sections in Chapter II.

Two general mechanisms can be envisaged for the oxidative addition of XY to d^8 complexes and are represented by equations (4) and (5), below. (M = metal atom, L = non-participating ligand, usually tertiary phosphine or carbon monoxide, ‡ represents the transition-state).

Table 1

Adduct Stability	Addendum	$\nu(\text{CO})$, cm^{-1} (CHCl_3 soln)	Relative oxid.state
Easily reversible	$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	1967	1.00
	O_2	2015	1.89
	SO_2	2021	2.00
	H_2	2034	2.24
Stable, reversible	HCl	2046	2.46
	CH_3I	2047	2.48
	C_2F_4	2052	2.57
	$\text{C}_2(\text{CN})_4$	2057	2.67
Stable, irreversible	BF_3	2067	2.85
	I_2	2067	2.85
	Br_2	2072	2.95
	ClI	2074	2.98
	Cl_2	2075	3.00

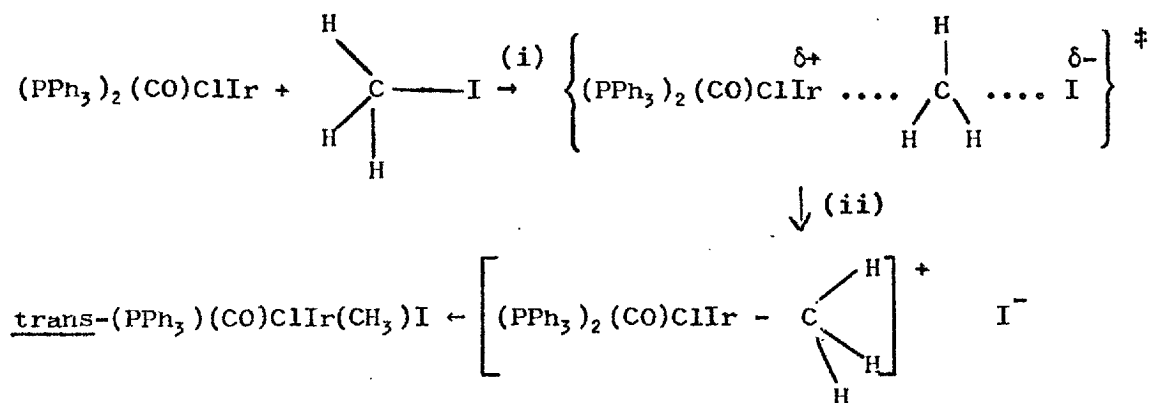
Table showing the observed $\nu(\text{CO})$ for various adducts of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, and their calculated relative oxidation states.



Equation (4) represents a single-step, concerted mechanism. The transition-state consists of the metal atom being equally bonded to both X and Y, while equation (5) represents a two-step mechanism in which the transition-state consists of the metal bound only to X or Y, giving rise to ionic products which subsequently associate to form the adduct LnMXY. The differences in the two reactions should be noted. If reaction proceeds via equation (4) then cis products would be expected, exclusively. If the reaction proceeds via a mechanism represented by equation (5) then, as a free ion is present, either cis or trans products could be expected. Also in the latter case, as ionic species are involved, one would expect reaction rates to be solvent-dependent. The exact stereochemistry of addition will depend upon various factors, i.e. trans-effect, steric hindrance, solvent effects, etc. The mechanism represented by equation (4) is favoured by addenda which have a low oxidising power and are symmetrical. Thus hydrogen has been shown to add in the cis configuration by Vaska.⁽¹⁵⁾ Similar cis additions have been shown to occur for hydrogen halides in anhydrous conditions, but trans addition has been reported in the presence of moisture or an ionising medium. These results will be discussed further in Chapter II but it is worth noting here that a mechanism represented by equation (5) seems to operate preferentially when possible. Apart from the addition of hydrogen and molecules XY which have multiple bonds, e.g. O₂, olefins, acetylenes, additions to d⁸ complexes seem to occur predominantly in the trans fashion. Early work by Chatt⁽²⁶⁾ showed that cis elimination of chlorine from PtCl₄ [P(Prⁿ)₃]₂ to give PtCl₂ [P(Prⁿ)₃]₂ took place and the

assumption was made on the grounds of microscopic reversibility that addition of chlorine and halogens in general would proceed with cis stereochemistry. However, this does not appear to be the case and Basolo and Pearson⁽¹⁴⁾ reported trans addition of halogens to various Pt(II) complexes. Collman and Sears⁽⁵⁾ have supported this finding. It would appear then that equation (5) must be operating with reaction proceeding in a similar way to the addition of bromine to olefins.⁽²⁷⁾ Evidence of this was provided by Collman and Roper⁽¹³⁾ when they isolated the ionic complex $[\text{OsX}(\text{CO})_2(\text{PPh}_3)_2]\text{X}$ from reaction mixtures of $\text{Os}(\text{CO})_3(\text{PPh}_3)_2$ and bromine or iodine (in the latter case excess iodine gave the I_3^- anion). Heating these complexes to 60° gave rise to loss of carbon monoxide and the formation of the neutral complex cis- $\text{OsX}_2(\text{CO})_2(\text{PPh}_3)_2$. Despite the contradictory reports of Collman and Sears⁽⁵⁾ who have observed trans addition of alkyl and acyl halides to $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ and Pearson and Muir⁽²⁸⁾ who have reported cis addition, the reaction of alkyl and acyl halides probably proceeds via a mechanism represented by equation (5).

Evidence is provided by Heck⁽²⁾ who observed the formation of trihalo-species $\text{MClX}_2(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{halide}$) from reactions of various alkyl halides with $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. If only the mechanism represented by equation (4) was operating then there appears to be no way that trihalo-species could have been formed, whereas reaction via equation (5) will give rise to halide ions capable of further reaction with the complexes to give the trihalo-species. Further evidence is provided by Chock and Halpern⁽¹⁶⁾ in their studies on the kinetics of addition of H_2 , O_2 and MeI to $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). They found that the reactions of H_2 and O_2 were similar and the following trend for change in the rate of reaction with change of X , i.e. $\text{I} > \text{Br} > \text{Cl}$ was found. They also found one set of activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, to apply to these two reactions. Reaction of MeI followed the opposite trend in the rate of reaction, i.e. $\text{X} = \text{Cl} > \text{Br} > \text{I}$, and completely different values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were found to apply. Also, they observed a change in rate of reaction with change of solvent for the MeI reaction, but no change for the H_2 and O_2 reactions. The conclusion derived was that the reactions with H_2 and O_2 proceeded via a concerted mechanism as represented by equation (4), while a polar mechanism as represented by equation (5) was operating for the MeI reaction, see Scheme 1.

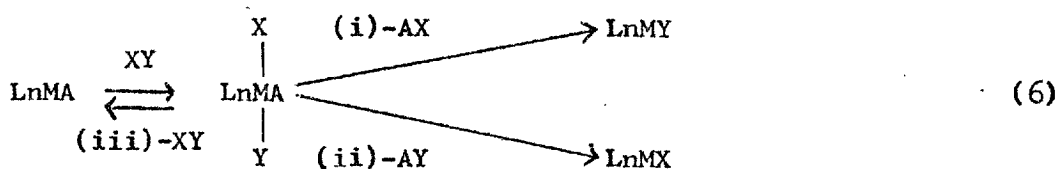
Scheme I

Scheme represents the reaction of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with MeI .

It will be noted that steps (i) and (ii) in Scheme 1 represent a simple $\text{S}_\text{N}2$ reaction. As is well known, inversion at the carbon atom always takes place in such reactions. Thus Labinger *et al.*⁽²⁹⁾ found that inversion occurred for optically active alkyl halides upon reaction with $\text{IrCl}(\text{CO})\text{L}_2$, confirming the $\text{S}_\text{N}2$ reaction suggested.

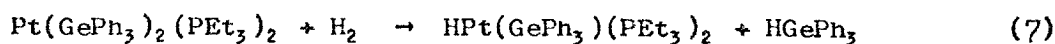
B. Reductive Elimination

Early work by Vaska⁽¹⁷⁾ on the oxidative addition of H_2 , O_2 and SO_2 to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ showed that these additions were reversible and a study of the "reversibility" of oxidative addition to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ has been made by Vaska,⁽²⁵⁾ as mentioned above. The reverse of an oxidative addition reaction is called a reductive elimination and this type of reaction will be referred to quite regularly in this thesis. Two other examples of reductive elimination reactions have been reported by Singer and Wilkinson⁽³⁾ for elimination of thiols from $\text{IrCl}(\text{RS})\text{H}(\text{CO})(\text{PPh}_3)_2$ (R = alkyl or aryl) and Chatt⁽²⁶⁾ for the elimination of chlorine from $\text{PtCl}_4[\text{P}(\text{Pr}^\text{n})_3]_2$. All the above reductive eliminations represent straight reverses of oxidative addition reactions: other possibilities can arise which are much more interesting. These are represented below:-



When XY is added to LnMA (M = Ir, Rh; A = anionic ligand, e.g. halide, alkyl, hydride, etc; L = π -acceptor ligand, tertiary phosphine or carbon monoxide) the product LnMAXY is formed. A reductive elimination may now take place in three different ways as shown in equation (6). Step (iii) is uninteresting and only yields starting materials. Steps (i) and (ii), however, not only yield new metal complexes but new compounds AX and AY, respectively. The factors which determine whether AX, AY or XY will be eliminated may be either thermodynamic or kinetic. Examples of this type of reaction are given below.

Commereuc, Douek and Wilkinson⁽³⁰⁾ have studied the reaction of $\text{RhCl}(\text{PPh}_3)_3$ with trifluoroacetic acid to give the complex $\text{RhH}(\text{CF}_3\text{CO}_2)\text{Cl}(\text{PPh}_3)_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}_2$ in dichloromethane. At refluxing benzene temperatures the complex loses hydrogen chloride to give $\text{Rh}(\text{CF}_3\text{CO}_2)(\text{PPh}_3)_2$. Cross and Glockling⁽³¹⁾ have used the following reaction to produce hydride complexes.



The reaction proceeds presumably via an oxidative addition of hydrogen to give $\text{PtH}_2(\text{GePh}_3)_2(\text{PEt}_3)_2$, which eliminates HGePh_3 . Similar reaction paths are probably followed for the formation of the hydride $\text{RhH}(\text{PPh}_3)_3$ from the reaction of hydrogen with the metal complex $\text{RhMe}(\text{PPh}_3)_3$ to eliminate methane, as studied by Keim.⁽³²⁾

This oxidative addition, followed by reductive elimination cycle is utilised in many catalytic reactions, e.g. hydrogenation, and hydroformylation of olefins. In the homogeneous catalytic hydrogenation of olefins a metal alkyl is formed by insertion of olefin into a metal-hydrogen bond; oxidative addition of hydrogen to this metal alkyl yields a metal dihydridoalkyl complex which then reductively eliminates alkane to re-form the metal hydride complex which can react with more olefin, and the cycle repeated. Other examples of the utilisation of this cycle in catalytic reactions have been reported by Singer and

Wilkinson⁽³³⁾ for the selective dimerisation of α -hydroxyacetylenes and by Furlani, Collamati and Sartori⁽³⁴⁾ for the catalytic polymerisation of phenylacetylene. These two reactions will be discussed in more detail with reference to the studies on the alkynyl complexes described in Chapter I.

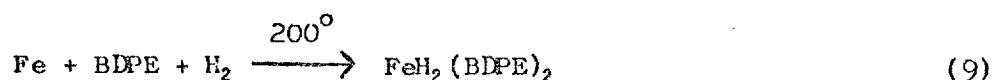
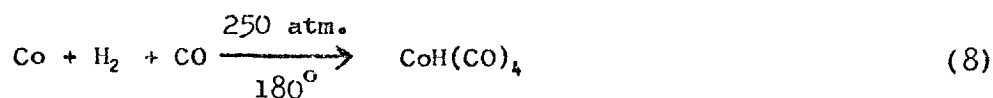
C. Hydride Complexes of Transition Metals

As mentioned above, this thesis is essentially a report of the reaction of hydride complexes with various substrates, thus a short discussion on the preparation and properties of transition metal hydrides is therefore not misplaced here.

The chemistry of transition metal hydrides is relatively new, the first ones prepared being the carbonyl hydrides $\text{FeH}_2(\text{CO})_4$ and $\text{CoH}(\text{CO})_4$ which were reported by Hieber in 1930. In 1955 Wilkinson and Birmingham reported the preparation of the hydrides $\text{MHCp}(\text{CO})_3$ ($\text{M} = \text{Cr}, \text{Mo}$). The first tertiary phosphine-containing hydride, the volatile trans- $\text{PtHCl}(\text{PEt}_3)_2$ was discovered by Chatt, Duncanson and Shaw. After these discoveries, during the period from about 1955 to the present day, many hydride complexes have been reported and recently an excellent review by Kaesz and Saillant⁽³⁵⁾ has appeared on the hydride complexes of transition metals. Other reviews of these hydrides have appeared by Ginsberg⁽³⁶⁾ and by Green and Jones.⁽³⁷⁾ Below is given a short summary of the methods of preparation of transition metal hydride complexes. In many cases there are close similarities between these preparations and the types of reactions already discussed in sections A and B.

1. Direct Hydrogenation

The hydrides $\text{CoH}(\text{CO})_4$ and $\text{FeH}_2(\text{BDPE})_2$ have been synthesised by direct interaction of the metal with hydrogen gas in the presence of the π -ligand, as given by equations (8),⁽³⁸⁾ and (9).



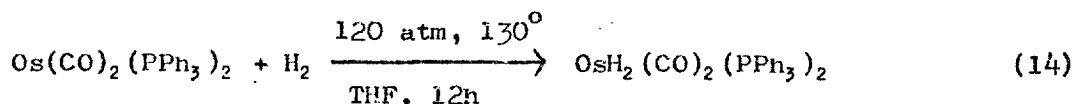
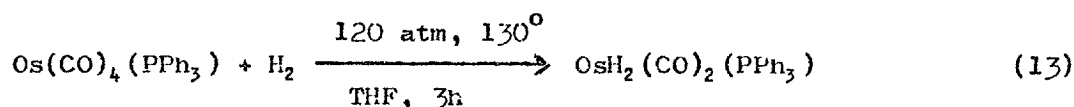
The formation of $\text{OsH}_2(\text{CO})_4$ has been studied by Eplattenier and Calderazzo⁽³⁹⁾ and various routes have been examined. (Equations (10)-(12))



Equations (11) and (12) represent a general route to the formation of hydridocarbonyl complexes, i.e. direct reaction of a metal carbonyl with hydrogen. This route has been studied by Kaesz *et al.*⁽⁴⁰⁾ and found to be widely applicable to the synthesis of most transition metal hydridocarbonyl complexes. It involves the displacement of carbon monoxide ligands by hydrogen, which brings us directly to the next general method for the synthesis of hydrides.

2. Displacement of Coordinated ligands by Hydrogen

In complexes with mixed ligands carbon monoxide is preferentially displaced to phosphine. Thus:

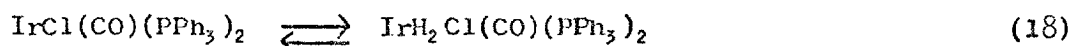


Hydrogen will also displace nitrogen in the following, (L = tertiary phosphine)



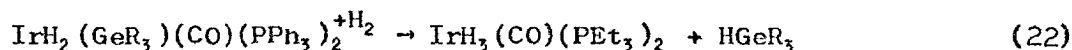
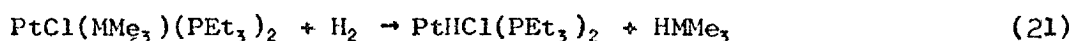
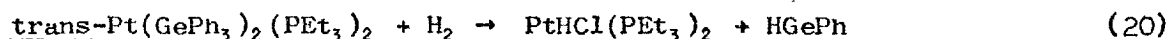
3. Oxidative Addition of Hydrogen

This is closely connected with the reactions studied in section A of this Introduction. Three examples will be given here in equations (17),⁽⁴¹⁾ (18),⁽⁴²⁾ (19)⁽⁴³⁾ (L = tertiary phosphine; X = halide; S = solvent).



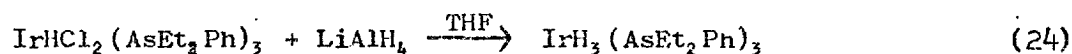
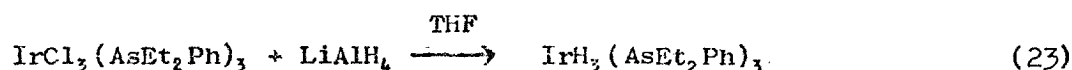
4. Hydrogenolysis of GpIV derivatives

This type of reaction described below in equations (20),⁽³¹⁾ (21),⁽⁴⁴⁾ (M = Si, Ge), and (21)⁽⁴⁵⁾ (R = Me, Et, Cl) have already been discussed in section B and the route by which the hydrides are formed can be represented by the oxidative addition-reduction elimination cycle described in that section.

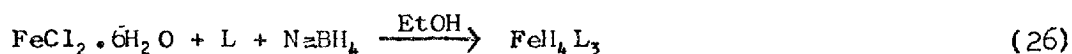
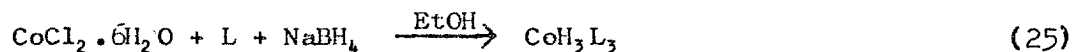


5. Reaction of MXL_n Complexes with Saline Hydrides

This is one of the most commonly used routes to the preparation of hydride complexes, where, effectively, the hydride anion is used to displace a halide ligand. Equations (23) and (24) represent this type of reaction.



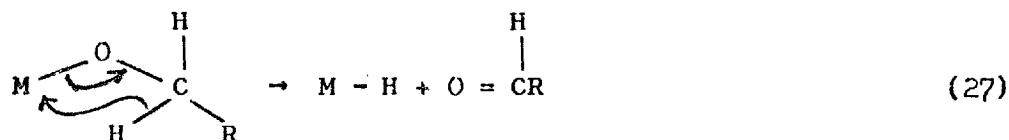
The metal halide phosphine complexes may be prepared in situ from the metal halide and tertiary phosphine and reduced immediately in a one-step synthesis. Thus the complexes CoH_3L_3 (L = PPh_3 , PEtPh_2 , PET_2Ph) have been prepared by Sacco and Rossi⁽⁴⁶⁾ (equation (25)); the complexes FeH_4L_3 (L = PEtPh_2 , PBuPh_2) by Aresta et al.⁽⁴⁷⁾ (equation (26)); and the complexes CoHL_4 and FeH_2L_3 (L = $\text{P}(\text{OEt})_3$) by Kruse and Atalla⁽⁴⁸⁾ using this method.



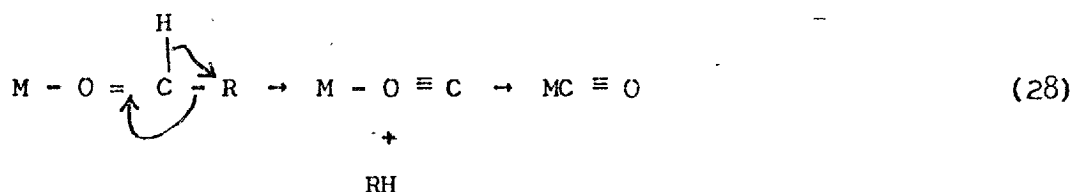
6. Hydrogen transfer from Solvent

In this method metal halide complexes are reduced to hydrides by the action of the alcoholic solvent in presence of base (usually potassium hydroxide, although triethylamine, sodium carbonate and other bases have

been used). This method was first used by Malatesta but in 1957 Chatt, Duncanson and Shaw developed it into a general method for synthesising the hydrides of Pt, Ir, Rh, Os and Ru. A mechanism for this reaction was proposed by Chatt and Shaw when they detected the presence of aldehyde in the reaction solutions. They proposed that an alkoxide group, formed by the action of base on the solvent, displaces halide ion and the following rearrangement occurs:-

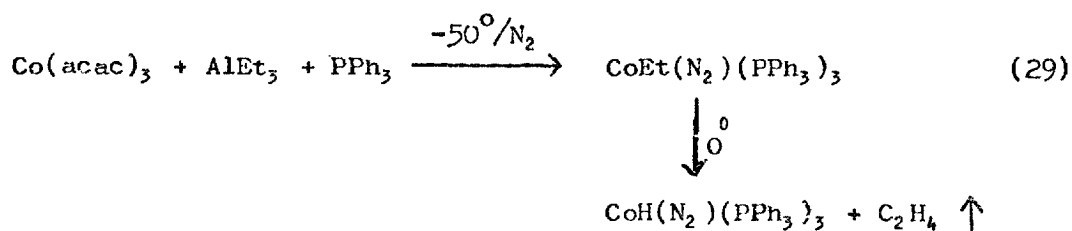


Chatt, Shaw and Field⁽⁴⁹⁾ have shown that further interaction of the aldehyde and metal complex can take place to form a carbonylhydride complex and alkane.



7. Reaction of MXL_n with Alkyls of Li, Mg and Al

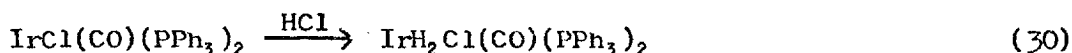
This method is similar in principle to the previous, i.e. an unstable complex is first formed which then decomposes to form the hydride. In this case metal alkyls are formed which eliminate olefin to give the hydride. Thus equation (29).⁽⁵⁰⁾



Generally when the methyls and phenyls of Li, Mg and Al are used, stable metal methyl and phenyls are obtained as these cannot eliminate olefins to give a hydride.

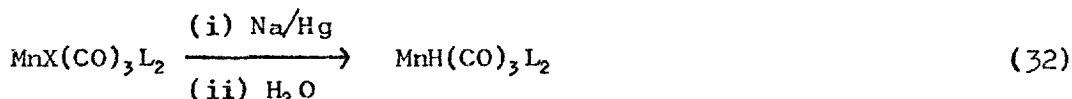
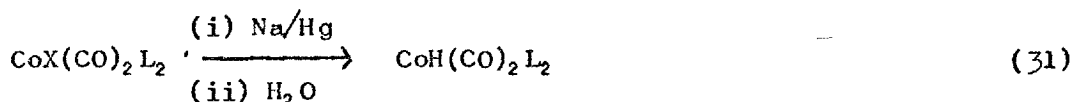
8. Oxidative Addition of Hydrogen Compounds

This has already been mentioned in section A and includes protonation of complexes by acids. A full discussion of this method will be given in Chapter II as it will be relevant to the type of reactions described in that chapter. One example here suffices.



9. Hydrolysis of Metal Anions

This method consists of preparing an anionic metal complex by sodium amalgam reduction of a metal halide complex, and hydrolysis of this by a weak acid or water. This method has been used a lot by Hieber, see equations (31), ⁽⁵¹⁾ and (32) ⁽⁵²⁾ (L = tertiary phosphine).



The above gives a very short account of the method of preparation of the hydride complexes but for a more detailed account reference should be made to the reviews mentioned at the beginning of this section. A short discussion on the properties of these hydride complexes now follows in order that the work described in Chapters I and II be presented in perspective to the known chemistry of transition metal hydride complexes.

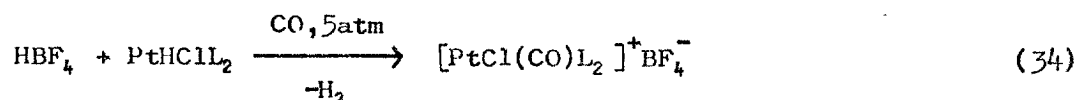
Transition metal hydride complexes are stabilised by ligands which stabilise low oxidation states, that is π -acceptor ligands. This is inherently due to the fact that many transition metal hydrides are in low oxidation states, but probably also due to the high σ -bond character of the metal to hydrogen bond which utilises the σ -electron-density on the metal thus weakening the σ -bonding to other ligands, especially the trans-ligand. This is noticed in the high trans-effect that the hydride ligand exhibits (i.e. owing to the weakening of σ -bonding to the trans-ligand and thus destabilisation of the ground state). Thus π -acceptor ligands, which utilise metal electron-density not available to the hydride ligand, are favoured, particularly in the trans position.

A general reaction that transition metal hydride complexes will undergo is with compounds containing labile hydrogen atoms, leading to loss of hydrogen. Such reactions have already been mentioned and will be discussed further in Chapters I and II. Two examples follow.

The simplest of this type of reaction is that involving two molecules of the hydride, resulting in catenation,



as studied by Ungvary and Marko.⁽⁵³⁾ Reaction of hydride complexes with strong acids can lead to loss of hydrogen and the formation of cationic species (equation (34)),⁽⁵⁴⁾ (L = tertiary phosphine).



Loss of hydrogen is also observed in the reaction of hydride complexes with halogens, hydrogenhalides, mercuric halides and with alkylhalides alkanes are obtained.



In the latter reaction (equation (38)) if carbon tetrachloride is used then chloroform is obtained and this is often used as a diagnostic test for a hydride; thus Kruse and Atalla⁽⁵⁵⁾ have used the detection of chloroform from reaction with carbon tetrachloride in determining the structures of $\text{FeH}_2[\text{P}(\text{OEt})_3]_4$ and $\text{CoH}[\text{P}(\text{OEt})_3]_4$. Sometimes reaction is not so straightforward and studies by Sacco and Rossi⁽⁴⁶⁾ on the interaction of carbon tetrachloride with $\text{CoH}(\text{N}_2)\text{L}_3$ (L = tertiary phosphine) have shown that not only chloroform, but perchloroethylene is obtained, accompanied by formation of CoCl_2L_3 .

Another general reaction that hydrides undergo is the insertion of alkenes into the metal-hydrogen bond to form alkyls, as studied by Chatt et al.⁽⁵⁶⁾ for the reversible addition of ethylene to trans- $\text{PtHBr}(\text{PEt}_3)_2$

to form trans-PtEtBr(PEt₃)₂. Olefins with substituted electronegative groups have often been used to study the insertion reactions, as these form more stable alkyls. Thus Mays and Wilkinson⁽⁵⁷⁾ have studied the formation of Co(C₂F₄H)(CN)₅³⁻ from CoH(CN)₅³⁻ and C₂F₄; and Wilford and Stone⁽⁵⁸⁾ the interaction of ReH(CO)₅ with C₂F₄, CF₂ = CFCl, CF₂ = CCl₂, and CF₃C ≡ CCF₃.

In the i.r. transition metal hydrides show absorption in the region 1850 to 2200 cm⁻¹. The intensity of the absorption can vary and it is sometimes broad; at times, therefore, the absorption is difficult to detect as in CoH(N₂)(PPh₃)₃. Church and Mays⁽⁵⁹⁾ have reported weak ν(PtH) for the complexes trans-[PtHLL'₂][ClO₄] (L = Me₃CNC, p-MeOC₆H₄NC; L' = PEt₃), while for L = Me₃CNC and L' = AsEt₃⁽⁶⁰⁾ ν(PtH) could not be detected in the i.r. However, when a carbonyl group is present there is mixing of the ν(MH) and ν(CO) modes, owing to their similar frequencies (and therefore energies). This results in strong intensity ν(MH) absorptions and also a shift in the observed frequencies attributed to ν(MH) and ν(CO) compared to the theoretical values. Thus when deuterium is substituted for hydrogen in hydridocarbonyl complexes a change in the observed ν(CO) frequency is noticed due to the smaller interaction between the ν(MD) and ν(CO) modes (i.e., there being a greater energy separation). Also, owing to this change in interaction, on substituting deuterium for hydrogen anomalous ν(MH)/ν(MD) values are obtained. These effects are greatest for hydride trans to carbon monoxide and are less marked for the second and third transition series than for the first. This behaviour observed on isotopic substitution has been used by Vaska^(61,62) to obtain information about the stereochemistry of particular hydridocarbonyl complexes.

The n.m.r. of the hydride ligand in these transition metal complexes occurs at high-field and usually falls in the range τ 15 - 35 (although in quite a few complexes resonances are observed outside this range). The reason for this high τ-value compared with that normally observed for protons in organic compounds (i.e. τ 0 - 10) has been explained as being due to two effects:

- (i) a paramagnetic shielding effect caused by the mixing of excited electronic states into the ground state; and
- (ii) the diamagnetic shielding caused by the electrons in the diffuse metal d-orbitals.

Studies on the change in position of the hydride resonance with changing trans-ligand have shown that for ligands with a high trans-influence resonance occurs at below τ 20, and for ligands with a low trans influence at above τ 20. Here, ligands with a high "trans-influence" is used to describe ligands with high trans-effects due to the weakening of the trans bond, i.e. destabilisation of the ground state. Such trends have been useful in the assignment of the stereochemistry of hydride complexes. Useful information on stereochemistry can also be obtained from the splitting patterns observed for the hydride resonance owing to spin-spin coupling with ^{31}P nuclei which have $I = \frac{1}{2}$. Studies have shown that trans phosphorus ligands give rise to a spin-spin coupling constant (J) of 60 to 180 Hz, while cis phosphorus ligands give rise to $J = 8.5$ to 30 Hz.

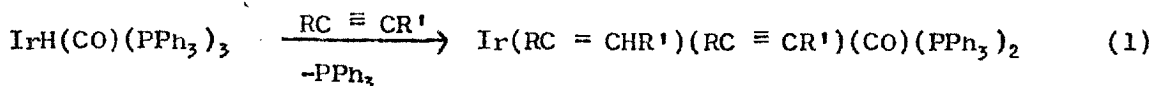
CHAPTER I

THE INTERACTION OF HYDRIDOCARBONYLTRIS(TRIPHENYLPHOSPHINE) COMPLEXES OF IRIIDIUM AND RHODIUM WITH ALK-1-YNES

A. INTRODUCTION

It has already been noted that the complexes $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ are the active catalysts for the hydroformylation and hydrogenation of alkenes and conjugated dienes and the intermediates involved in these reactions have been characterised.^(63,64) However, although these complexes will act as hydrogenation catalysts^(65,66) for alk-1-ynes they will not hydroformylate the latter under the mild conditions (e.g. 1 atm 25°) which are used for the hydroformylation of alk-1-enes.⁽⁶⁷⁾ Under more forcing conditions though (i.e. 100° , 700 lb in.⁻²; Co/H_2 , 1:1; in molten PPh_3) hydroformylation occurs and hex-1-yne is completely converted to *n*-heptanal and 2-methylhexanal (4:1) in less than 12 hr. These facts led to the supposition that fairly stable intermediates were formed from the interaction of these complexes with alk-1-ynes.

Preliminary investigations showed that refluxing solutions of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ in benzene containing an excess of hex-1-yne turned from pale yellow to orange and on addition of ethanol a pale yellow complex could be crystallised. This complex shows no absorption attributable to $\nu(\text{IrH})$ in the i.r. or any high-field resonance in the n.m.r.; furthermore, the i.r. of this complex showed a weak absorption in the $2100\text{--}2130\text{ cm}^{-1}$ region which is characteristic of a carbon-carbon triple bond. Absence of an absorption in the $1750\text{--}1600\text{ cm}^{-1}$ region excluded the possibility of the presence of a vinylic group formed by insertion of the acetylene into the iridium-hydrogen bond, as observed by Baddley and Fraser⁽⁶⁸⁾ in the interaction of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ with certain activated acetylenes, e.g. dicyanoacetylene, methyl- and ethylpropiolate, ethylphenylpropiolate, viz:-



[R = R' = CN; R = H, R' = CO₂Me or CO₂Et; R = Et, R' = CO₂Ph]

Elemental analysis finally confirmed that the new complex could be formulated as Ir(C $\equiv$ CC₄H₉)(CO)(PPh₃)₃ (if prepared in the presence of an excess of triphenylphosphine).

B. PREPARATION AND DESCRIPTION OF THE COMPLEXES

Iridium Complexes The new complexes are of the general formula Ir(C $\equiv$ CR)(CO)(PPh₃)_χ (χ = 2 or 3; R = alkyl or substituted alkyl) and can be formed by the direct interaction of an excess of the appropriate alk-1-yne (gaseous alk-1-ynes were bubbled through the refluxing solution) and IrH(CO)(PPh₃)₃ in refluxing benzene. Crystallisation by addition of ethanol affords the complexes which will crystallise either as bis- or tris(triphenylphosphine) species. A mixture of these species is obtained directly from using IrH(CO)(PPh₃)₃ but inclusion of a five-fold excess of triphenylphosphine in the reaction mixture affords the pale yellow pure tris(triphenylphosphine) complex. The orange-yellow pure bis(triphenylphosphine) complex is obtained when IrH(CO)₂(PPh₃)₂ is used as the starting material and this can easily be converted to the tris(triphenylphosphine) complex by recrystallisation from benzene-ethanol solution containing a five-fold excess of triphenylphosphine.

The complexes may also be prepared from the direct reaction between the alk-1-yne and the π-allyl species Ir(η^3 -C₃H₅)(CO)(PPh₃)₂, whereupon propene is quantitatively eliminated.

Rhodium Complexes The rhodium analogues of the iridium alkynyl complexes described above cannot be prepared using similar preparative conditions to the latter. The RhH(CO)(PPh₃)₃ - alk-1-yne system is acutely sensitive to oxygen and when attempts to prepare rhodium complexes using these conditions were made only triphenylphosphine oxide could be obtained. When RhH(CO)(PPh₃)₃ is added to a solution of freshly distilled hex-1-yne in benzene containing an excess of triphenylphosphine and this system exposed to an atmosphere of oxygen at room temperature,

slow uptake of the gas can be observed and the initially yellow solution turns to deep red. Large yields of triphenylphosphine oxide can be obtained from such solutions and catalytic oxidation of triphenylphosphine is evidently taking place. Exclusion of the hex-1-yne in a similar experiment affords no triphenylphosphine oxide and the oxidation catalyst is presumably a rhodium/acetylene complex. Solid products from these catalytic solutions could not be isolated and the nature of the catalytic species remains unknown. The catalytic oxidation of triphenylphosphine by rhodium complexes under similar mild conditions has been previously reported.⁽⁶⁹⁾

The preparation of the rhodium(I) analogues of the iridium alkynyl complexes from $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ was effected by interaction with alk-1-yne in benzene in a sealed Carius tube, with rigorous exclusion of oxygen. Red-brown solutions were obtained at room temperature from which the yellow bis(triphenylphosphine) complexes, $\text{Rh}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$, could be crystallised by addition of ethanol. The yields obtained from these reactions were low (ca 50%) and could not be improved by longer reaction times, higher reaction temperatures or by crystallisation at -80° . The deeper yellow tris(triphenylphosphine) complexes could be obtained by inclusion of a five-fold excess of triphenylphosphine in the reaction mixture.

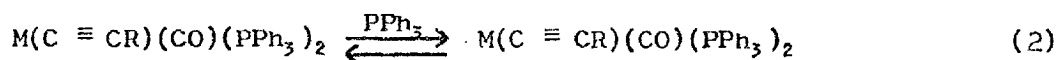
The rhodium alkynyl complexes (both bis- and tris(triphenylphosphine) species) are stable to air in the solid and only slowly decomposed in solution. The iridium analogues are also slowly decomposed by air in solution but the tris(triphenylphosphine) complex is fairly stable to air in the solid whereas the bis(triphenylphosphine) complex is slowly decomposed by air even in the solid.

The complexes are soluble in aromatic hydrocarbons, chloroform and methylene chloride, but insoluble in petroleum ether, diethyl ether and alcohols.

C. INFRA-RED AND ^1H N.M.R. SPECTRA

The infra-red and ^1H n.m.r. of the alkynyl complexes are listed in Table 1.1.

The iridium and rhodium alkynyl complexes show strong absorption in the region $1960-1985\text{ cm}^{-1}$ and weak absorption in the region $2100-2130\text{ cm}^{-1}$. The former absorption is assigned to $\nu(\text{CO})$ by comparison with similar carbonylphosphine complexes and the latter absorption to $\nu(\text{C} \equiv \text{C})$ and are in the same region as those observed for the complexes cis- and trans- $\text{Pt}(\text{C} \equiv \text{CPh})_2(\text{PPh}_3)_2$,⁽⁷⁰⁾ $\text{PtH}_2(\text{C} \equiv \text{CR})_2(\text{PPh}_3)_2$,⁽⁷¹⁾ $\text{IrHCl}(\text{C} \equiv \text{CCO}_2\text{Et})(\text{CO})(\text{PPh}_3)_2$,⁽⁷²⁾ and the gold complexes, e.g. $\text{Au}(\text{C} \equiv \text{CBu}^t)(\text{PPh}_3)_2$.⁽⁷³⁾ The bis- and tris(triphenylphosphine) alkynyl complexes have different carbonyl stretching frequencies, the separation being ca 16 cm^{-1} for the rhodium complexes. As expected the tris(triphenylphosphine) complexes show the higher $\nu(\text{CO})$ frequencies, there being less electron density available for back-bonding to the carbon monoxide antibonding orbitals. In the n.m.r. the complexes exhibit no coupling between the (e.g.) methyl group in $\text{Rh}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_2$, $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_2$ or $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ and ^{31}P or ^{103}Rh nuclei. Addition of triphenylphosphine to the solution of a bis(triphenylphosphine) complex in benzene gave rise to a shift in the resonance of the methyl group towards high-field. This shift reflected the shift in equilibrium in the following reaction:-



D. REACTIONS OF THE ALKYNYL COMPLEXES WITH UNSATURATED FLUOROCARBONS

The similarity of the alkynyl complexes with the chloro-complexes $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ is evident. As already discussed a characteristic reaction of these d^8 complexes is their ability to add oxidatively small molecules to form 1:1 adducts.^(2,12,15,25) This section describes the addition of unsaturated fluorocarbons to the new alkynyl complexes to form adducts in which the alkynyl group remains intact.

In general the addition of an unsaturated fluorocarbon, e.g. $\text{CF}_3\text{C} \equiv \text{CCF}_3$, to a d^8 complex (four- or five-coordinate) will give rise to a six-coordinate complex. Depending upon the amount of electron transfer (see Introduction, section A) the new complex may be described as being a d^8 π -bonded complex, (I) or a d^6 σ -bonded complex (II) (see Scheme 1.1).

Table 1.1

Infra-red (a) and ^1H n.m.r. (b) data of the iridium and rhodium alkynyl complexes.

Complex	Infra-red data		n.m.r.	
	$\nu(\text{CO})\text{S}$	$\nu(\text{CC})\text{W}$	τ value	J(Hz)
$\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_2$	1968	2131	8.52 s	-
$\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$	1974	2132	8.60 s ^(c)	-
$\text{Ir}(\text{C} \equiv \text{CEt})(\text{CO})(\text{PPh}_3)_2$	-	-	8.20 q,	7.5
			9.38 t	7.5
$\text{Ir}(\text{C} \equiv \text{CEt})(\text{CO})(\text{PPh}_3)_3$	1974	2124	-	-
$\text{Ir}(\text{C} \equiv \text{CBu}^{\text{n}})(\text{CO})(\text{PPh}_3)_3$	1970	2115	-	-
$\text{Ir}(\text{C} \equiv \text{CBu}^{\text{t}})(\text{CO})(\text{PPh}_3)_2$	1962	2098	9.24 s	-
$\text{Ir}(\text{C} \equiv \text{CBu}^{\text{t}})(\text{CO})(\text{PPh}_3)_2$	1971	2112	-	-
$\text{Ir}(\text{C} \equiv \text{CC}_6\text{H}_4)(\text{CO})(\text{PPh}_3)_3$	1971	2097	-	-
$\text{Ir}(\text{C} \equiv \text{CCH}_2(\text{OH}))(\text{CO})(\text{PPh}_3)_3$ (d)	1977	2123	-	-
$\text{Ir}(\text{C} \equiv \text{CC}(\text{OH})\text{Me}_2)(\text{CO})(\text{PPh}_3)_3$ (e)	1976	2118	-	-
$\text{Ir}(\text{C} \equiv \text{CC}_6\text{H}_4(\text{OH}))(\text{CO})(\text{PPh}_3)_3$ (f)	1979	2104	-	-
$\text{Rh}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_2$	1967	2124	8.53 s	-
$\text{Rh}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$	1983	2128	8.65 s ^(c)	-
$\text{Rh}(\text{C} \equiv \text{CEt})(\text{CO})(\text{PPh}_3)_2$	1967	2126	8.13 q,	7.5
			9.49 t	7.5
$\text{Rh}(\text{C} \equiv \text{CEt})(\text{CO})(\text{PPh}_3)_3$	1985	2119	-	-
$\text{Rh}(\text{C} \equiv \text{CBu}^{\text{n}})(\text{CO})(\text{PPh}_3)_3$	1978	2129	-	-

(a) Nujol mulls, cm^{-1} , all complexes show bands associated with coordinated triphenylphosphine.

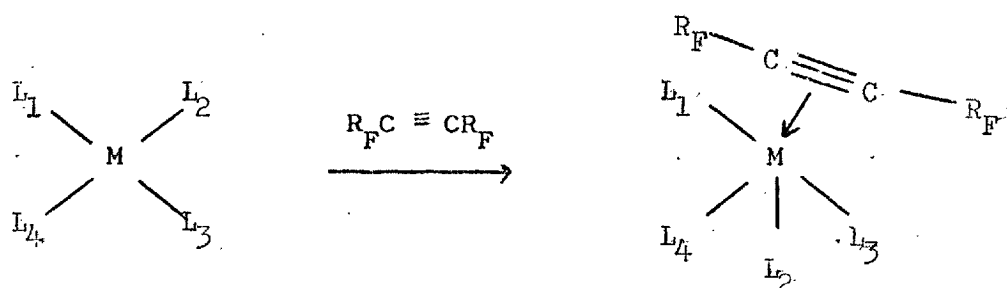
(b) In benzene at 100 MHz.

(c) In the presence of an excess of triphenylphosphine.

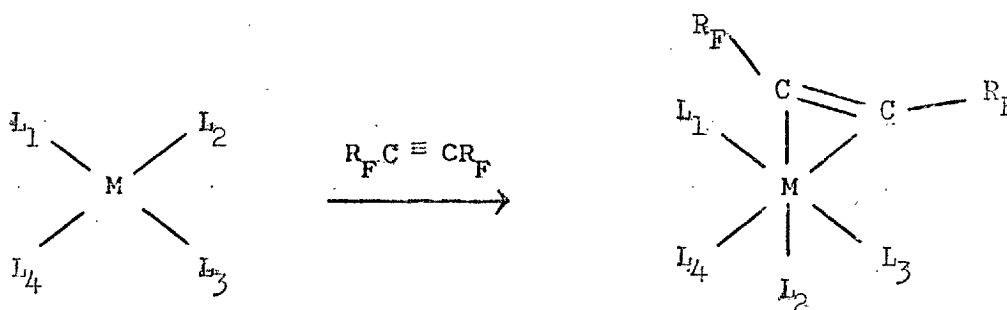
(d) $\nu(\text{OH})$ 3585 w.

(e) $\nu(\text{OH})$ 3580 w.

(f) $\nu(\text{OH})$ 3575 w.



(I)

 d^8 , π -bonded

(II)

 d^6 , σ -bondedSCHEME 1.1

(I) and (II) show the possible electronic configurations of the adducts formed between d^8 complexes and unsaturated fluorocarbon ligands.

In the former case if the metal is iridium or rhodium the central metal atom in the adduct remains in the +1 oxidation state. The latter will represent an oxidation state of +3. These two possibilities represent theoretical extremes and in practice the fluorocarbon adducts formed can rarely be assigned as having the electronic configuration represented by one or the other of these extremes (i.e. (I) or (II)), they lie somewhere between the two. When one of the other non-participating ligands (represented in Scheme 1.1 by L) is a carbonyl group the $\nu(\text{CO})$ frequency observed in the i.r. can be used as a fairly accurate indication of the extent that the adduct can be represented by the d^6 , σ -bonded configuration, (II), the more accurately that the complex can be represented as (II) (i.e. metal atom in the +3 oxidation state in the case of Ir and Rh), the higher will the frequency of $\nu(\text{CO})$ be observed. The validity of using the $\nu(\text{CO})$ value to predict the formal oxidation state of the metal atom has been discussed in section A of the Introduction. Another difference between the "extreme" structures (I) and (II) is that in (I) the carbon-carbon bond of the fluorocarbon remains formally as a triple bond whereas in (II) it is formally a double bond. If the unsaturated fluorocarbon initially had a double bond then type (I) adduct will have a carbon-carbon double bond and type (II) adduct a carbon-carbon single bond. Thus σ -bonding of an unsaturated fluorocarbon implies a reduction in the bond-order by one degree. Use can be made of this fact in the observation of the $\nu(\text{CC})$ absorption of the fluorocarbon in the i.r. and its value used as a check on the results obtained from the $\nu(\text{CO})$ values observed. The i.r. data for the fluorocarbon adducts is collected in Table 1.2 and the values observed are discussed at the end of the section. The Table also contains $\Delta\nu(\text{CO})$ values for the difference in $\nu(\text{CO})$ between the adduct and the uncomplexed bistrisphenylphosphine alkynyl, $\text{Ir}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$.

(i) Hexafluorobut-2-yne On bubbling hexafluorobut-2-yne through a solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ in benzene at room temperature rapid polymerisation of the fluorocarbon occurs to form a viscous mass. This is a similar result to that obtained by Mague and Wilkinson⁽⁷⁴⁾ for the reaction of $\text{RhCl}(\text{PPh}_3)_3$ and the above fluorocarbon. The

polymer obtained in the latter case has the same properties as that obtained from the present system and analysis of this polymer confirmed it was poly-hexafluorobut-2-yne, $(C_4F_6)_n$ (Found: F, 67.9; C, 29.0 Required: F, 70.4; C, 29.6%). Extraction from the viscous mass with chloroform excludes the insoluble polymer and the complex $Ir(C \equiv CMe)[C_2(CF_3)_2](CO)(PPh_3)_2$ may be crystallised from the solution by addition of ethanol. The complex forms as white crystals and in the solid the i.r. shows multiple bands for $\nu(CO)$ and $\nu(CC)$ (alkynyl group) suggesting solid lattice effects rather than the presence of isomers, as only a single band is observed for each of the $\nu(CO)$ and $\nu(CC)$ absorptions in chloroform solution.* There is no evidence from the i.r. that a metallo-cyclopentadiene system is formed as was observed in the interaction of hexafluorobut-2-yne with $RhCl(SbPh_3)_3$ ⁽⁷⁴⁾ or a cyclopentadienone complex as observed with $Fe(CO)_5$.

(ii) Perfluorobut-2-ene The adduct $Ir(C \equiv CMe)[(CF_3)CF \cdot CF(CF_3)](CO)(PPh_3)_2$ could be prepared by shaking a solution of $Ir(C \equiv CMe)(CO)(PPh_3)_3$ in benzene with perfluoro-but-2-ene at 3 atm. for 72 h. The complex is obtained as white crystals and the i.r. evidence suggests that the perfluorobut-2-ene is σ -bonded in a three-membered metallo ring.

(iii) Hexafluorobuta-1,3-diene The white crystals obtained by bubbling hexafluorobutadiene through a benzene solution of $Ir(C \equiv CMe)(CO)(PPh_3)_3$ at room temperature have the formula $Ir(C \equiv CMe)[CF_2CF:CF \cdot CF_2](CO)(PPh_3)_2$. The i.r. of the complex suggests that the hexafluorobutadiene is acting as a bidentate σ -bonding ligand.

(iv) Hexafluoroacetone (Although this is strictly not a fluorocarbon it fits into this section more conveniently than any other).

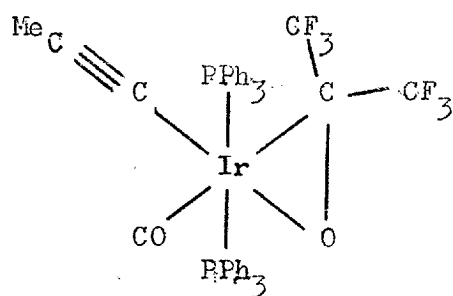
$Ir(C \equiv CMe)(CO)(PPh_3)_3$ in benzene solution reacts with hexafluoroacetone at 3 atm. and 80° to give a cream adduct, $Ir(C \equiv CMe)[(CF_3)_2CO](CO)(PPh_3)_2$ similar to $IrCl[(CF_3)_2CO](CO)(PPh_3)_2$ formed by the interaction of $IrCl(CO)(PPh_3)_2$ and hexafluoroacetone. Both the latter adduct and the present one do not show absorption in

* The possibility of isomers is not completely excluded, though, as the band observed in chloroform tends to be broad, as is expected in a polar solvent.

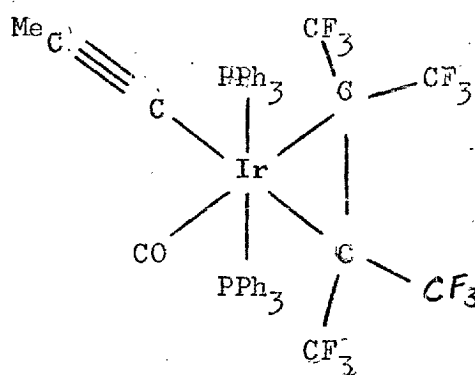
the i.r. attributable to a keto group (free $(\text{CF}_3)_2\text{CO}$ has $\nu(\text{CO})$ 1810 cm^{-1} (s)). The chloro-complex, however, is reported to exist as isomers,^(76,77) showing multiple $\nu(\text{CO})$ bands in the i.r. No evidence of isomers has been obtained with the present alkynyl complex, which shows a single, sharp absorption for $\nu(\text{CO})$.

The rhodium alkynyl complexes would not react with any of the above fluorocarbons.

(v) Discussion of the i.r. of fluorocarbon adducts As can be seen from Table 1.2 the values for $\Delta\nu(\text{CO})$ for the fluorocarbon adducts are in the range 60 - 80 for the hexafluoroacetone, hexafluorobutadiene and perfluorobut-2-ene adducts but lower for the hexafluorobut-2-yne adduct. The high shifts observed for the first group suggests that these three adducts can be regarded as being formally Ir(III) complexes and that the fluorocarbons are σ -bonded to the iridium atom. Further evidence for this lies in the fact that there was no absorption attributable to a carbon-carbon double bond for the perfluorobut-2-ene adduct or attributable to carbon-oxygen double bond for the hexafluoroacetone adduct. This suggests that these ligands are σ -bonded to the iridium forming three-membered heterocyclic rings (III and IV), the carbon-carbon and carbon-oxygen bonds being reduced by one order.

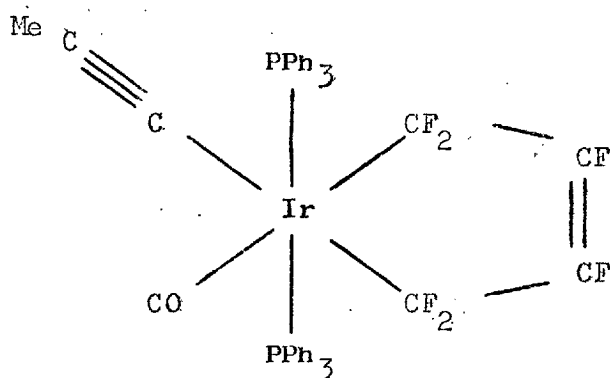


III



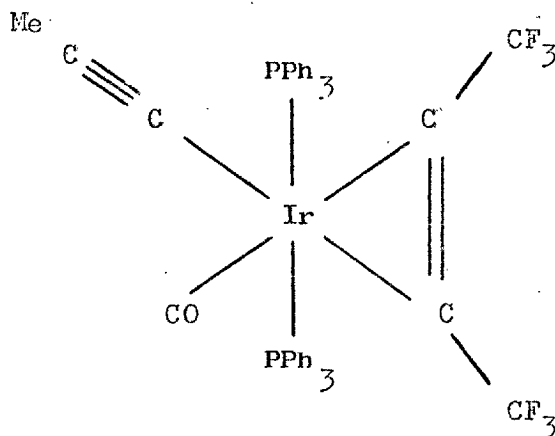
IV

For the hexafluorobutadiene adduct a strong band at 1786 cm^{-1} was observed in the i.r. A similar adduct between hexafluorobutadiene and $\text{Fe}(\text{CO})_5$ ⁽⁷⁸⁾ shows a strong band in this region which is attributable to the $\text{C} = \text{C}$ bond in the metallo-heterocycle which is formed (V).



V

The perfluorobut-2-yne adduct shows a strong band at 1749 cm^{-1} which is characteristic of a $\text{C} = \text{C}$ stretch and this suggests that the ligand is acting formally as a bidentate σ -bonded ligand (VI).



VI

As mentioned before, though, the $\Delta\nu(\text{CO})$ value for this adduct suggests that the complex cannot be represented as being $\text{Ir}(\text{III})$. This anomaly may be due to other factors effecting the $\nu(\text{CO})$ frequency (e.g. trans-effect).

Table 1.2

Infra-red data for fluorocarbon adducts of the alkynyl complexes^(a)

Complex	$\nu(\text{CO})$ (s)	$\Delta\nu(\text{CO})$	$\nu \text{CC}^{(b)}$ (w)	$\nu \text{CC}^{(c)}$ (s)
$\text{Ir}(\text{C} \equiv \text{CMe})[\text{C}_2(\text{CF}_3)_2](\text{CO})(\text{PPh}_3)_2$	(d)	-	(d)	1749
$\text{Ir}(\text{C} \equiv \text{CMe})[\text{CF}_2 \cdot \text{CF} : \text{CF} \cdot \text{CF}_2](\text{CO})(\text{PPh}_3)_2$	2041	73	2117	1786
$\text{Ir}(\text{C} \equiv \text{CMe})[(\text{CF}_3)_2\text{CO}](\text{CO})(\text{PPh}_3)_2$	2030	62	(e)	-
$\text{Ir}(\text{C} \equiv \text{CMe})[\text{CF}_3 \cdot \text{CF} : \text{CF} \cdot \text{CF}_3](\text{CO})(\text{PPh}_3)_2$	2046	78	2112	-

- (a) Nujol mulls, cm^{-1} , all complexes show bands associated with coordinated triphenylphosphine.
- (b) Alkynyl group.
- (c) Fluorocarbon group.
- (d) Multiple bands obtained in the solid at $\nu(\text{CO})$ 2016, 1989, 1986 cm^{-1} ; $\nu(\text{CC})$ 2136, 2142, 2152 cm^{-1} . In chloroform solution $\nu(\text{CO})$ 1998, $\nu(\text{CC})$ 1750 cm^{-1} .
- (e) $\nu(\text{CC})$ not discernible.

E. ^1H AND ^{19}F N.M.R. OF THE FLUOROCARBON ADDUCTS

The ^1H n.m.r. data for the adducts is listed in Table 1.3; the ^{19}F n.m.r. data is included in the text below for convenience.

There is little shift in the methyl proton resonance for the adducts except for the hexafluorobut-2-yne adduct which is shifted downfield. The signal is a narrow triplet (J ca 2.5) resulting from coupling with two equivalent or nearly equivalent ^{31}P nuclei, suggesting that both phosphines are cis to the propynyl group.

^{19}F n.m.r. spectra of the adducts were measured at 35° and 94.2 MHz relative to trifluoromethylbenzene (0 p.p.m.) in chloroform and summarized below.

(i) $\text{Ir}(\text{C} \equiv \text{CMe})[(\text{CF}_3)_2\text{C}_2](\text{CO})(\text{PPh}_3)_2$. This shows two resonances at -10.75 and -11.80 p.p.m. owing to the non-equivalent CF_3 groups. These signals each show complex splitting owing to methyl coupling and probably also with ^{31}P nuclei.⁽⁷⁹⁾ The higher field signal may be resolved as a quartet of triplets (J_1 , ca 6 Hz; J_2 , ca 3 Hz) although the lower field signal is not well resolved.

(ii) $\text{Ir}(\text{C} \equiv \text{CMe})[(\text{CF}_3)\text{CF}:\text{CF}(\text{CF}_3)](\text{CO})(\text{PPh}_3)_2$. This adduct shows a four-line spectrum with two quartets (J , ca 10 Hz) at +2.73 and +5.22 p.p.m. assigned as non-equivalent CF_3 groups, and complex multiplets at +104 and +124 p.p.m. assigned as the olefinic fluorines.

(iii) $\text{Ir}(\text{C} \equiv \text{CMe})[\text{CF}_2\cdot\text{CF}:\text{CF}:\text{CF}_2](\text{CO})(\text{PPh}_3)_2$. Studies on $\text{Fe}[\text{CF}_2\cdot\text{CF}:\text{CF}:\text{CF}_2](\text{CO})_4$ have shown an A_2X_4 pattern with two peaks of intensity ratio 2:1.⁽⁷⁸⁾ By contrast, the lack of symmetry of the iridium complex is expected to reduce this to an $AA'X_2X_2'$ pattern. Thus two signals of equal intensity centered at +29.6 and +39.7 p.p.m. are associated with the non-equivalent CF_2 groups. Both appear as a doublet of doublets with each line showing further splitting. The major coupling constants for the lower field resonance are 144 and 42 Hz while those for the higher field signal are 72 and 23 Hz. It thus seems that unequal coupling of the CF_2 groups with the A and A' olefinic fluorines gives the observed spectrum. A very complex resonance centred at +99.6 p.p.m. may be assigned to the two CF groups which are less affected by the asymmetry of the molecules and thus overlap.

(iv) $\text{Ir}(\text{C} \equiv \text{CMe})[(\text{CF}_3)_2\text{CO}](\text{CO})(\text{PPh}_3)_2$. Two multiplet signals of equal intensity at +6.95 and +9.86 p.p.m. are attributed to the non-equivalent CF_3 groups. They are in similar positions to those reported⁽⁷⁶⁾ for $\text{IrCl}[(\text{CF}_3)_2\text{CO}](\text{CO})(\text{PPh}_3)_2$, although in that case only a single signal was observed indicating equivalence of the CF_3 groups. The lower-field signal was resolved as a quartet of triplets (J_1 , ca 14.0; J_2 , ca 1.5 Hz) and the signal at higher field, although less well resolved may be associated with mutual couplings with two ^{31}P nuclei.

Table 1.3

^1H n.m.r. data^(a) for the fluorocarbon adducts

Complex	^1H n.m.r.	
	τ value	J (Hz)
$\text{Ir}(\text{C} \equiv \text{CMe})[\text{C}_2(\text{CF}_3)_2](\text{CO})(\text{PPh}_3)_2$	8.26 t	1.6
$\text{Ir}(\text{C} \equiv \text{CMe})[\text{CF}_2 \cdot \text{CF} : \text{CF} \cdot \text{CF}_2](\text{CO})(\text{PPh}_3)_2$	8.53 t	2.5
$\text{Ir}(\text{C} \equiv \text{CMe})[(\text{CF}_3)\text{CF} : \text{CF}(\text{CF}_3)](\text{CO})(\text{PPh}_3)_2$	8.53 t	2.5
$\text{Ir}(\text{C} \equiv \text{CMe})[(\text{CF}_3)_2\text{CO}](\text{CO})(\text{PPh}_3)_2$	8.71 t	2.5

(a) At 35° , 100 MHz. In CDCl_3 . t = triplet

F. OTHER REACTIONS

In addition to the fluorocarbons the alkynyl complexes will add the following - carbon monoxide, sulphur dioxide, oxygen, tetracyanoethylene, dimethylacetylenedicarboxylate, and methyl iodide, as described below. Again the shift in $\nu(\text{CO})$ (i.e. $\Delta\nu(\text{CO})$) is measured and discussed. See Table 1.4 for the i.r. data of these adducts.

(i) Carbon Monoxide On passing CO gas through the yellow solutions of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ in benzene the colour disappears and the i.r. spectrum shows new absorptions at 2020 and 1950 cm^{-1} associated with the dicarbonyl species $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})_2(\text{PPh}_3)_2$. The reaction is reversible on passage of N_2 through the solution. Attempts to isolate the solid dicarbonyl complex by filtration under CO fail, and starting material is recovered. No insertion of carbon monoxide into the metal-carbon bond is observed under these conditions and when the solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_2$ in benzene is treated with CO at 55 atm. and 80° for 12 h. loss of the alkynyl group occurs and an insoluble uncharacterised iridium-carbonyltriphenylphosphine species is formed which is also formed on treatment of $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ with CO under the same conditions. With CO and H_2 gas (1:1) at 60 atm. and 50° for 10 h. quantitative conversion of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_2$ into $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ occurs. The rhodium alkynyl complexes showed no reaction with CO at 1 atm. and 25° .

(ii) Sulphur Dioxide When sulphur dioxide is passed into a solution of $\text{Ir}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_3$ in benzene the solution becomes bright green and addition of ethanol yields the green complexes, $\text{Ir}(\text{C} \equiv \text{CR})(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$. These release sulphur dioxide on heating in vacuo at 100° with regeneration of the orange $\text{Ir}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$.

The rhodium alkynyls also add sulphur dioxide at 1 atm. and room temperature to yield the bright yellow adducts, $\text{Rh}(\text{C} \equiv \text{CR})(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$. Reaction is much slower than in the iridium case and solutions of $\text{Rh}(\text{C} \equiv \text{CR})(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$ lose sulphur dioxide to reform $\text{Rh}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$ merely on sweeping with N_2 for ca 15 min.

The i.r. spectra of both the iridium and rhodium adducts have strong bands at ca 1190 and 1040 cm^{-1} , which are assigned to the coordinated SO_2 . These are similar to the bands observed in the SO_2 adducts of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Rh}(\text{C}_2\text{F}_4\text{H})(\text{CO})(\text{PPh}_3)_2$ ⁽⁶³⁾ and hence the structures of both the iridium and rhodium adducts are probably similar to that of $\text{IrCl}(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$. ⁽⁸⁰⁾

(iii) Oxygen The bis(triphenylphosphine) iridium complexes, $\text{Ir}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$ readily add oxygen even as dry solids but the tris(triphenylphosphine) complexes are stable in air. In benzene solution both bis- and tris(triphenylphosphine) complexes readily add oxygen to form cream adducts, $\text{Ir}(\text{C} \equiv \text{CR})(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$, which are much less soluble than the starting materials. Oxygen cannot be removed from these adducts on heating at 100° in vacuo.

The medium-intensity band at 832 cm^{-1} (Table 1.4) in the i.r. is assigned to the O - O stretch by comparison with $\text{IrCl}(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$ and the alkynyl adducts probably have a similar structure. ⁽¹⁹⁾

The rhodium alkynyl complexes do not react with oxygen either in the solid state or in solution. This is surprising in view of the necessity to rigorously exclude oxygen during their preparation.

(iv) Sulphur Dioxide and Oxygen The reaction of the oxygen adduct with SO_2 or of the SO_2 adduct with O_2 to give the sulphato complex is known for $\text{Pt}(\text{O}_2)(\text{PPh}_3)_2$ ⁽⁸¹⁾ and $\text{IrCl}(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$.

For the present system, the sulphato complex, $\text{Ir}(\text{C} \equiv \text{CMe})(\text{SO}_4)(\text{CO})(\text{PPh}_3)_2$, is obtained when either $\text{Ir}(\text{C} \equiv \text{CMe})(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$ reacts with SO_2 or $\text{Ir}(\text{C} \equiv \text{CMe})(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$ reacts with O_2 , both at room temperature and atmospheric pressure.

(v) Tetracyanoethylene When a benzene solution of $\text{Ir}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$ or $\text{Rh}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$ is treated with a small excess of tetracyanoethylene at 25° an immediate reaction occurs and addition of ethanol precipitates the adducts $\text{M}(\text{C} \equiv \text{CR})[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)_2$ which are white for $\text{M} = \text{Ir}$ and yellow for $\text{M} = \text{Rh}$. These adducts have i.r. spectra similar to that for $\text{IrCl}[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)_2$. ^(72,83)

(vi) Dimethylacetylenedicarboxylate A rapid reaction occurs between dimethylacetylenedicarboxylate and a benzene solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_2$ in the cold, and addition of ethanol precipitates the white complex, $\text{Ir}(\text{C} \equiv \text{CMe})[\text{C}_2(\text{CO}_2\text{Me})_2](\text{CO})(\text{PPh}_3)_2$. The large $\Delta\nu(\text{CO})$ value (see Table 1.4) and the lowering of $\nu(\text{CC})$ for the ligand to 1745 cm^{-1} is consistent with octahedral iridium(III) with $\text{C}_2(\text{CO}_2\text{Me})_2$ acting as a bidentate ligand. ⁽⁷²⁾

The rhodium alkynyls do not add dimethylacetylenedicarboxylate.

(vii) Methyl Iodide The white crystalline adduct $\text{Ir}(\text{C} \equiv \text{CBu}^n)\text{MeI}(\text{CO})(\text{PPh}_3)_2$ was prepared by reaction of $\text{Ir}(\text{C} \equiv \text{CBu}^n)(\text{CO})(\text{PPh}_3)_3$ in benzene with a 1 molar equivalent of MeI at room temperature.

N.m.r. spectra of these Adducts The methyl proton resonance of the adducts of the iridium and rhodium propynyl complexes is generally shifted downfield relative to the starting materials (see Table 1.4), which is consistent with the metal being in a higher oxidation state. The signal is a narrow triplet (J ca 2.5 Hz) resulting from coupling with two equivalent or nearly equivalent ^{31}P nuclei, suggesting that both phosphine groups are cis to the alkynyl group. Similar splittings are probably responsible for the complex multiplet observed for the low-field CH_2 signal of adducts of the hex-1-ynyl complexes and although no splitting of the low-field quartet was resolved in the adducts of the but-1-ynyl complexes these signals are significantly broadened.

Reactions with acetylene gas and phenylacetylene When acetylene gas is bubbled through a refluxing solution of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ or $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ in benzene a deep red colour rapidly appears. Addition of ethanol to the cooled solution affords a deep red solid. Purification of this material by chromatography on alumina yields an orange solid which shows the following in the i.r.: strong bands at 1990 and 1981 cm^{-1} ; a weak band at 2120 cm^{-1} assigned as $\nu(\text{CC})$ of an ethynyl group; and a medium-intensity band at 3285 cm^{-1} assigned as $\nu(\text{CH})$ of a $-\text{C} \equiv \text{C} - \text{H}$ group. It seems that the orange material contains the complex $\text{Ir}(\text{C} \equiv \text{CH})(\text{CO})(\text{PPh}_3)_2$ and the n.m.r. of the orange material has a singlet resonance at τ 7.92 in benzene (acetylinic proton). Treatment of this orange material with oxygen gives rise to new bands in the i.r. at 2015 and 832 cm^{-1} , the band at 1981 cm^{-1} disappearing; these new bands are assigned as being $\nu(\text{CO})$ and $\nu(\text{OO})$ of the adduct $\text{Ir}(\text{C} \equiv \text{CH})(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$. Two medium-intensity bands are now observed 3290 and 3280 cm^{-1} ($\nu(\text{CH})$) while the weak band at 2120 cm^{-1} ($\nu(\text{CC})$) and the band at 1990 cm^{-1} remains unchanged. The n.m.r. now shows a triplet at τ 7.83 in benzene and τ 8.42 in chloroform ($J = 1.7$ Hz). These facts seem to confirm the presence of the complex $\text{Ir}(\text{C} \equiv \text{CH})(\text{CO})(\text{PPh}_3)_2$ ($\nu(\text{CO}) = 1981 \text{ cm}^{-1}$), similar to the alkynyl complexes described above, if one considers all the spectroscopic evidence (see Figure 1.1). The band at 1990 cm^{-1} seems to be due to some inseparable impurity which could be purely organic (i.e. polymeric), or organometallic in nature. A meaningful analysis could not be obtained for the orange material.

Table 1.4

Infra-red ^(a) and ¹H n.m.r. ^(b) data for some adducts of the alkynyl complexes

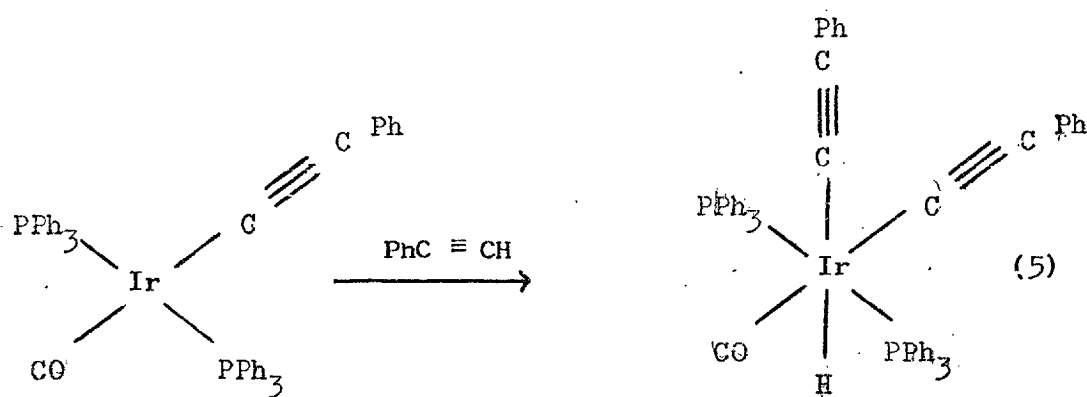
Complex	Infra-red				N.m.r.	
	$\nu(\text{CO})$ S	$\Delta\nu(\text{CO})$	$\nu(\text{CC})$ W	Other bands	τ	J (Hz)
$\text{Ir}(\text{C} \equiv \text{CMe})(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$	1998	30	2146	$\nu(\text{OO})$ 832 M	8.14 t	1.5
$\text{Ir}(\text{C} \equiv \text{CEt})(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$	1998	-	2144	$\nu(\text{OO})$ 833 M	7.72 q 9.21 t	7.5
$\text{Ir}(\text{C} \equiv \text{CBu}^t)(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$	1998	36	2133	$\nu(\text{OO})$ 834 M	-	-
$\text{Ir}(\text{C} \equiv \text{CMe})(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$	2011	43	2135	$\nu(\text{SO}_2)$ 1190 S, 1042 S	8.48 t	2.5
$\text{Ir}(\text{C} \equiv \text{CMe})(\text{SO}_4)(\text{CO})(\text{PPh}_3)_2$	2049	81	(c)	(d)	-	-
$\text{Ir}(\text{C} \equiv \text{CMe})[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)_2$	2058	90	2159	$\nu(\text{CN})$ 2229 M	8.32 t ^(e)	2.5
$\text{Ir}(\text{C} \equiv \text{CMe})[\text{C}_2(\text{CO}_2\text{Me})_2](\text{CO})(\text{PPh}_3)_2$	2004	36	2134	$\nu(\text{CC})$ 1745 S ^(f)	7.97 s ^(e) 8.48 t	
$\text{Ir}(\text{C} \equiv \text{CBu}^n)\text{MeI}(\text{CO})(\text{PPh}_3)_2$	2041	-	(c)	-	8.98 t ^(g)	5.5
$\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})_2(\text{PPh}_3)_2$ ^(h)	2027 1979	-	(c)	-	8.49 s	-
$\text{Rh}(\text{C} \equiv \text{CEt})[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)_2$	2079	112	(c)	$\nu(\text{CN})$ 2220 M	7.91 q 9.19 t	7.5 7.5
$\text{Rh}(\text{C} \equiv \text{CMe})(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$	2027	60	2118	$\nu(\text{SO}_2)$ 1200 S 1044 S	8.53 s ⁽ⁱ⁾	-

- (a) Nujol mulls, cm^{-1} , all complexes show bands associated with coordinated triphenylphosphine.
- (b) In benzene at 100 MHz.
- (c) $\nu(\text{CC})$ not discernible.
- (d) Bands consistent with bidentate sulphate coordination, at 1260 s, 1165 s, 882 s, 862 s and 660 s cm^{-1} , c.f. C.D. Cook and G.S. Janhal, J. Amer. Chem. Soc., 1967, 89, 3066.
- (e) In CDCl_3 .
- (f) Also $\nu(\text{CO}_2\text{Me})$ 1695 s, 1681 s.
- (g) Methyl attached to iridium; n-butyl signals at τ 9.18 t (J , 6.5 Hz), 8.48 m, 7.34 m (probably triplet of triplets, $J_1 = 6.0$, $J_2 = 2.0$ Hz).
- (h) Compound isolated under CO at room temperature containing $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_2$ impurity.
- (i) Signal broader than that of $\text{Rh}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_2$ but splittings unresolved.

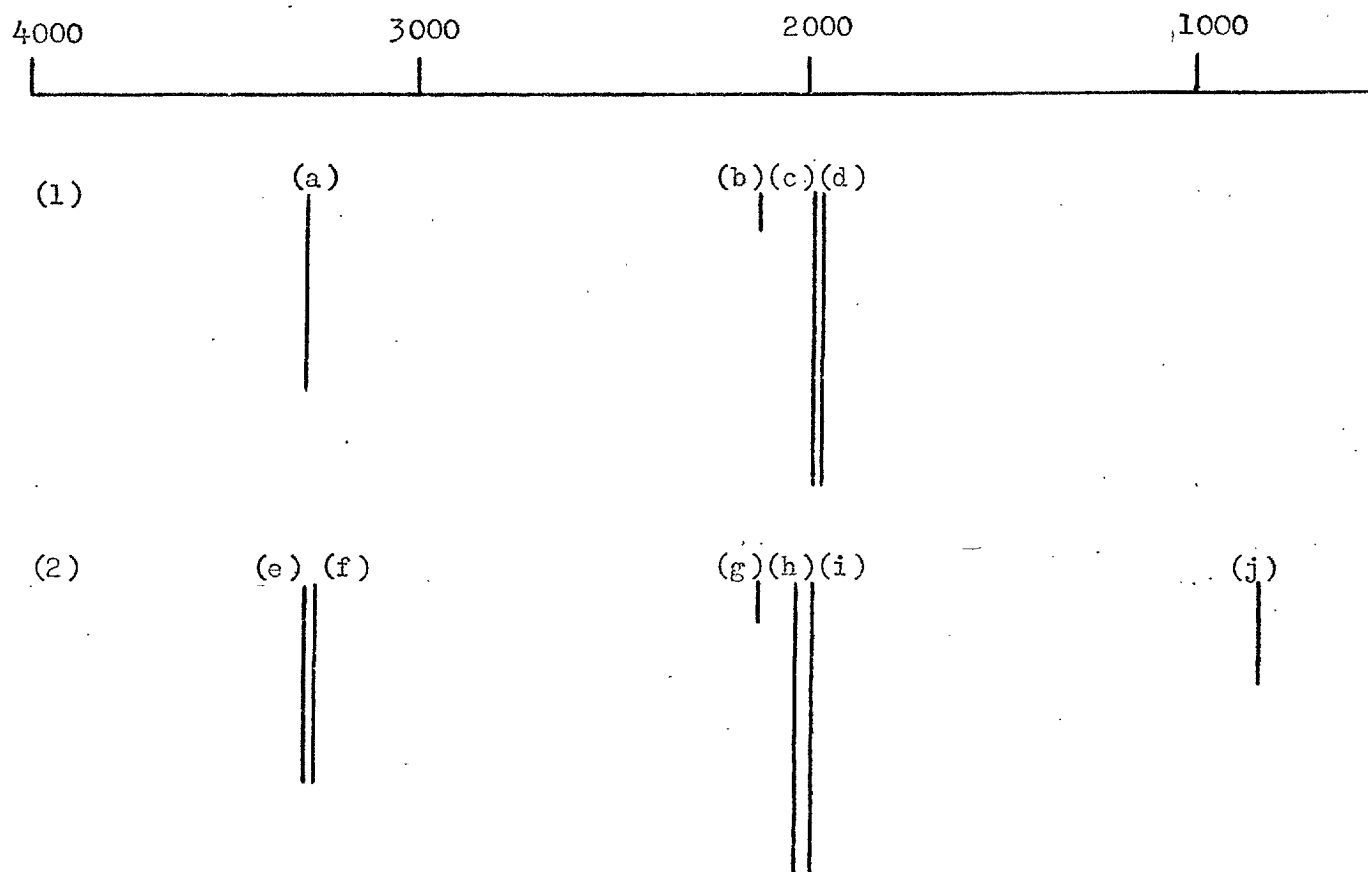
Baddley and Fraser⁽⁶⁸⁾ have reported that phenylacetylene reacts with $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ to give a white complex which analyses for two phenylacetylene molecules per $\text{Ir}(\text{CO})(\text{PPh}_3)_2$ group and having an Ir-H bond, but no further details were given.

$\text{Ir}(\text{CO})(\text{PPh}_3)_3$ Interaction of $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ or $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ in refluxing benzene with an excess of phenylacetylene gives a deep red-brown solution very rapidly from which a pale brown solid may be obtained by addition of ethanol. This solid shows absorption in the i.r. at 2152 (M), 2108 (M) and 2001 (S) cm^{-1} . This solid contains large quantities of polyphenylacetylene but chromatography on alumina leads to a white iridium complex, presumably similar to the one reported above. The i.r. of this solid shows bands at 2110 (M) and 2024 (S) cm^{-1} assigned as $\nu(\text{IrH})$ and $\nu(\text{CO})$, respectively. Both the crude material and the purified complex are very soluble in benzene to give deep red and pale yellow solutions, respectively and both show a high-field triplet resonance at τ 18.83 ($J = 15.5 \text{ Hz}$).

The complex is assigned as being $\text{IrH}(\text{C} \equiv \text{CPh})_2(\text{CO})(\text{PPh}_3)_2$ formed by the oxidative addition of phenylacetylene to the intermediate complex $\text{Ir}(\text{C} \equiv \text{CPh})(\text{CO})(\text{PPh}_3)_2$ which has been formed in an analogous manner to the other alkynyls described above, viz.



The $\nu(\text{IrH})$ band probably obscures the $\nu(\text{CC})$ absorption which could not be detected, but absence in the n.m.r. of a resonance attributable to olefinic protons precludes the possible formation of a vinylic derivative.

Figure 1.1

Infra-red spectra of orange material obtained from reaction of $\text{IrH(CO)(PPh}_3)_3$ showing change with reaction with oxygen.

- (1) Before reaction with oxygen.
- (2) After reaction with oxygen.

See Table 1.5 for actual frequencies of the bands shown.

Table 1.5

	Frequency (cm ⁻¹)	Assignment
(a)	3285 M	$\nu(\text{CH})$ (acetylinic) either in a polymer or in a complex
(b)	2120 W	$\nu(\text{CC})$, either in complex or in polymer
(c)	1990 S	-
(d)	1981 S	$\nu(\text{CO})$ in complex $\text{Ir}(\text{C} \equiv \text{CH})(\text{CO})(\text{PPh}_3)_2$
(e)	3290 M	$\nu(\text{CH})$ (acetylinic) either in a polymer or a complex
(f)	3280 M	As (e)
(g)	2120 W	$\nu(\text{CC})$ either in a complex or in a polymer
(h)	2015 S	$\nu(\text{CO})$ in oxygen adduct $\text{Ir}(\text{C} \equiv \text{CH})(\text{O}_2)(\text{PPh}_3)_2$
(i)	1990 S	-
(j)	832 M	$\nu(\text{OO})$ in oxygen adduct in (h), above

Table shows frequency values and assignments to bands given in Figure 1.1.

Furlani, Collamati and Sartori⁽³⁴⁾ have reported that the complexes $\text{Pt}(\text{PPh}_3)_4$, $\text{Pt}(\text{PPh}_3)_2$, $\text{PtCl}_2(\text{PPh}_3)_2$, $\text{PtHCl}(\text{PPh}_3)_2$ and $\text{Pt}(\text{HC} \equiv \text{CPh})(\text{PPh}_3)_2$ will act as catalysts for the polymerisation of phenylacetylene, and the catalytic behaviour of the complex $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ was studied here by the following reaction.

$\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ was heated with large excess of phenylacetylene (mole ratio 1:100) at 80° and after 24 h. all of the phenylacetylene had been converted to polymer and the complex mentioned above could be shown to be present in this mixture (i.e., by i.r. and n.m.r.). The resulting mixture from this reaction was a dark red viscous material from which the orange-yellow polymer could be obtained as a powder by dissolution in benzene and precipitation with hexane. Analysis of the powder by g.l.c. showed it to contain approximately 6% of 1, 3, 5- and 1, 2, 4-triphenylbenzene (ratio approx. 1:1), but no other volatile constituent was detected. It appears then that the polymer is predominantly linear. Analogous results were obtained by Furlani *et al.* using the platinum complexes listed above, i.e. small amounts of cyclic polymers were detected and the rest was identified as linear polymers having molecular weights in the range 1400 - 1600.

Exchange reactions Interaction of the complex $\text{Ir}(\text{C} \equiv \text{CEt})(\text{CO})(\text{PPh}_3)_3$ with phenylacetylene (six-fold excess) in a sealed n.m.r. tube (solvent, benzene) showed a rapid displacement of the but-1-ynyl group as but-1-yne (detected by n.m.r.) and the partial formation of the complex $\text{IrH}(\text{C} \equiv \text{CPh})_2(\text{CO})(\text{PPh}_3)_2$ detected by the observation of the growth of a high-field resonance at τ 18.83. Addition of a twenty-five fold excess of phenylacetylene to a solution of $\text{Ir}(\text{C} \equiv \text{CEt})(\text{CO})(\text{PPh}_3)_3$ in benzene in a sealed n.m.r. tube and heating to 80° led to:

- (a) the disappearance of the acetylenic proton resonance due to phenylacetylene;
 - (b) the growth of a high-field line at τ 18.83; and
 - (c) the growth of resonances attributable to but-1-yne.
- (a) is undoubtedly due to the polymerisation of phenylacetylene.

Similar results to the ones observed above were found in using ethylpropiolate instead of phenylacetylene. Reaction of $\text{Ir}(\text{C} \equiv \text{CEt})(\text{CO})(\text{PPh}_3)_3$ with ethylpropiolate in a sealed n.m.r. tube leads to the disappearance of the acetylenic proton resonance of ethylpropiolate and the growth of the acetylinic proton resonance due to but-1-yne. Also, growth of a high-field resonance is observed and is assigned to the formation of $\text{IrH}(\text{C} \equiv \text{CCO}_2\text{Et})_2(\text{CO})(\text{PPh}_3)_2$. Attempts to prepare the latter complex have yielded mixtures of materials which contain polyethylpropiolate and the i.r. of the mixture suggests the presence of the above complex hydride, although it has not been obtained pure.

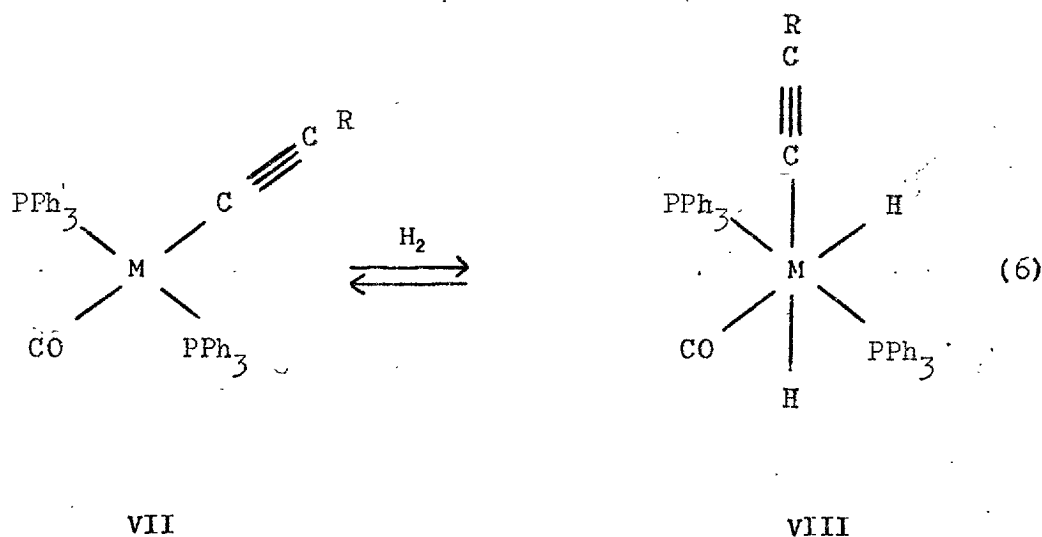
When $\text{Ir}(\text{C} \equiv \text{CEt})(\text{CO})(\text{PPh}_3)_3$ is heated with a 15-fold excess of prop-1-yne in a sealed n.m.r. tube no exchange reaction is observed, even after 48 h. at 70° . However, on heating to 190° the but-1-ynyl group is slowly displaced as free but-1-yne and the propynyl complex is formed. After 24 h. under these conditions ca 60% exchange takes place.

Although polymerisation of simple alk-1-ynes was not observed in the iridium system, treatment of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ with an excess of propylene or but-1-yne in a sealed n.m.r. tube at 80° led to the complete disappearance of the sharp resonances of the initial alkynes and their replacement by broad signals of the polymers. Polymerisation of the alk-1-yne under the conditions described in the absence of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ was not found to take place.

G. Discussion

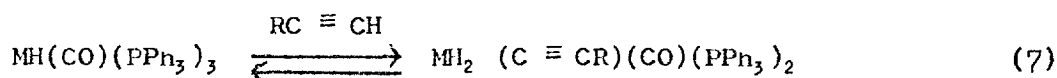
As noted above, investigations into the preparations and reactions of the alkynyl complexes described were originally prompted by a desire to prove that stable intermediates were formed by the interaction of alk-1-ynes and the complexes $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$. As expected, therefore, no reaction was observed between the alkynyl complexes and hydrogen gas at 1 atmosphere and room temperature. The analogy between trans- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and the iridium alkynyl complexes has already been mentioned and it is well known that the former complex reversibly adds hydrogen. It is interesting to note that a change in one of the ligands can significantly change the behaviour of the complex.

This change is probably due to the greater electron-accepting powers of the alkynyl group compared to chloride, thus reducing the electron density available for bonding. Both the iridium and rhodium alkynyl complexes, however, will react with hydrogen under more severe conditions (50 atm, 70⁰) and in the presence of a two-fold excess of triphenylphosphine. Reaction was shown to occur by isolating and identifying the complexes $\text{MH}(\text{CO})(\text{PPh}_3)_3$ ($\text{M} = \text{Ir}, \text{Rh}$) which was formed by the hydrogenation reaction. For $\text{Rh}(\text{C} \equiv \text{C Br}^{\text{n}})(\text{CO})(\text{PPh}_3)_3$ the organic product was shown to be n-hexane by g.l.c. It is clear, then, that the following equilibrium exists and lies more favourably to the left.



Once the dihydride is formed, presumably $\text{RC} \equiv \text{CH}$ is eliminated to give $\text{MH}(\text{CO})(\text{PPh}_3)_3$ (i.e. in the presence of PPh_3) and hydrogenation proceeds normally.^(65,66) Thus the following suggested mechanism for the formation of the alkynyl complexes seems feasible, that is $\text{RC} \equiv \text{CH}$ oxidatively adds to $\text{MH}(\text{CO})(\text{PPh}_3)_3$ as $\text{RC} \equiv \text{C}-$ and $-\text{H}$ to give the dihydride complex, (VIII). This is followed by the elimination of hydrogen to give the alkynyl complex, (VII). This oxidative addition - reductive elimination cycle has already been discussed in the Introduction.

The formation of VIII by the following reaction



can in theory be quite slow and thermodynamically not too favourable

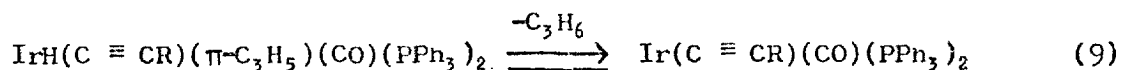
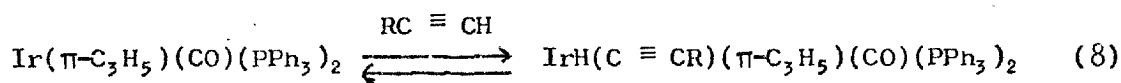
(as, indeed, seems to be the case *), but once formed will very quickly lose hydrogen to give VII via the very favourably reverse of the reaction represented in equation (7). There certainly seems to be enough precedent to suggest that the above mechanism is likely.

Collman⁽⁷²⁾ has prepared the hydridoalkynyl complexes, $\text{IrHCl}(\text{C} \equiv \text{CCO}_2\text{Et})(\text{CO})(\text{PPh}_3)_2$ by the reaction of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with ethylpropiolate.

A double oxidative addition has been proposed for the formation of $\text{PtH}_2(\text{C} \equiv \text{CR})_2(\text{PPh}_3)_2$ ⁽⁷¹⁾ from certain alk-1-ynes and $\text{Pt}(\text{PPh}_3)_4$.

Similarly, the complexes $\text{Pt}(\text{C} \equiv \text{CPh})_2(\text{PPh}_3)_2$ may be formed by the oxidative addition of phenylacetylene using $\text{Pt}(\text{PPh}_3)_4$, $\text{Pt}(\text{PPh}_3)_2$, cis- and trans- $\text{PtCl}_2(\text{PPh}_3)_2$ and trans- $\text{PtHCl}(\text{PPh}_3)_2$.⁽³⁴⁾ A mechanism similar to the one proposed above has also been proposed by Singer and Wilkinson⁽³³⁾ for the selective dimerisation of α -hydroxyacetylenes using $\text{RhCl}(\text{PPh}_3)_3$.

It was shown that the alkynyl complexes could be prepared from the reaction of $\text{Ir}(\pi\text{-C}_3\text{H}_5)(\text{CO})(\text{PPh}_3)_2$ and alk-1-yne to give propene. A similar mechanism to the one discussed above can explain this observation adequately, viz.

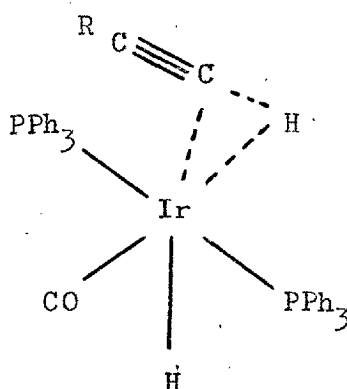


Attempts to prepare the alkynyl complexes from $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ ⁺ and alk-1-yne failed, even in the presence of triethylamine (as a hydrogen chloride acceptor). Consequently the reaction of HCl with the iridium and rhodium alkynyl complexes yielded $\text{IrHCl}_2(\text{CO})(\text{PPh}_3)_2$ and $\text{RhHCl}_2(\text{CO})(\text{PPh}_3)_2$, respectively. Clearly then, the intermediates $[\text{IrHCl}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2]$ and $[\text{RhHCl}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2]$, formed by the oxidative addition of HCl to the alkynyl complexes, are unstable with respect to loss of alk-1-yne and yield the chloro-complexes. (The $\text{MHCl}_2(\text{CO})(\text{PPh}_3)_2$ complexes are formed by the further addition of HCl to the chlorides).

* Note reaction times and conditions required to prepare the alkynyl complexes.

⁺ The reaction of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and alk-1-yne led to rapid polymerisation of the latter.

Although this mechanism for the formation of the alkynyl complexes is acceptable it is worth noting that complete oxidative addition of the alk-1-yne, i.e. total cleavage of the acetylenic hydrogen to carbon bond, $\equiv \text{C-H}$, need not necessarily take place to give formally $\text{IrH}_2(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$, as suggested above. As has been pointed out by Furlani *et al.*⁽³⁴⁾ in the termination step in the mechanism of polymerisation of phenylacetylene (which will be discussed below), coordination of phenylacetylene followed by transfer of acetylenic proton may occur without the formation of a hydride complex. Thus, although the intermediate $[\text{IrH}_2(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2]$ has been suggested above, it may be more accurate to represent the intermediate as IX.



IX

This may be thought of as being a hybrid of the purely π -bonded complex $\text{IrH}(\text{HC} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$ and the σ -bonded complex $\text{IrH}_2(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$. The important point to note here is that the acetylenic hydrogen to carbon bond has been weakened sufficiently to allow its cleavage, and thus the elimination of hydrogen. Indeed, this explanation seems to be more palatable than the first proposed mechanism, in the light of certain considerations.

If the alk-1-yne could oxidatively add to give a formal hydride then two points come to light:

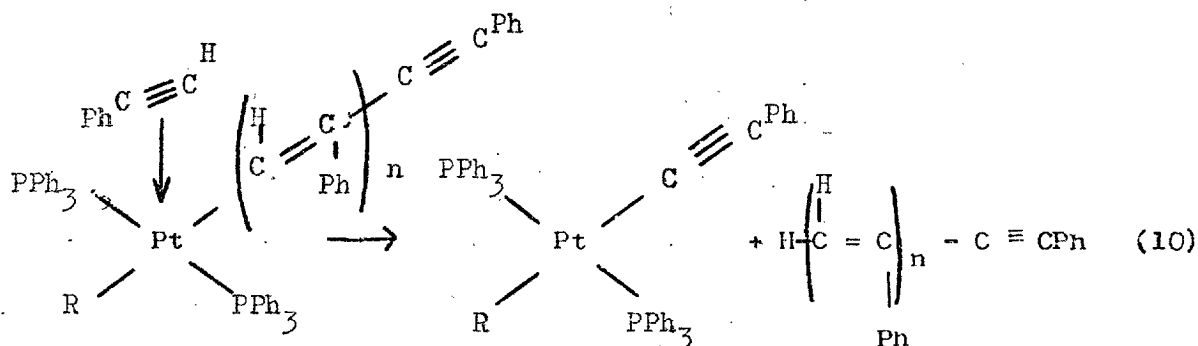
- (i) once $\text{Ir}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$ had been formed, it would be reasonable to assume that another molecule of $\text{RC} \equiv \text{CH}$ would add to this to give the hydrido-complex, $\text{IrH}(\text{C} \equiv \text{CR})_2(\text{CO})(\text{PPh}_3)_2$, as observed in the case of $\text{PhC} \equiv \text{CH}$ and $\text{HC} \equiv \text{CCO}_2\text{Et}$. Although some interaction of alk-1-yne and $\text{Ir}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$ is indicated, e.g. by (a), the orange colour of the reaction solutions from which the alkynyl complexes are obtained (this may be due to coordination of $\text{RC} \equiv \text{CH}$ to give the π -complex $\text{Ir}(\text{C} \equiv \text{CR})(\text{HC} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$ in solution) and (b) the evident polymerisation of alk-1-yne by $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, it is certainly not of such significance as for $\text{PhC} \equiv \text{CH}$ and $\text{HC} \equiv \text{CCO}_2\text{Et}$;
- (ii) the formation of $\text{IrHCl}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$ from the interaction of simple alk-1-yne, $\text{RC} \equiv \text{CH}$, and trans- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ would be expected as for ethylpropiolate.

From here on the intermediates in the formation of the alkynyl complexes will be represented by formulae of the type $[\text{MH}(\text{X})(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2]$ but it should be borne in mind that a better representation may be given by IX.

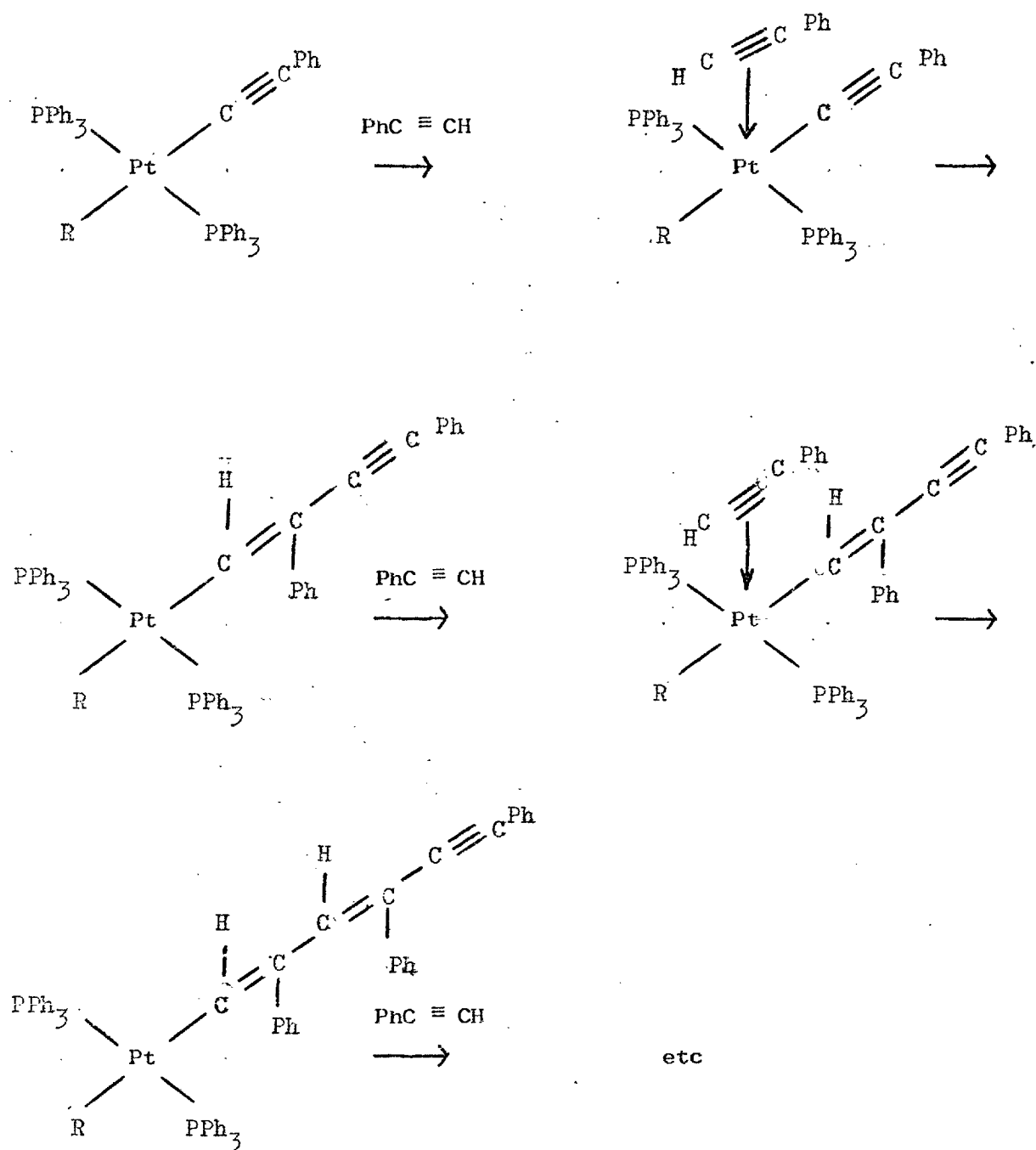
The exchange reactions observed may now be explained in a similar manner to that for the formation of the alkynyl complexes. Total displacement of the alkynyl group by phenylacetylene and ethylpropiolate to give complexes of the type $\text{IrH}(\text{C} \equiv \text{CR})_2(\text{CO})(\text{PPh}_3)_2$ ($\text{R} = \text{Ph}, \text{CO}_2\text{Et}$) can be explained by the total oxidative addition of these acetylenes to give $[\text{IrH}(\text{C} \equiv \text{CR})(\text{C} \equiv \text{CR}')(\text{CO})(\text{PPh}_3)_2]$ ($\text{R}' = \text{simple alkyl}$) which loses $\text{R}'\text{C} \equiv \text{CH}$ to give $\text{Ir}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_2$. Further addition of $\text{RC} \equiv \text{CH}$ would then yield the complexes $\text{IrH}(\text{C} \equiv \text{CR})_2(\text{CO})(\text{PPh}_3)_2$. Exchange reactions using simple alk-1-ynes only goes in 60% conversion. Presumably once the $[\text{IrH}(\text{C} \equiv \text{CR})(\text{C} \equiv \text{CR}')(\text{CO})(\text{PPh}_3)_2]$ ($\text{R}, \text{R}' = \text{alkyl}$) is formed there is little to choose between the elimination of $\text{RC} \equiv \text{CH}$ or $\text{R}'\text{C} \equiv \text{CH}$.

It was noted that reaction with phenylacetylene, ethylpropiolate and simple alk-1-ynes (in the latter case, only with rhodium system) led to polymerisation of the acetylenes. Reference is made again to Furlani, Collamati and Sartori⁽³⁴⁾ and their work on the polymerisation of phenylacetylene using the platinum catalysts (i.e. $\text{Pt}(\text{PPh}_3)_4$, $\text{Pt}(\text{PPh}_3)_2$, $\text{PtHCl}(\text{PPh}_3)_2$, $\text{PtCl}_2(\text{PPh}_3)_2$ and $\text{Pt}(\text{HC} \equiv \text{CPh})(\text{PPh}_3)_2$). Here the active

catalyst was shown to be $\text{Pt}(\text{C} \equiv \text{CPh})_2(\text{PPh}_3)_2$, presumably formed by a double oxidative addition of $\text{PhC} \equiv \text{CH}$ followed by reductive elimination of hydrogen, and the mechanism for linear polymerisation was suggested to proceed via insertion of a phenylacetylene group into a platinum to phenylacetylide bond, see Scheme 1.2. They point out that the formation of a hydride complex by formal oxidative addition of phenylacetylene followed by reductive elimination of the polymer to yield $\text{Pt}(\text{C} \equiv \text{CPh})_2(\text{PPh}_3)_2$ need not necessarily take place in order that the chain be terminated. It may occur when the acidic proton of the coordinated phenylacetylene is transferred to the chain to give back the catalyst $\text{Pt}(\text{C} \equiv \text{CPh})_2(\text{PPh}_3)_2$, as represented below in equation (10).



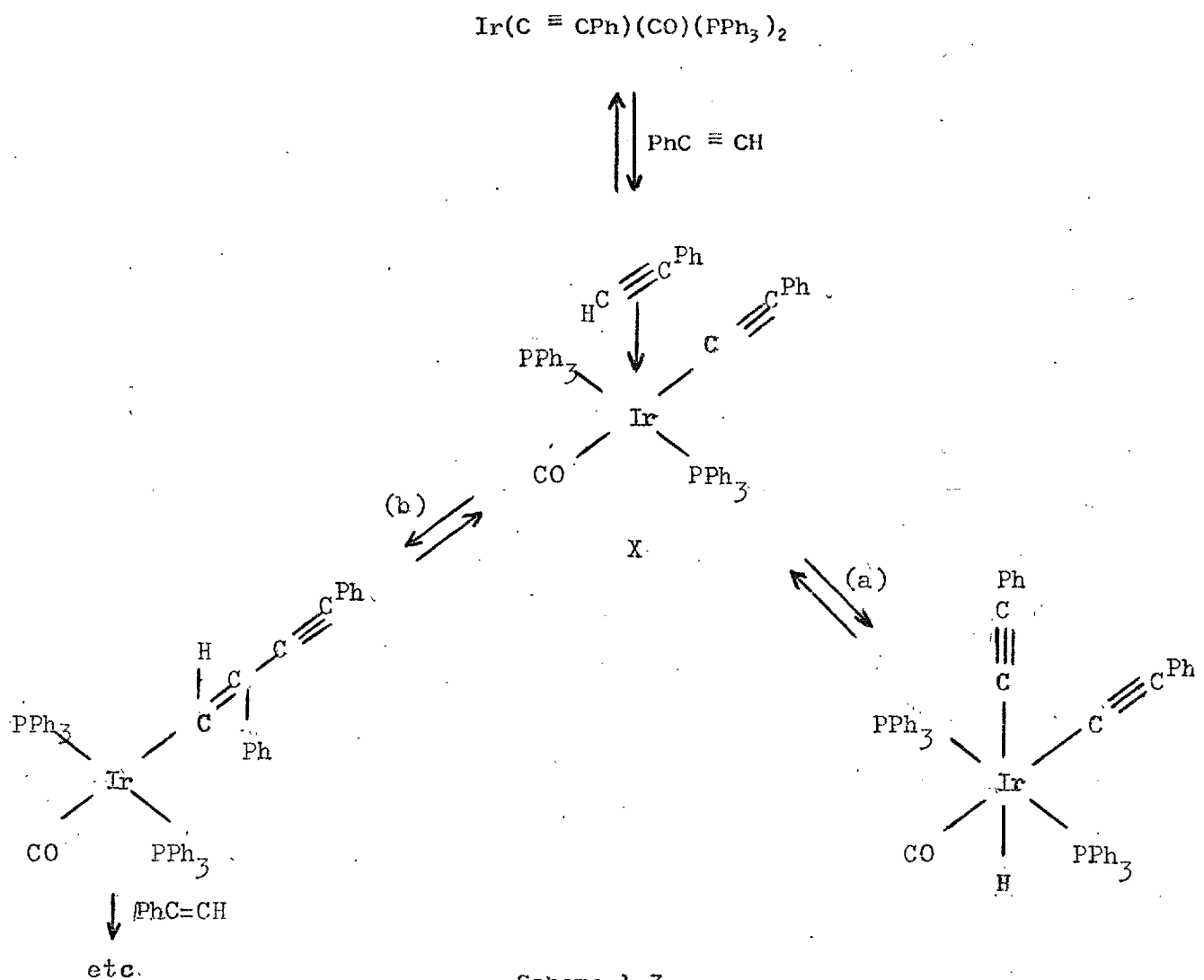
In the present case, for the polymerisation of phenylacetylene by $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ or $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$, a similar mechanism is probably operating although the nature of the catalyst is more difficult to determine. It is unlikely to be $\text{IrH}(\text{C} \equiv \text{CPh})_2(\text{CO})(\text{PPh}_3)_2$, as this is coordinatively saturated and has no vacant coordination sites available to accommodate a further phenylacetylene molecule for polymerisation to occur. The catalyst is more likely to be the complex $\text{Ir}(\text{C} \equiv \text{CPh})(\text{CO})(\text{PPh}_3)_2$ which has already been suggested as being formed as an intermediate in the formation of $\text{IrH}(\text{C} \equiv \text{CPh})_2(\text{CO})(\text{PPh}_3)_2$. The addition of a second molecule of phenylacetylene to this complex probably occurs via the π -complex $\text{Ir}(\text{C} \equiv \text{CPh})(\text{HC} \equiv \text{CPh})(\text{CO})(\text{PPh}_3)_2$ (X) formed by simple complexation of phenylacetylene. This seems likely and Chatt⁽⁸⁴⁾ has prepared the π -complex, $\text{Pt}(\text{HC} \equiv \text{CPh})(\text{PPh}_3)_2$ by simple interaction of $\text{Pt}(\text{PPh}_3)_4$ or $\text{Pt}(\text{PPh}_3)_2$ with phenylacetylene. The complex X can then rearrange to give the hydridodiacetylide species or may proceed to rearrange by



Scheme 1.2

Showing the insertion of phenylacetylene into platinum to phenylacetylide bond giving rise to linear polymerisation.

by insertion of the coordinated $\text{PhC} \equiv \text{CH}$ into the iridium-acetylide bond in a manner similar to that proposed by Furlani *et al.*, see Scheme 1.3.

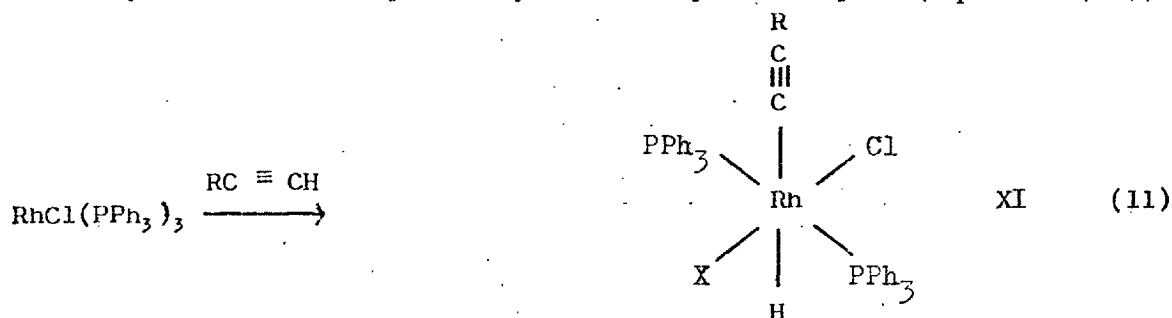


Scheme 1.3

Scheme showing a possible pathway for the polymerisation of phenylacetylene in its reaction with $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ and also the formation of the complex $\text{IrH}(\text{C} \equiv \text{CPh})_2(\text{CO})(\text{PPh}_3)_2$.

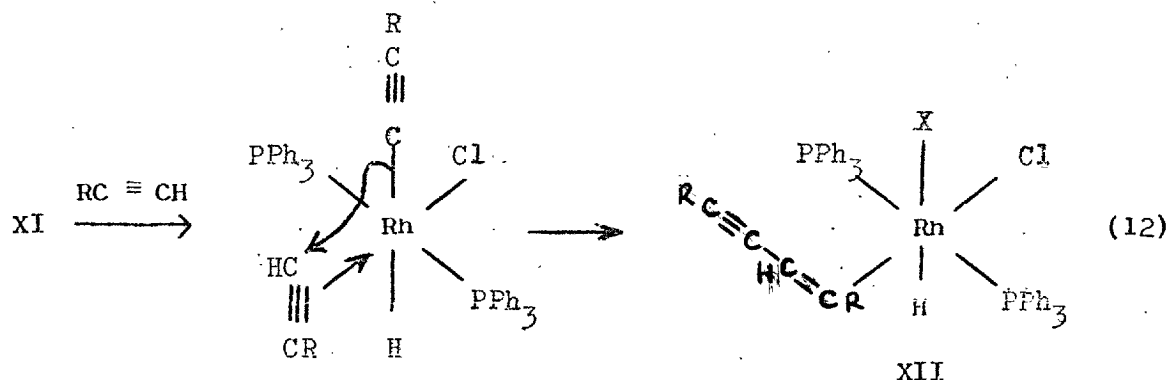
Routes (a) and (b) are reversible and in presence of excess phenylacetylene route (b) is favoured.

The mechanism described in Scheme 1.3 is similar to that proposed for the selective dimerisation of α -hydroxyacetylenes and phenylacetylene using $\text{RhCl}(\text{PPh}_3)_3$ as catalyst, as studied by Singer and Wilkinson.⁽³³⁾ Here they suggest that initial oxidative addition of acetylene occurs to give a hydrido-acetylide complex (equation (11)).



(R = Ph, α -hydroxyalkyl; X = vacant coordination site)

Another molecule of the acetylene now reacts with the complex XI to fill the vacant site, and insertion of the coordinated acetylene into the Rh-C bond occurs (equation (12)).



XII can now reductively eliminate the 3-yne-1-ene to give back the catalyst for recyclisation.

The interesting point in relation to the present discussion is that in the above case polymerisation ceases when the dimer is formed, whereas in the cases of the platinum and iridium catalysed polymerisations, reaction proceeds to give long chain polymers. The difference here is attributed to the fact that in the rhodium system the active intermediate is the hydride $\text{RhH}(\text{C} \equiv \text{CR})\text{Cl}(\text{PPh}_3)_2$, whereas the active intermediates

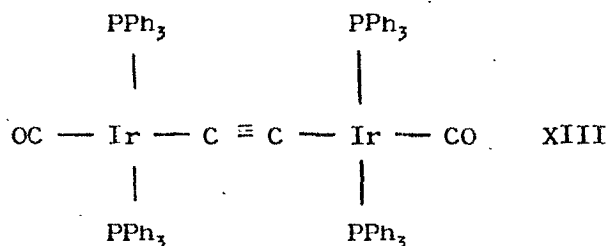
in the other systems are not hydrides, i.e. $\text{Ir}(\text{C} \equiv \text{CPh})(\text{CO})(\text{PPh}_3)_2$ and $\text{Pt}(\text{C} \equiv \text{CPh})_2(\text{PPh}_3)_2$. Thus for the rhodium case a hydrogen atom is always readily available for transfer to the metal-carbon bond, whereas for platinum and iridium, the hydrogen atom must be acquired from a coordinated acetylene molecule, in which case the insertion reaction will be in competition with the termination reaction.

As recorded above the reaction of acetylene gas with $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ or $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ yielded a mixture of products which could not be separated satisfactorily. The presence of $\text{Ir}(\text{C} \equiv \text{CH})(\text{CO})(\text{PPh}_3)_2$ was noted as one of the constituents but the other constituent(s) of the mixture could not be identified. The possibility of polymer formation was also noted. There seems to be very little work done on the complexing of acetylene gas in which the C-H bond is cleaved, and the common complexes contain π -bonded acetylenes. Two factors complicate the reaction of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ with acetylene.

- (i) The possibility that acetylene can act as a bidentate group, having the C-H bonds available for activation.
- (ii) The size of the acetylene molecule, which could allow certain modes of reactions which are not available to the other substituted acetylenes.

Bearing these two points in mind, the following possibilities are reasonable for the interaction of acetylene and $\text{IrH}(\text{CO})(\text{PPh}_3)_3$.

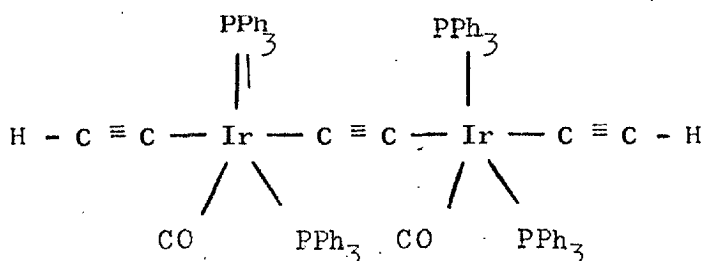
The acetylene loses both its C-H bonds and bonds to two iridium atoms, giving



This could be the complex giving rise to the band at 1990 cm^{-1} which remains unchanged on reaction with oxygen (see Figure 1.1).

Another possibility is that the acetylene molecule has formed a π -complex with $\text{Ir}(\text{C} \equiv \text{CH})(\text{CO})(\text{PPh}_3)_2$ which then inserts into the $\text{Ir} - \text{C} \equiv$ bond giving $\text{Ir} - \text{CH} = \text{CH} - \text{C} \equiv \text{CH}$. Repetition of this could yield polymers as in the case of phenylacetylene, although no evidence of this was noted.

Yet another possibility is that the complex XIII add two more molecules of acetylene, one to each iridium, and then eliminates hydrogen to yield the following:



Other suggestions are possible, but it would be pointless to speculate further; the suggestions given above are sufficient to illustrate the possibilities.

CHAPTER II

The Interaction of Hydridocarbonyltris(triphenylphosphine) Complexes of Iridium and Rhodium with Organic Acids

A. INTRODUCTION

In the previous chapter complexes of the type $MA(CO)(PPh_3)_3$ ($M = Ir, Rh$) were described where A was an alkynyl group. These complexes were prepared from the direct interaction of alk-1-yne on the hydrido complexes $IrH(CO)(PPh_3)_3$ and $RhH(CO)(PPh_3)_3$ and it was suggested that they were formed via dihydrido intermediates of the type $MH_2A(CO)(PPh_3)_2$, or pseudo-dihydrido intermediates, $[MH(H...C \equiv CR)(CO)(PPh_3)_2]$ formed by oxidative addition (or partial oxidative addition) of alk-1-yne to the hydrido complex. Thoughts on the mechanism of this reaction led to the idea of extending this type of reaction to include other substrates.

Considering the general formula of alk-1-yne as being HA, where H is the acetylinic proton then the formation of the alk-1-yne complexes can be represented by equation (1).

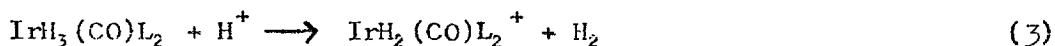
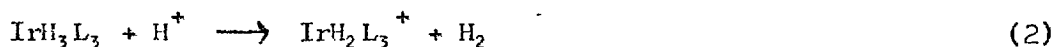


It seems reasonable to assume that if other substrates which can be represented by the general formula HA are used then similar mechanisms will operate and similar products will result. HA will represent a substrate with H being a labile or acidic proton and A being a group which can exist as an anionic moiety having a lone pair through which it can coordinate to the metal.

The addition of substrates of the type HA as described above (termed here as organic acids) to d^8 complexes to give hydrido, d^6 species has been studied extensively. For example, Wilkinson et al. have carried out the following reactions: $RhCl(PPh_3)_3$ and $IrCl(CO)(PPh_3)_2$ with hydrogen cyanide, hydrogen sulphide, toluene thiols, fluorocarboxylic,

nitric and perchloric acids to give hydrido species;⁽³⁾ $\text{RhCl}(\text{PPh}_3)$ with hydrogen chloride to give $\text{RhHCl}_2(\text{PPh}_3)_2$,⁽¹⁰⁾ with trichlorosilane to give $\text{RhH}(\text{SiCl}_3)\text{Cl}(\text{PPh}_3)_2$,⁽¹¹⁾ and with trifluoroacetic acid to give $\text{RhHCl}(\text{CF}_3\text{CO}_2)(\text{PPh}_3)_2 \cdot \frac{1}{2}$ solvent.⁽³⁰⁾ Vaska⁽⁴⁾ has studied the addition of hydrogen halides to $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$; Shaw and Steinbank⁽⁸⁵⁾ the addition of hydrogen chloride and benzoic acid to $\text{IrCl}(\text{CO})\text{L}_2$ ($\text{L} = \text{PMe}_2\text{Ph}$, PBu^tMe_2 , PBu^tEt_2 , Pbu^nEt_2 , $\text{PBu}^t\text{Pr}^n_2$, PBu^t_2Me , $\text{PBu}^t_2\text{Pr}^n$, PBu^t_2Et); and Roundhill, Tripathy and Renoe the addition of hydrogen cyanide, formic and acetic acids, picric acid, thioacetic and thiobenzoic acid and 2-mercaptobenzothiazole to $\text{Pt}(\text{PPh}_3)_4$ (the latter is a d^{10} complex, but in this example it reacts in a directly analogous way to the d^8 complexes). Similar additions to d^8 species should therefore yield d^6 dihydrido species analogous to the products obtained above.

In this particular case, however, reductive elimination of molecular hydrogen (which, energetically, is very favourable) is possible yielding a new d^8 complex in which the hydrido group has effectively been replaced by the conjugate base of the acid in question. Of course, elimination of hydrogen may not occur, and the factors which determine whether it will, have been discussed. Elimination of hydrogen by reaction of a hydrido species with an acid is a well-known reaction, but by no means does it always occur when a hydride complex is treated with acid. An interesting reaction is that studied by Malatesta, Caglio and Angoletta⁽⁸⁷⁾ in which the trihydrido species IrH_3L_3 and $\text{IrH}_3(\text{CO})\text{L}_2$ ($\text{L} = \text{tertiary phosphine}$) were reacted with acid to give dihydrido cationic complexes with elimination of hydrogen.



Further reaction of the cationic complex with acid to eliminate a second molecule of hydrogen does not occur. Cationic dihydrido species of the type indicated above have been prepared by other routes

have been shown to be stable. Collman, Vastine and Roper⁽⁸⁸⁾ have prepared $[\text{IrH}_2(\text{CO})_2(\text{PPh}_3)_2]^+$ by protonation of $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ with

Table 2.1

Infra-red (a) and n.m.r. (b) data for complexes described in Chapter II.

Complex	Infra-red			N.m.r.	
	$\nu(\text{CO})\text{S}$	$\nu(\text{IrH})\text{S}$	Other	τ	J (Hz)
$\text{Ir}(\text{OC}_6\text{H}_4\text{NO}_2)(\text{CO})(\text{PPh}_3)_2$	1941	-	-	-	-
$\text{IrH}(\text{pyS})_2(\text{PPh}_3)$	-	2143	(c)	32.3d ^(d) 31.2d ^(e)	22 22
$\text{IrH}(\text{pyS})_2(\text{PPh}_3)_2$	-	2151	(c)	31.8t ^(d) 31.5t ^(e)	17 17
$\text{Ir}(\text{C}_2\text{H}_5)(\text{pyS})_2(\text{PPh}_3)_2$	-	-	-	9.33t ^(e) 8.87m ^(e)	6.5
$[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{BPh}_4$	2000	2139, 21080	-	-	-
$\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$	2040	2243	$\nu(\text{CO}_2)$ 1700s, 1678 ^(f)	27.09t	11
$\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$	1979	-	$\nu(\text{CO}_2)$ 1710s, 1694s ^(f)	-	-
$\text{Rh}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$	1990	-	$\nu(\text{CO}_2)$ 1692s ^(f)	-	-
$[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{CF}_3\text{SO}_3$	2005	2115, 2170	(f,g)	19.61 ^(e,h) 20.9bt	
$[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{CF}_3\text{SO}_3 \cdot \text{CF}_3\text{SO}_3\text{H}$	2000	-	(f,g)	-	-

(a) Nujol mulls, cm^{-1} , all complexes show bands associated with coordinated triphenylphosphine. (b) At 100 MHz, 35°

(c) Bonds associated with coordinated pyridine-2-thiolato, i.e. 1582S, 1551M, 1148M, 1135M cm^{-1} (d) In deuteriochloroform

(e) In deuteriobenzene (f) Strong $\nu(\text{CF})$ bands in 1200-1130 cm^{-1} region.

(g) Bands in the 1450-1350 cm^{-1} region due to $\nu(\text{SO}_3)$.

(h) Virtual quartet.

hexafluorophosphoric acid; and Kong and Roundhill⁽⁸⁹⁾ have prepared $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^+$ by protonation of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ with trifluoroacetic acid.

In the present studies reaction of the complexes $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ with various organic acids has been investigated in the hope of arriving at a convenient, general synthesis of d^8 complexes via the dihydrido d^6 intermediates followed by elimination of molecular hydrogen. Although this general route has not been fully realised, success has been obtained with the following acids: p-nitrophenol, pyridine-2-thiol, trifluoroacetic and trifluoromethylsulphonic acids.

The iridium hydrido complex was observed to react also with the following acids, although products which gave consistently reliable analyses could not be obtained: 2:4-dinitrophenol, α -nitroso- β -naphthol, 2-aminothiophenol, benzothiazole-2-thiol, salicylaldehyde, o-allylphenol and thiophenol. The following acids were also tried, but no reaction was observed: phenol, p-fluorophenol, pentafluorophenol, nitromethane, o-cresol, p-cresol, ethylsalicylate, o-hydroxyacetophenone, 8-hydroxyquinoline, acetylacetone, benzyl- α -dioxime and 1,1,1-trifluoroethanol.

The reactions which gave isolable products are described below, as are the n.m.r. and i.r. data (see Table 2.1).

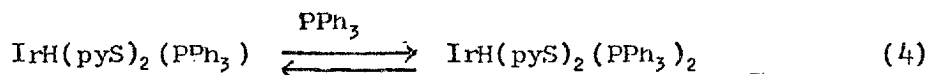
B. PREPARATION AND DESCRIPTION OF THE COMPLEXES

p-Nitrophenol Although no reaction occurred between phenol and $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ or $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ under the conditions studied, the interaction of p-nitrophenol with $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ yielded p-nitrophenato-carbonyltris(triphenylphosphine)iridium(I), $\text{Ir}(\text{OC}_6\text{H}_4\text{NO}_2)(\text{CO})(\text{PPh}_3)_2$. This complex was obtained as pale yellow microcrystals by refluxing the hydride complex and p-nitrophenol in toluene, cooling and crystallisation by addition of ethanol. The complex was characterised by i.r. spectroscopy, analysis and molecular weight measurements.

The p-nitrophenato group could be displaced from the complex as p-nitrophenol by reaction with a strong acid, e.g. HCl to give $\text{IrHCl}_2(\text{CO})(\text{PPh}_3)_2$.

p-Nitrophenol did not appear to react with the rhodium analogue, $\text{RhH}(\text{CO})(\text{PPh}_3)_3$.

Pyridine-2-thiol (pySH) The interaction of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ with pyridine-2-thiol in refluxing toluene yields a yellow complex on crystallisation with ethanol. The i.r. of the complex in the region $2400 - 1800 \text{ cm}^{-1}$ showed only a single, sharp band which was assigned as $\nu(\text{IrH})$. Absorption attributable to a carbonyl stretching mode was not observed. This yellow complex was therefore assigned the formula $\text{IrH}(\text{pyS})_2(\text{PPh}_3)_X$. When a six-fold excess of triphenylphosphine was included in the reaction mixture the pure complex, reliably analysing for $\text{IrH}(\text{pyS})_2(\text{PPh}_3)_2$ was obtained. Normally (i.e., omission of an excess of PPh_3) a mixture was obtained where $X = 1$ or 2 . Thus, recrystallisation of this mixture from toluene-ethanol yields the pure mono(triphenylphosphine) complex, $\text{IrH}(\text{pyS})_2(\text{PPh}_3)$. The following equilibrium in solution is thus suggested.

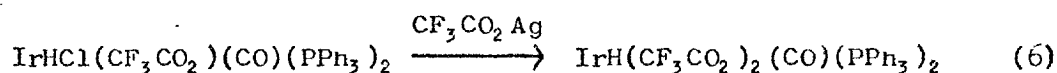
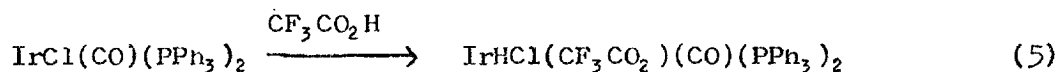


N.m.r. studies confirmed this equilibrium. A high-field doublet (see Table 2.1) was observed for a solution of the pure mono(triphenylphosphine) complex in benzene. On addition of a six-fold excess of PPh_3 to this solution a new high-field resonance, which was a triplet, grew in intensity at the expense of the initial high-field doublet. This reaction was only very slow at 35° ; a sharp triplet being obtained only after 48 h. when no doublet could be detected.

$\text{IrH}(\text{pyS})_2(\text{PPh}_3)_2$ failed to react with ethylene at 3 atm. pressure and room temperature in an n.m.r. tube, even after 48 h., but on heating this system to 85° and holding it at this temperature for 16 h., the high-field triplet collapsed and was replaced by a normal lower-field ethyl resonance. Reaction was quantitative, the relative intensities of the final ethyl group to the initial hydride being 5:1. The ethyl complex appears to be unstable with respect to loss of ethylene at atmospheric pressure and seems only to exist under pressure in a sealed system and attempts to prepare the solid ethyl complex, $\text{Ir}(\text{C}_2\text{H}_5)(\text{pyS})_2(\text{PPh}_3)_X$ failed.

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$ was found to react with pyridine-2-thiol to give a dark red complex which could not be characterised.

Trifluoroacetic Acid When $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ is refluxed in toluene with a large excess of trifluoroacetic acid a colourless solution is obtained from which a white complex may be precipitated by addition of light petroleum or ether. This complex was shown to be $\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$ and has previously been prepared by Singer and Wilkinson⁽³⁾ by the following reactions (equations (5) and (6)).



The present synthesis is obviously more convenient.

The complex was assigned the formula $\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$ by considering analytical data and by comparing the spectral properties of this complex and the complex obtained by Singer and Wilkinson.

Independent studies by Kong and Roundhill⁽⁸⁹⁾ on the reaction of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ with trifluoroacetic acid in chloroform in the cold showed that a colourless salt, formulated by them as being $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3][(\text{CF}_3\text{CO}_2)_2\text{H}]$, is formed. This work confirmed the previous studies of Commereuc, Douek and Wilkinson⁽³⁰⁾ on the reaction of trifluoroacetic acid and $\text{IrH}(\text{CO})(\text{PPh}_3)_3$, in which the cation $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^+$ was identified, but not the anion.

The present work has yielded a similar complex by reaction in cold toluene and, although good analyses have not been obtained, the i.r. and n.m.r. spectra observed were identical to that observed by Wilkinson et al * (above). However, the dihydrido cation may be precipitated as a tetraphenylborate salt, $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{BPh}_4$, for which good analysis has been obtained.

* That is, three resonances at (i) τ 19.4, (ii) τ 20.7 and (iii) τ 21.9. (i) was a virtual quartet, (ii) and (iii) were triplets; and the integration was 2:1:1, respectively,

If the salt $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3][(\text{CF}_3\text{CO}_2)_2\text{H}]$ (prepared in cold toluene) is heated in refluxing toluene for ca 30 min. the complex $\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$ may be obtained from the solution.

It was found that in the preparation of $\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$ solutions of the latter were pale yellow when hot but colourless when cold. This suggested that some dissociation of acid was occurring at high temperatures to give a new species. Thus when $\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$ is refluxed in toluene containing a large excess of triethylamine the solution remains yellow when cold and the yellow complex $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ can be isolated. The function of the triethylamine, here, is presumably to mop up the dissociated acid.

The yellow complex, above, showed a band in the i.r. at 1978 cm^{-1} assignable to $\nu(\text{CO})$ but absorptions attributable to $\nu(\text{IrH})$ were not observed. Carboxylate bands and bands assignable to $\nu(\text{CF})$ were observed indicating the presence of a trifluoroacetato group. High-field resonances could not be detected in the n.m.r. Molecular weight measurements on the $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ complex gave half the expected value and conductivity measurements in dichloromethane and nitromethane showed that the complex was a non-electrolyte in these solvents. Thus, dissociation of a triphenylphosphine ligand would appear to be indicated.

On bubbling oxygen through a benzene solution of $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ for ca 10 h. a yellow complex $\text{Ir}(\text{O}_2)(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ ($\nu(\text{CO}) = 2011$, $\nu(\text{OO}) = 860\text{ cm}^{-1}$) is obtained. This, however, is contaminated with unconverted $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$. Sweeping the solution of $\text{Ir}(\text{O}_2)(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2 / \text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ with nitrogen gave back the pure $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ complex.

Reaction between $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ and acetic acid was not observed and in an attempt to obtain the acetato complex by reaction of sodium acetate with $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{BPh}_4$ only yellow $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (identified by i.r. and n.m.r.) and acetic acid (identified by g.l.c.) was obtained.

Immediate reaction is observed between $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ and trifluoroacetic acid in cold toluene, with effervescence, to give a pale yellow solution from which the complex $\text{Rh}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ can be obtained by addition of light petroleum or ether. This complex shows i.r. absorption

attributable to $\nu(\text{CO})$, $\nu(\text{CO}_2)$ (carboxylate) and $\nu(\text{CF})$. A medium-intensity peak is also observed at 832 cm^{-1} . A similar complex has been prepared via a different route by Mitchell, Ruddick and Wilkinson.⁽⁹⁰⁾ They prepared the complex by addition triphenylphosphine and lithium trifluoroacetate to a refluxing solution of Rh_2^{4+} in methanol (prepared by the protonation of $\text{Rh}_2(\text{OAc})_4$). This preparation was repeated and a complex identical to that obtained by the present reaction, was obtained. The complex, $\text{Rh}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$, prepared by the alternative route, also shows the medium-intensity peak at 832 cm^{-1} . The origin of this peak is uncertain and will be discussed later.

Trifluoromethylsulphonic acid The interaction of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ with an excess of trifluoromethylsulphonic acid in the cold gives a colourless solution from which the complex $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{CF}_3\text{SO}_3$ ($\nu(\text{IrH}) = 2115$, $\nu(\text{CO}) = 2005 \text{ cm}^{-1}$; $\tau 19.61 \text{ q}$, $\tau 20.96 \text{ t}$) can be obtained. This was identified by i.r. and n.m.r. spectroscopy and by analogy with the similar trifluoroacetate complex, $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3](\text{CF}_3\text{CO}_2)\text{H}$.

When $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{CF}_3\text{SO}_3$ or $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ is refluxed in toluene with an excess of trifluoromethylsulphonic acid a colourless solution is obtained from which a white complex could be obtained. The complex showed strong bands at 2065 cm^{-1} (assigned as $\nu(\text{CO})$) and 2285 cm^{-1} (assigned as $\nu(\text{IrH})$) and is formulated as $\text{IrH}(\text{CF}_3\text{SO}_3)_2(\text{CO})(\text{PPh}_3)_2$ by analogy with $\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$. However, analysis of the complex, even after repeated crystallisations, is inconsistent for $\text{IrH}(\text{CF}_3\text{SO}_3)_2(\text{CO})(\text{PPh}_3)_2$. The consistent observation of a weak absorption in the i.r. at 1990 cm^{-1} $\nu(\text{CO})$ suggests the presence of an impurity, probably $\text{Ir}(\text{CF}_3\text{SO}_3)(\text{CO})(\text{PPh}_3)_2$, formed by dissociation of acid. Recrystallisation of the $\text{IrH}(\text{CF}_3\text{SO}_3)_2(\text{CO})(\text{PPh}_3)_2$ complex from solutions containing an excess of the acid also failed to eliminate the peak at 1990 cm^{-1} and to produce analytically pure samples.

Attempts to prepare the trifluoromethylsulphonato complex $\text{Ir}(\text{CF}_3\text{SO}_3)(\text{CO})(\text{PPh}_3)_2$, analogous to $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ also failed. Therefore, when a solution of the impure $\text{IrH}(\text{CF}_3\text{SO}_3)_2(\text{CO})(\text{PPh}_3)_2$ was refluxed in toluene with an excess of triethylamine (to mop up any dissociated acid) only an intractable yellow solution was obtained from

which only oils could be obtained. Similar intractable solutions were obtained when the complex $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{CF}_3\text{SO}_3$ was refluxed in toluene alone. When the reaction with triethylamine was tried in ethanol hydride abstraction from solvent occurred to give yellow $\text{IrH}(\text{CO})(\text{PPh}_3)_3$.

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$ reacts with trifluoromethylsulphonic acid in cold toluene, with effervescence, to yield pale yellow solutions from which a pale yellow salt analysing for $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{CF}_3\text{SO}_3 \cdot \text{CF}_3\text{SO}_3\text{H}$ is obtained. The conductivity of this complex in nitromethane was found to be $97.05 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ in 10^{-3} M solution, and this value is slightly higher than that expected for a 1:1 electrolyte, and supports the formulation above, in which a trifluoromethylsulphonic acid of crystallisation has been included. This formulation is directly analogous to $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3](\text{CF}_3\text{CO}_2)_2\text{H}$, as suggested by Kong and Roundhill.⁽⁸⁹⁾ An anomaly, however, is the absence of a low-field resonance in the n.m.r. attributable to an acidic proton. Absence of a high-field resonance precluded the existence of a rhodium hydrido species and this is supported by the absence of a band attributable to $\nu(\text{RhH})$ in the i.r. The existence of the $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]^+$ cation is confirmed by precipitation of the latter as the tetraphenylborate salt, $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{BPh}_4$ which does not show bands in the i.r. attributable to a trifluoromethylsulphonate group (i.e. $\nu(\text{CF})$ and $\nu(\text{SO}_3)$) which proves that the trifluoro-sulphate is not coordinated to the rhodium. The $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{BPh}_4$ complex is analogous to the complex, $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{BF}_4$ as prepared by Wilkinson *et al.*⁽⁹¹⁾ and shows a similar i.r. to the latter.

C. DISCUSSION

As mentioned in the Introduction the aim of the experiments described in this chapter was to find a general, simple synthesis of complexes of the type $\text{MA}(\text{CO})(\text{PPh}_3)_2$ from the readily available hydrido complexes $\text{MH}(\text{CO})(\text{PPh}_3)_3$. The fact that this aim has not been achieved brings to light several important points.

It is impossible to predict whether a particular acid will react with the complexes knowing only the pK_a of the acid in water. In fact, except for strong acids, there seems to be little correlation between

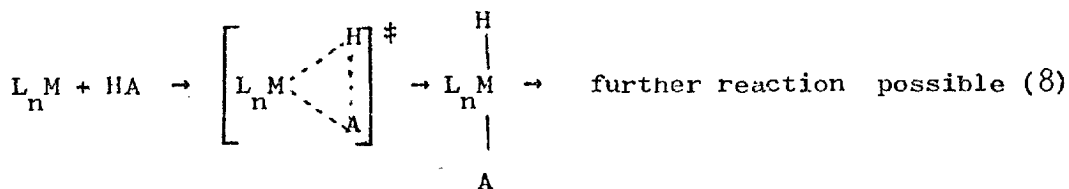
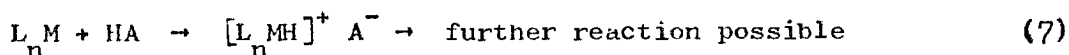
the tendency of the acid to react and the pKa alone. Two factors seem to be of importance.

- (i) the pKa of the acid,
- (ii) the affinity of the conjugate base, A^- , for the metal atom in question.

This can easily be explained by the fact that (i) represents the ease of dissociation of the A-H bond and (ii) the strength of the new M-A bond formed. Both factors are obviously of importance.

For example, in Chapter I the reaction of $MH(CO)(PPh_3)_3$ with alk-1-yne was seen to proceed with ease, as was the reaction between $MH(CO)(PPh_3)_3$ and trifluoroacetic acid in this chapter. As alk-1-ynes have a pKa about 22, (i) plays little part in influencing the reaction and the fact that the alk-1-ynyl group has two π -bonds capable of delocalising d-electron density (i.e. high nephelauxetic effect) obviously means that (ii) plays the major role in the formation of the alkynyl complexes. For the case of trifluoroacetic acid, which is a strong acid, (ii) plays a big role in the formation of say, the complex $[IrH_2(CO)(PPh_3)_3]-(CF_3CO_2)_2H$ and, as the trifluoroacetate is not in the primary coordination sphere, obviously (ii) plays little part.

Two mechanisms can be suggested for the reaction of acids with d^8 complexes. (The mechanisms are similar to those suggested for the possible mechanisms of the general oxidative addition reaction). Equations (7) and (8) represent these mechanisms.



$\ddagger$ represents the transition-state.

The general formula $L_n M$ has been used to represent the d^8 complexes in question, as the arguments used to explain reaction of $MH(CO)(PPh_3)_3$ can be extended to other similar complexes which do not contain hydrido

ligands. If (as is the case for the reactions described in this chapter) one of the ligands, L, is a hydride, or an equally labile ligand, then, as suggested in equations (7) and (8), further reaction may occur. This will be discussed subsequently.

Considering the suggested mechanisms, then, equation (7) relies heavily upon the effect of (i) (i.e. pK_a of the acid) while equation (8) upon (ii). These represent the possible extreme pathways that the reaction may follow and in the present context represent the alk-1-yne reactions (equation (8)) and the trifluoroacetic acid reaction (equation (7)). Of course, acids that have pK_a values higher than trifluoroacetic acid and whose conjugate bases have lower affinities for the metal than does the alkynyl group (e.g. p-nitrophenol) can follow a pathway which may be represented as a hybrid of equations (7) and (8); after all, in the transition-state in equation (8) the 'A' group may be considered as having a partial negative charge and thus approaching to A⁻.

Studies by Vaska⁽⁴⁾ upon the stereochemistry of addition of the acids HF, HCl, HBr, HI and H₂S to solid IrCl(CO)(PPh₃)₂ indicate that only cis addition is taking place. This was confirmed by the results of similar work carried out by Chatt, Johnson and Shaw.⁽⁹²⁾ Here it seems that a mechanism of the type in equation (8) is taking place. Later studies by Collman and Sears⁽⁵⁾ showed that addition of hydrogen halides to IrCl(CO)-(PPh₃)₂ in benzene yielded both cis and trans adducts. This was cleared up by Blake and Kubota⁽⁹³⁾ who found that the addition in benzene produced only cis products in anhydrous benzene but that in the presence of traces of moisture both cis and trans adducts were formed, as was the case when the ionising solvents and solvent systems, CH₂Cl₂, dimethylformamide, benzene-acetonitrile, benzene-methanol were used. Thus, it would appear that (owing to the strong acidity of hydrogen halides) the alternative mechanism, represented by equation (7), can operate in the presence of ionising media.

Reductive elimination of hydrogen halide (HX) from IrHXCl(CO)L₂ (L = tertiary phosphine) was shown by Deeming and Shaw⁽⁹⁴⁾ to take place by reaction with base. They found that elimination from cis-HX adducts occurred more rapidly than from trans-HX adducts. The inference here is that elimination from cis adducts can be represented by the reverse of

equation (8) and that elimination from trans adducts is represented by the reverse of equation (7). The fact that different rates are observed suggests different mechanisms. It is to be expected that reaction as in equation (8), representing a concerted reaction, will occur more rapidly than in equation (7), in which the H-A bond has to be completely broken.

Further evidence for the operation of equation (7) was provided by Cariati, Ugo and Bonati⁽²²⁾ who obtained products of the type $[PtHL_3]A$ from reaction of $Pt(0)$ complexes with H_2SO_4 , HNO_3 , and $HClO_4$. Similarly, in 1955 Wilkinson and Birmingham made the dihydride cation $[ReH_2Cp_2]^+$ by protonation of $ReHCp$; Drinkard et al⁽⁹⁵⁾ protonated $Ni[P(OEt)_3]_4$ to give $\{HNi[P(OEt)_3]_4\}^+$; Vaska⁽⁶¹⁾ showed the existence of $[IrH_2(CO)L_3]Cl$ formed by the reaction of HCl with $IrH(CO)L_3$ (L = tertiary phosphine); and the cationic dihydrides $[IrH_2(CO)(PPh_3)_3]^+$ and $[IrH_2(CO)_2(PPh_3)_2]^+$ have already been mentioned.^(30,88) Deeming and Shaw⁽⁸⁾ have shown that when protonation, as represented by equation (7) occurs the extent of protonation is directly dependent on the pK_a of the acid used.

At this point it is worth repeating that for any particular reaction described in this chapter, it is difficult (except, perhaps, for the trifluoroacetic and trifluoromethylsulphonic acid reactions) to determine whether equation (7) or (8) is operating, but it is as well to be aware of the possibilities.

Similar studies to the present work have been carried out by Roundhill, Tripathy and Renoe⁽⁸⁶⁾ in which various organic acids were reacted with $Pt(PPh_3)_4$ in an attempt to get hydride complexes. The results and conclusions of these studies support the present work. For example, it was found that HF (pK_a 3.5), acetylacetone (pK_a 9.0), phenol (pK_a 9.9), *p*-nitrophenol (pK_a 7.2), 2:4-dinitrophenol (pK_a 4.0) and nitromethane (pK_a 10.2) did not react, while HCN (pK_a 8-12), H_2S , thiophenol, thioacetic (pK_a 3.33) and thiobenzoic acids, benzothiazole-2-thiol, hydrogen bromide, picric and trifluoroacetic acid all reacted. Acetic (pK_a 4.76) and formic (pK_a 3.75) acids reacted to give unstable products which were easily decomposed in the cold by diethyl ether. The only disagreements between the above work and the present are the results obtained with *p*-nitrophenol, 2:4-dinitrophenol, acetic and formic acids, although the

latter two results are not serious disagreements. As can be seen from Roundhill's and the present work, prediction as to whether reaction will take place is impossible if only pKa values are considered, as this would only take into consideration reaction via a pathway similar to that in equation (7). As Roundhill points out, the nephelauxetic effect of the conjugate base of the acid concerned is also of vital importance. This is closely connected with the fact that both platinum and iridium behave as "soft" acids, to use Pearson's⁽⁹⁶⁾ terminology. This clearly explains why reaction was observed between the complexes and thio-acids, even though the pKas of these acids were not sufficiently low to predict reaction. This final point about the nephelauxetic effect of the conjugate base and the "hard-soft" criteria is of greater importance to the pathway represented by equation (8).

Thus, with these criteria in mind, reaction was not observed between $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ and phenol, presumably because of the low acidity and low affinity of iridium for oxygen prohibiting both equations (7) and (8) to be operative. p-Nitrophenol, being more acidic, and the p-nitrophenato group having a greater nephelauxetic effect, reacts, and presumably an intermediate of the type $\text{IrH}_2(\text{pnp})(\text{CO})(\text{PPh}_3)_2$, or $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3](\text{pnp})$ (pnp = p-nitrophenato), or a hybrid of the two, is formed. Loss of hydrogen can then occur to give the product, $\text{Ir}(\text{pnp})(\text{CO})(\text{PPh}_3)_2$. That $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ does not react with p-nitrophenol reflects the lower tendency for rhodium(I) to oxidatively add, compared to iridium(I).^(7,12) The p-nitrophenato group could be displaced as p-nitrophenol by reaction with HCl to give $\text{IrHCl}_2(\text{CO})(\text{PPh}_3)_2$, presumably by a mechanism similar to that involved in the formation of $\text{Ir}(\text{pnp})(\text{CO})(\text{PPh}_3)_2$, i.e. via an intermediate of the type $\text{IrHCl}(\text{pnp})(\text{CO})(\text{PPh}_3)_2$, which is unstable to loss of p-nitrophenol. This oxidative addition, followed by reductive elimination sequence is quite common and similar to the formation of dimethylfumarate from the reaction of $\text{Rh}(\text{RC} = \text{CHR})(\text{CO})(\text{PPh}_3)_2$ ($\text{R} = \text{CO}_2 \text{ Me}$) with HCl, as studied by Booth and Lloyd.⁽⁹⁷⁾

The reaction of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ with pyridine-2-thiol, as seen above, results in the formation of $\text{IrH}(\text{pyS})_2(\text{PPh}_3)_2$ (pyS = pyridine-2-thiolato). The greater affinity of iridium for sulphur is undoubtedly of importance

Table 2.2

<u>Reaction</u>	<u>No Reaction</u>
Trifluoroacetic acid	phenol
trifluoromethylsulphonic acid	o-cresol
p-nitrophenol	p-cresol
2:4-dinitrophenol	p-fluorophenol
salicylaldehyde	pentafluorophenol
α -nitroso- β -naphthol	o-hydroxyacetophenone
o-allyophenol	8-hydroxyquinoline
thiophenol	acetylacetone
2-aminophenol	nitromethane
benzothiazole-2-thiol	benzyl- α -dioxime
pyridine-2-thiol	1,1,1-trifluoroethanol

Table gives a list of the substrates reacted with $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, and the results obtained.

here in the formation of the complex. Also, chelation of the pyridine-2-thiolate group via nitrogen is another factor which makes the addition of the latter very favourable. In fact so favourable is this addition that what is obviously happening is that a second molecule of pyridine-2-thiol reacts with the iridium(I) intermediate formed (maybe $\text{Ir}(\text{pyS})(\text{CO})(\text{PPh}_3)_2$ or $\text{Ir}(\text{pyS})(\text{PPh}_3)_2$) to give an iridium(III) hydride. The use of pyridine-2-thiol as a strong chelating ligand is well-known.⁽⁹⁸⁾ So strong is the chelating power of this ligand that it displaces the carbonyl group and a precedent for the loss of CO by chelation is found in the formation of $\text{Rh}(\text{abt})_3$ ($\text{abt} = o\text{-aminobenzenethiol}$) from reaction of $(\text{Rh}(\text{CO})_2\text{Cl})_2$ with abt .⁽³⁰⁾

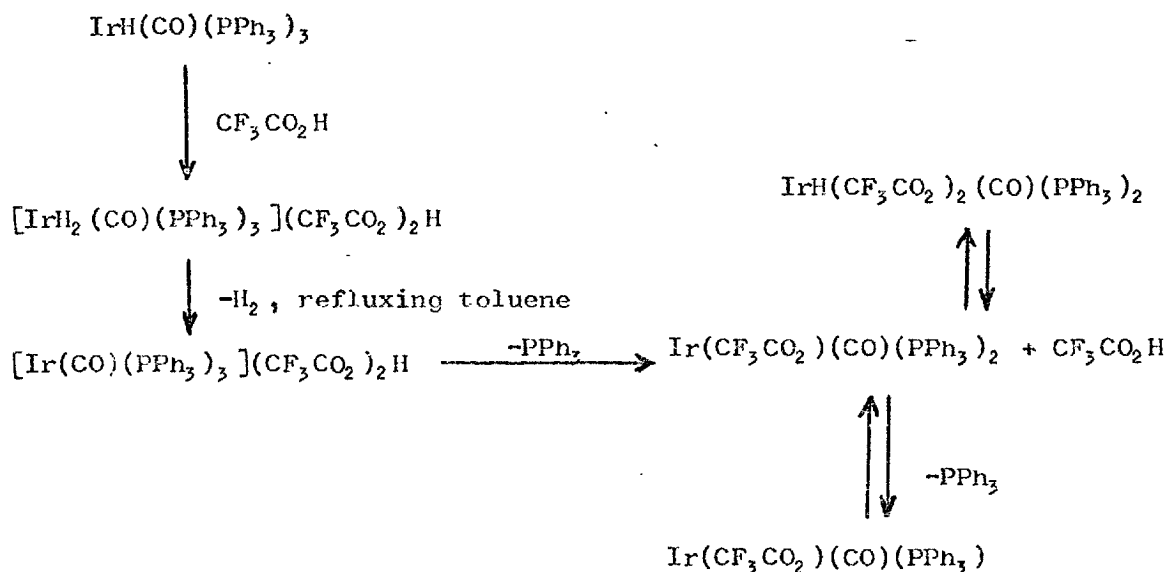
Insertion of ethylene into the metal-hydrogen bond of the complex $\text{IrH}(\text{pyS})_2(\text{PPh}_3)_2$ was observed under the conditions described above and indicates that a free coordination site is present. This is possible by either the loss of a triphenylphosphine group or the "de-chelation" of one of the pyridine-2-thiolato groups through the nitrogen. Insertion is reversible and is similar to the behaviour observed by Chatt et al⁽⁵⁶⁾ for insertion into $\text{PtHBr}(\text{PEt}_3)_2$. The solid $\text{Ir}(\text{C}_2\text{H}_5)(\text{pyS})_2(\text{PPh}_3)_2$ is unstable to loss of ethylene at atmospheric pressure and room temperature and decomposition of this complex occurs to yield the hydride and ethylene as in the platinum system.

The reaction of the iridium hydride complex, $\text{IrH}(\text{CO})(\text{PPh}_3)_3$, with trifluoroacetic acid provides an excellent illustration of the mechanism represented by equation (7), as reaction stops in the cold at the stage represented by $[\text{L}_n\text{MH}]^+$ in this equation and the products may be studied. Further reaction of this product may then be observed by heating and the manner in which such complexes rearrange can be studied.

The reaction stops in the cold when the cationic dihydride $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^+$ is formed. The counter-ion in this case is assumed to be $(\text{CF}_3\text{CO}_2)_2\text{H}^-$, as suggested by Roundhill and Kong.⁽⁸⁹⁾ A precedent for this is the report by Vaska⁽⁶¹⁾ who obtained $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{HCl}_2$ (i.e. the anion is HCl_2^-) from reactions of HCl with $\text{IrH}(\text{CO})(\text{PPh}_3)_3$. Heating this complex was found to give a different, neutral hydride, $\text{IrH}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$. This complex was identified by comparison with the identical complex prepared by Singer and Wilkinson.⁽³⁾ In the present

case the species $[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]^+$ is unstable to loss of molecular hydrogen at high temperatures and reductive elimination of H_2 occurs to give $[\text{Ir}(\text{CO})(\text{PPh}_3)_3]^+$ which in the presence of $(\text{CF}_3\text{CO}_2)_2\text{H}^-$ gives the neutral $\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$. This latter complex loses acid on heating to give $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$. This loss of acid is similar to that observed by Commereuc, Douek and Wilkinson⁽³⁰⁾ for the complex $\text{RhHCl}(\text{CF}_3\text{CO}_2)(\text{PPh}_3)_2 \cdot \frac{1}{2}\text{CH}_2\text{Cl}$, only in this case HCl was lost on heating to give $\text{Rh}(\text{CF}_3\text{CO}_2)(\text{PPh}_3)_2$. The $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ was also found to dissociate a triphenylphosphine molecule, as mentioned above. Thus, the complete $\text{IrH}(\text{CO})(\text{PPh}_3)_3 / \text{CF}_3\text{CO}_2\text{H}$ system, as known, is given in Scheme 2.1.

Scheme 2.1



Scheme showing the $\text{IrH}(\text{CO})(\text{PPh}_3)_3 / \text{CF}_3\text{CO}_2\text{H}$ system.

The reaction of $\text{CF}_3\text{CO}_2\text{H}$ with the rhodium analogue $\text{RhH}(\text{CO})(\text{PPh}_3)_3$, gave $\text{Rh}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$, which has been obtained previously by Mitchell, Ruddick and Wilkinson⁽⁹⁰⁾ via an alternative route. Here, the $\text{Rh}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ complex is presumably formed via the $[\text{RhH}_2(\text{CO})(\text{PPh}_3)_3]^+$ species, analogous to the iridium system, but here, loss of hydrogen occurs spontaneously at room temperature.

Reference is made here to the anomalous peak observed at 832 cm^{-1} in the i.r., which was also observed for the similar complex prepared by Mitchell, Ruddick and Wilkinson. Here, they assumed that this peak was owing to a $\nu(\text{OO})$ absorption from the complex $\text{Rh}(\text{O}_2)(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ which was formed by aerial oxidation of $\text{Rh}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$. Attempts to prepare the complex under oxygen-free conditions persistently gave products which showed absorption at 832 cm^{-1} , furthermore, the following did not change the i.r. spectrum in any way.

- (a) pumping on the complex for several days at 10^{-2} mm ,
- (b) sweeping a solution of the complex in toluene with a stream of nitrogen for several hours,
- (c) sweeping a solution of the complex with oxygen for a few hours.

As will be recalled, the complex $\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ was found to form the oxygen adduct $\text{Ir}(\text{O}_2)(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ only very slowly and not to completion at atmospheric pressure. The fact that rhodium(I) undergoes oxidative addition more reluctantly than does iridium(I), it seems highly unlikely that the analogous rhodium complex, $\text{Rh}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$ will form an adduct with oxygen, let alone an irreversible one. It is the opinion here, therefore, that the band at 832 cm^{-1} is not owing to coordinated oxygen but its origin remains a mystery.

As mentioned above, the reaction of trifluoromethylsulphonic acid with the rhodium and iridium hydrides yields products which are similar to that obtained with trifluoroacetic acid, and it is assumed that reaction proceeds in a similar manner. The following differences were observed.

- (i) The counter-ion for the cation $[\text{IrH}_2(\text{CO})(\text{PPh}_3)]^+$ was CF_3SO_3^- and not $(\text{CF}_3\text{SO}_3)_2\text{H}$.
- (ii) The complex $\text{IrH}(\text{CF}_3\text{SO}_3)_2(\text{CO})(\text{PPh}_3)_2$ could not be obtained analytically pure.

(iii) For the rhodium case the product of reaction was ionic and assigned as $[\text{Rh}(\text{CO})(\text{PPh}_3)_2]\text{CF}_3\text{SO}_3 \cdot \text{CF}_3\text{SO}_3\text{H}$.

These differences are attributable to the lower coordinating power of the trifluoromethylsulphonato groups compared to trifluoroacetato, and its preference to exist as a free ion, CF_3SO_3^- .

EXPERIMENTAL

A. General

Microanalyses were carried out by the Microanalytical Laboratory, Imperial College, and the data collected in Tables E.I and E.II.

Molecular weights were obtained using a Hitachi-Perkin-Elmer Model 115 osmometer at 37° under nitrogen and melting points (uncorrected) were measured on an Electrothermal apparatus.

N.m.r. spectra were measured on Perkin-Elmer Models R14 and R12A at 35° and 100 MHz and 60 MHz, respectively for protons. Fluorine n.m.r. spectra were measured on the Perkin-Elmer R14 at 35° and 94.1 MHz.

I.r. spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer as nujol mulls.

G.l.c. measurements were carried out on a Perkin-Elmer Model F11 chromatograph fitted with flame ionisation detectors.

Hydridocarbonyltris(triphenylphosphine)-iridium(I) and -rhodium(I) were prepared using literature methods. Chloroiridic acid and rhodium trichloride trihydrate was obtained from Johnson-Matthey Limited; triphenylphosphine from Albright and Wilson Limited.

All solvents were of reagent grade and were dried and saturated with nitrogen before use. All experiments were carried out under an atmosphere of nitrogen.

B. Chapter I

All samples were washed with ethanol and vacuum dried.

(i) Propynyl- and but-1-ynyl-carbonylbis(triphenylphosphine)iridium(I)

A slow stream of propyne or but-1-yne was passed through a refluxing solution of $\text{IrH}(\text{CO})_2(\text{PPh}_3)_2$ (0.20 g) in benzene (30 ml) for ca 4 h. Ethanol (30 ml) was added to the cold orange solution and the precipitated orange-yellow complex collected (ca 0.16 g, 80%).

(ii) Propynyl- and but-1-ynyl-carbonyltris(triphenylphosphine)iridium(I)

A slow stream of propyne or but-1-yne was passed through a refluxing

solution of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (0.20 g) and triphenylphosphine (0.26 g) in benzene (30 ml) for ca 4 h. Ethanol (30 ml) was added to the cold orange solution and the precipitated yellow complex collected (ca 0.17 g, 80%).

(iii) Alk-1-ynylcarbonyltris(triphenylphosphine)iridium(I)

$\text{Ir}(\text{C} \equiv \text{CR})(\text{CO})(\text{PPh}_3)_3$ ($\text{R} = \text{Bu}^n, \text{Bu}^t, \text{CH}_2\text{OH}, \text{C}_6\text{H}_{11}, \text{C}_6\text{H}_{10}\text{OH}, \text{C}(\text{OH})\text{Me}_2$). A ten-fold excess of alk-1-yne was added to a solution of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (0.20 g) and triphenylphosphine (0.26 g) in benzene (30 ml) and the mixture refluxed for ca 6 h. Ethanol (30 ml) was added to the cold, orange solution and the precipitated yellow complex collected (ca 80%).

(iv) Propynyl-, But-1-ynyl-, and Hex-1-ynyl-carbonylbis(triphenylphosphine)-rhodium(I)

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (0.50 g) was placed in a Carius tube attached to the vacuum line and thoroughly degassed toluene (20 ml) was added by distillation. After similar addition of propyne or but-1-yne (equivalent to ca 3 atm.) or hex-1-yne (10 ml) the tube was sealed. After ca 24 h. at room temperature the yellow complex was obtained from the deep red solution by addition of ethanol (30 ml) (ca 0.19 g, 50%).

(v) Propynyl-, But-1-ynyl- and Hex-1-ynyl-carbonyltris(triphenylphosphine)iridium(I)

As for the bistriphenylphosphine complexes above, except that triphenylphosphine (0.71 g) was added with the solid rhodium complex.

Addition Reactions The reaction conditions described below for the propynyl complex have in most cases been applied to other acetylide complexes.

(vi) Propynyl(oxygen)carbonylbis(triphenylphosphine)iridium

A slow stream of oxygen was passed over a stirred solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (30 ml) for ca 1 h. Addition of ethanol (30 ml) gave the white complex (0.15 g, 96%; m.p. 180° decomp.).

(vii) Propynyl(sulphur dioxide)carbonylbis(triphenylphosphine)iridium

A slow stream of sulphur dioxide was passed through a solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (30 ml) for ca 1 h. Addition

of ethanol (30 ml) to the green solution gave the bright green complex (0.15 g, 92%). The complex loses sulphur dioxide on heating the solid in vacuo.

(viii) Propynyl(sulphato)carbonylbis(triphenylphosphine)iridium(III)

Oxygen was passed through a solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$ (0.15 g) in benzene (25 ml) at room temperature for ca 2 h. Addition of ethanol (25 ml) precipitated the cream complex (0.14 g, 90%; decomp. ca 218°).

(ix) Propynyl(tetracyanoethylene)carbonylbis(triphenylphosphine)iridium

A solution of freshly-sublimed tetracyanoethylene (0.075 g) in benzene (10 ml) was added to a solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (25 ml) and the mixture stirred for ca 15 min. Addition of ethanol (50 ml) to the dark brown solution gave the white complex (0.16 g, 92%; decomp. ca 245°).

(x) Propynyl(dimethylacetylenedicarboxylate)carbonylbis(triphenylphosphine)iridium

A solution of dimethylacetylenedicarboxylate (0.082 g) in benzene (25 ml) was added to a solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (25 ml). After stirring for ca 15 min. addition of ethanol (50 ml) gave the white complex (0.16 g, 90%; m.p. 178° decomp.).

(xi) Hex-1-ynylmethyliodocarbonylbis(triphenylphosphine)iridium(III)

To a solution of $\text{Ir}(\text{C} \equiv \text{CBn}^n)(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (30 ml) was added 1 mole equivalent of methyl iodide in dilute benzene solution. After stirring for ca 15 min., addition of ethanol (30 ml) gave the white complex (0.14 g, 80%).

(xii) Propynyl(hexafluoroacetone)carbonylbis(triphenylphosphine)iridium

A solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (20 ml) was heated at ca 80° for 72 h. with hexafluoroacetone (3 atm.) in a sealed tube. Subsequent addition of ethanol (20 ml) gave the white complex (0.14 g, 77%; decomp. ca 134°).

(xiii) Propynyl(hexafluorobut-2-yne)carbonylbis(triphenylphosphine)iridium

A slow stream of hexafluorobut-2-yne was passed into a solution of

$\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (30 ml). The bright yellow solution rapidly turned pale and excess hexafluorobut-2-yne was polymerised to a pale yellow solid. A mixture of the complex and the polymer was obtained on addition of ethanol (30 ml). The complex was extracted with chloroform and recovered by precipitation with ethanol (0.15 g, 81%; m.p. 153° decomp.).

(xiv) Propynyl(perfluorobut-2-ene)carbonylbis(triphenylphosphine)iridium

A solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (20 ml) was shaken for ca 72 h. with perfluorobut-2-ene (3 atm.) at room temperature. Addition of ethanol (30 ml) to the pale yellow solution afforded the complex (0.14 g, 73%; m.p. 162° decomp.).

(xv) Propynyl(hexafluorobutadiene)carbonylbis(triphenylphosphine)iridium

A slow stream of perfluorobutadiene was passed through a solution of $\text{Ir}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (30 ml) for ca 10 min. Addition of ethanol (30 ml) precipitated the cream complex (0.15 g, 81%; m.p. 168° decomp.).

(xvi) Propynyl(sulphur dioxide)carbonylbis(triphenylphosphine)rhodium

Sulphur dioxide was bubbled through a solution of $\text{Rh}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (30 ml) for ca 2 hr. Addition of ethanol (30 ml) gave the bright yellow complex (0.15 g, 94%). The complex loses sulphur dioxide on warming the solid.

(xvii) Propynyl(tetracyanoethylene)carbonylbis(triphenylphosphine)rhodium

A solution of tetracyanoethylene (0.083 g) in benzene (10 ml) was added to a stirred solution of $\text{Rh}(\text{C} \equiv \text{CMe})(\text{CO})(\text{PPh}_3)_3$ (0.20 g) in benzene (25 ml). After ca 1 h. ethanol (30 ml) was added to the dark red solution and the yellow-brown complex collected (0.14 g, 81%; decomp. ca. 174°).

Table E.I

Analytical Data (Chapter I)

Complex	Found (%)			Required (%)		
	C	H	Others	C	H	Others
$\text{Ir}(\text{C}\equiv\text{CMe})(\text{CO})(\text{PPh}_3)_2$	60.3	4.5		60.4	4.3	
$\text{Ir}(\text{C}\equiv\text{CMe})(\text{CO})(\text{PPh}_3)_3$	65.3	4.7	P, 8.6	66.5	4.6	P, 8.9
$\text{Ir}(\text{C}\equiv\text{CEt})(\text{CO})(\text{PPh}_3)_2$	60.9	4.8		61.7	4.4	
$\text{Ir}(\text{C}\equiv\text{CEt})(\text{CO})(\text{PPh}_3)_3$	66.9	4.9		66.8	4.9	
$\text{Ir}(\text{C}\equiv\text{CBu}^n)(\text{CO})(\text{PPh}_3)_3$	66.5	5.1		67.3	5.0	
$\text{Ir}(\text{C}\equiv\text{CBu}^t)(\text{CO})(\text{PPh}_3)_2$	62.5	4.8	P, 7.8	62.5	4.7	P, 7.5
$\text{Ir}(\text{C}\equiv\text{CBu}^t)(\text{CO})(\text{PPh}_3)_3$	66.6	4.7		67.3	5.0	
$\text{Ir}(\text{C}\equiv\text{CC}_6\text{H}_{11})(\text{CO})(\text{PPh}_3)_3$	66.8	5.1	P, 7.6	67.9	5.0	P, 8.3
$\text{Ir}[\text{C}\equiv\text{CCH}_2(\text{OH})](\text{CO})(\text{PPh}_3)_3$	64.1	5.2		65.5	4.5	
$\text{Ir}[\text{C}\equiv\text{CC}(\text{OH})\text{Me}_2](\text{CO})(\text{PPh}_3)_3$	66.4	5.0		66.1	4.8	
$\text{Ir}[\text{C}\equiv\text{CC}_6\text{H}_{10}(\text{OH})](\text{CO})(\text{PPh}_3)_3$	65.8	4.7		66.9	4.9	
$\text{Rh}(\text{C}\equiv\text{CMe})(\text{CO})(\text{PPh}_3)_2$	69.2	5.0	P, 9.3	69.2	4.8	P, 9.0
$\text{Rh}(\text{C}\equiv\text{CMe})(\text{CO})(\text{PPh}_3)_3$	72.6	5.2		72.8	5.0	
$\text{Rh}(\text{C}\equiv\text{CEt})(\text{CO})(\text{PPh}_3)_2$	68.3	5.1		69.5	4.9	
$\text{Rh}(\text{C}\equiv\text{CEt})(\text{CO})(\text{PPh}_3)_3$	72.6	5.6		73.0	5.2	
$\text{Rh}(\text{C}\equiv\text{CBu}^n)(\text{CO})(\text{PPh}_3)_3$	72.9	5.7		73.3	5.4	
$\text{Ir}(\text{C}\equiv\text{CMe})(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$	58.8	4.3		58.8	4.0	
$\text{Ir}(\text{C}\equiv\text{CEt})(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$	60.4	4.6		59.3	4.2	
$\text{Ir}(\text{C}\equiv\text{CBu}^n)(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$	59.3	4.8		60.1	4.6	
$\text{Ir}(\text{C}\equiv\text{CBu}^t)(\text{O}_2)(\text{CO})(\text{PPh}_3)_2$	60.4	4.8		60.1	4.6	
$\text{Ir}(\text{C}\equiv\text{CMe})(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$	58.1	4.2		56.6	3.9	
$\text{Ir}(\text{C}\equiv\text{CBu}^n)(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$	58.2	4.6		58.0	4.4	
$\text{Ir}(\text{C}\equiv\text{CMe})(\text{SO}_4)(\text{CO})(\text{PPh}_3)_2$	53.6	3.9	S, 3.5	54.5	3.8	S, 3.6
$\text{Ir}(\text{C}\equiv\text{CEt})(\text{SO}_4)(\text{CO})(\text{PPh}_3)_2$	54.6	4.0		55.0	3.9	
$\text{Ir}(\text{C}\equiv\text{CMe})[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)_2$	60.7	3.8	N, 6.1	60.5	3.6	N, 6.1
$\text{Ir}(\text{C}\equiv\text{CBu}^n)[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)_2$	61.9	4.3	N, 5.6	61.6	4.1	N, 5.9
$\text{Ir}(\text{C}\equiv\text{CMe})[\text{C}_2(\text{CO}_2\text{Me})_2](\text{CO})(\text{PPh}_3)_2$	59.8	4.4		59.8	4.2	
$\text{Ir}(\text{C}\equiv\text{CBu}^n)\text{MeI}(\text{CO})(\text{PPh}_3)_2$	54.8	4.5		54.5	4.3	
$\text{Ir}(\text{C}\equiv\text{CMe})[\text{C}_2(\text{CF}_3)_2](\text{CO})(\text{PPh}_3)_2$	55.7	3.6	P, 6.7	55.8	3.5	P, 6.5

Table E.I continued

Complex	Found (%)			Required (%)		
	C	H	Others	C	H	Others
$\text{Ir}(\text{C}\equiv\text{CMe})[\text{CF}_2\cdot\text{CF}:\text{CF}\cdot\text{CF}_2](\text{CO})-(\text{PPh}_3)_2$	55.9	3.4	P, 6.3	55.8	3.5	P, 6.5
$\text{Ir}(\text{C}\equiv\text{CMe})[\text{CF}_3\cdot\text{CF}:\text{CF}\cdot\text{CF}_3](\text{CO})-(\text{PPh}_3)_2$	53.7	3.5	P, 6.4	53.7	3.4	P, 6.3
$\text{Ir}(\text{C}\equiv\text{CMe})[(\text{CF}_3)_2\text{CO}](\text{CO})(\text{PPh}_3)_2$	54.1	3.7	P, 6.3	54.3	3.5	P, 6.5
$\text{Rh}(\text{C}\equiv\text{CMe})[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)_2$	67.0	4.2	N, 6.7	66.6	4.0	N, 6.8
$\text{Rh}(\text{C}\equiv\text{CEt})[\text{C}_2(\text{CN})_4](\text{CO})(\text{PPh}_3)_2$	67.2	4.6	N, 6.4	67.5	4.2	N, 6.7
$\text{Rh}(\text{C}\equiv\text{CEt})(\text{SO}_2)(\text{CO})(\text{PPh}_3)_2$	63.4	4.8	S, 4.5	63.7	4.5	S, 4.2

C. Chapter II

All samples were vacuum dried.

(i) p-Nitrophenolato(carbonyl)bis(triphenylphosphine)iridium(I)

$\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (0.2 g) and p-nitrophenol (0.1 g) were refluxed in toluene (40 ml) for ca 2 hr. After cooling the volume was reduced to 15 ml and an approximately equal volume of ethanol added to precipitate the complex as yellow microcrystals which were filtered off and washed with ethanol (ca 0.15 g, 85%, m.p. $210 - 214^\circ$ decomp.).

(ii) Hydridobis(pyridine-2-thiolato)(triphenylphosphine)iridium(III)

$\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (0.2 g) and pyridine-2-thiol (0.2 g) were refluxed in toluene (40 ml) for ca 3 hr. After cooling the volume was reduced to 10 ml and ethanol (20 ml) was added to precipitate the complex as yellow microcrystals which were filtered off and washed with ethanol and ether (ca 0.12 g, 90%).

(iii) Hydridobis(pyridine-2-thiolato)bis(triphenylphosphine)iridium(III)

$\text{IrH}(\text{pyS})_2(\text{PPh}_3)$ (0.2 g) was refluxed in toluene (50 ml) containing triphenylphosphine (0.5 g) for ca 1 h. After cooling the volume was

reduced to 15 ml and the complex precipitated as yellow microcrystals by the addition of an equal volume of ethanol. The complex was filtered off and washed with ethanol and ether (ca 0.25 g, 90%; m.p. 175 - 176 decomp.).

(iv) Hydridobis(trifluoroacetato)carbonylbis(triphenylphosphine)iridium(III)

$\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (0.2 g) was refluxed in toluene (50 ml) with trifluoroacetic (1 ml) acid for ca 1.5 h. After cooling the solvent was removed and the colourless, sticky residue was treated with ether (35 ml). The complex was precipitated as white microcrystals, collected by filtration and washed with ether (ca 0.2 g, 95%; m.p. yellow at 140° and then melts with decomp. at 210 - 215°).

(v) Trifluoroacetato(carbonyl)bis(triphenylphosphine)iridium(I)

$\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$ (0.2 g) was refluxed in toluene (50 ml) with triethylamine (2 ml) for ca 4 h; the solution turned yellow and remained yellow on subsequent cooling. The volume was reduced to ca 20 ml and the yellow complex was precipitated by addition of light petroleum (30 ml). The complex was filtered off, washed with petroleum and dried in vacuo. When dry the impure complex was washed with water and redried in vacuo (0.15 g, 90%; m.p. 200 - 203 decomp.). [If the complex was not washed in water it was contaminated with traces of $\text{Et}_3\text{NHO}_2\text{CCF}_3$ which caused partial reconversion to $\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$ after about 2 days].

(vi) Trifluoroacetato(carbonyl)bis(triphenylphosphine)rhodium(I)

$\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (0.2 g) was stirred in toluene (40 ml) and 1 ml trifluoroacetic acid was added. Immediate effervescence occurred and the solution became a paler yellow. After stirring for 30 min. the solvent was removed and the residue was treated with ether (30 ml). The yellow complex was collected by filtration and washed with ether (ca 0.15 g, 90%; m.p. 184 - 187° decomp.).

(vii) Dihydridocarbonyltris(triphenylphosphine)iridium(III) Hydrogen Bis(trifluoroacetate)

$\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (0.2 g) was stirred with trifluoroacetic acid (1 ml) in toluene in the cold for ca 1 h. The colourless solution was evaporated

to dryness and the colourless residue treated with ether (30 ml). White microcrystals were formed and were collected by filtration and washed with ether (ca 0.23 g, 90%; m.p. turns yellow at 143 - 144° and then melts with decomp. at 200 - 205°).

(viii) Dihydridocarbonyltris(triphenylphosphine)iridium(III) Tetraphenylborate

$[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3](\text{CF}_3\text{CO}_2)_2\text{H}$ (0.2 g), prepared as described above was dissolved in acetone (15 ml) and a solution of NaBPh_4 (0.14 g) in acetone (5 ml) was added; the mixture was stirred for ca 30 min. Methanol (5 ml) and water (5 ml) were added and the volume of the solution reduced slowly to ca 20 ml whereupon a white precipitate formed. The white microcrystals were filtered off and washed with acetone-water (1:1) (ca 0.18 g, 90%; m.p. 175 - 178° decomp.).

(ix) Dihydridocarbonyltris(triphenylphosphine)iridium(III) Trifluoromethylsulphonate

$\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (0.5 g) was stirred at room temperature in toluene (50 ml) with trifluoromethylsulphonic acid (0.5 ml) for ca 1 h. The volume was reduced to ca 15 ml and 35 ml diethyl ether was added to precipitate the cream-coloured complex which was filtered off, washed with a little ether, and dried in vacuo. The complex was washed with water until the washings were acid-free and then re-dried in vacuo at 95°. Dissolution of the complex in a minimum of ethanol, filtration, and crystallisation by careful addition of toluene and slow evaporation followed by cooling to -70° afforded the cream-coloured microcrystals which were filtered off, washed with a little cold toluene and ether, and dried in vacuo (0.35 g, 60% decomp. 198° and then melts at 203 - 204°).

(x) Carbonyltris(triphenylphosphine)rhodium(I) Trifluoromethylsulphonate

To a solution of $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ (0.2 g) in toluene (50 ml) was added ca 0.5 ml trifluoromethylsulphonic acid. Immediate effervescence occurred and the solution was stirred for ca 1 h. The toluene was removed by vacuum evaporation and the pale yellow residue dissolved in ether (30 ml). Pale yellow microcrystals of the complex precipitated out of solution upon standing overnight at -25°. The microcrystals

were filtered off, washed with ether, and dried in vacuo (ca 0.18 g, 85%; m.p. 159 - 163 decomp.).

(xi) Hydridobis(trifluoromethylsulphonato)carbonylbis(triphenylphosphine)-iridium(III)

To a solution of $\text{IrH}(\text{CO})(\text{PPh}_3)_3$ (0.5 g) in toluene (50 ml) was added 0.5 ml trifluoromethylsulphonic acid and the solution refluxed for ca 6 h. The volume was reduced to ca 10 ml and ether (15 ml) was added to complete precipitation of the pale yellow complex which was filtered off, washed with ether, and dried in vacuo. The complex was further washed with water until the washings were acid-free and dried in vacuo at 75°. Dissolution of the complex in a minimum of ethanol, filtration, and crystallisation by careful addition of toluene and slow evaporation followed by cooling to -70° afforded the pale yellow complex which was filtered off, washed with a little cold toluene and ether, and dried in vacuo (0.38 g, 73%; m.p. decomp. 247° then melts 252 - 255°). This complex could not be obtained analytically pure (Found: C = 47.6; H = 3.3; S = 6.8. $\text{C}_{39}\text{H}_{31}\text{F}_6\text{IrO}_7\text{P}_2\text{S}_2$ requires C = 44.8; H = 3.0; S = 6.1%. Molecular weight determined as being 557, requires 1043).

Table E.II

Analytical Data (Chapter II)

Complex	Found				Required			
	C	H	Others	M	C	H	Others	M
$\text{Ir}(\text{OC}_6\text{H}_4\text{NO}_2)(\text{CO})(\text{PPh}_3)_2$	58.6	3.9	N, 1.6 P, 6.7	890	58.5	3.9	N, 1.6 P, 7.0	882
$\text{IrH}(\text{pyS})_2(\text{PPh}_3)_2$	58.6	4.0	N, 2.9 P, 7.0 S, 7.2	470	58.9	4.2	N, 3.0 P, 6.8 S, 6.6	937
$\text{IrH}(\text{CF}_3\text{CO}_2)_2(\text{CO})(\text{PPh}_3)_2$	49.4	3.4		960	50.6	3.2		971
$[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{BPh}_4$	72.1	5.0	P, 7.3	650	71.4	5.1	P, 7.0	1327
$\text{Ir}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$	55.3	3.5		445	54.6	3.5		857
$\text{Rh}(\text{CF}_3\text{CO}_2)(\text{CO})(\text{PPh}_3)_2$	59.6	3.9			61.0	3.9		
$[\text{IrH}_2(\text{CO})(\text{PPh}_3)_3]\text{CF}_3\text{SO}_3$	58.1	4.1	S, 2.8 P, 8.1	1157	58.5	4.0	S, 2.5 P, 7.7	1125
$[\text{Rh}(\text{CO})(\text{PPh}_3)_3]\text{CF}_3\text{SO}_3\text{CF}_3\text{SO}_3\text{H}$	56.0	3.8	S, 5.3		56.3	3.8	S, 5.3	

REFERENCES

1. J. Halpern, Accounts Chem. Res., 1970, 3, 386.
2. R.F. Heck, J. Amer. Chem. Soc., 1964, 86, 2796.
3. H. Singer and G. Wilkinson, J. Chem. Soc. (A), 1968, 2516.
4. L. Vaska, J. Amer. Chem. Soc., 1966, 88, 5325.
5. J.P. Collman and C.T. Sears Jr., Inorg. Chem., 1968, 7, 27.
6. A.J. Deeming and B.L. Shaw, J. Chem. Soc. (A), 1968, 1128.
7. R.S. Nyholm and K. Vrieze, J. Chem. Soc., 1965, 5337.
8. A.J. Deeming and B.L. Shaw, J. Chem. Soc. (A), 1969, 1802.
9. L. Vallarino, J. Inorg. Nucl. Chem., 1958, 8, 288.
10. M.C. Baird, J.T. Mague, J.A. Osborn and G. Wilkinson, J. Chem. Soc. (A), 1967, 1347.
11. F. de Charentenay, J.A. Osborn and G. Wilkinson, J. Chem. Soc. (A), 1968, 787.
12. J.P. Collman and W.R. Roper, J. Amer. Chem. Soc., 1965, 87, 4008.
13. J.P. Collman and W.R. Roper, J. Amer. Chem. Soc., 1966, 88, 3504.
14. F. Basolo and R.G. Pearson, Prog. Inorg. Chem., 1962, 4, 331.
15. L. Vaska and J.W. Diluzio, J. Amer. Chem. Soc., 1962, 84, 679.
16. P.B. Chock and J. Halpern, J. Amer. Chem. Soc., 1966, 88, 3511.
17. L. Vaska, Science, 1963, 140, 800.
18. G.T. Takaki and R.T.M. Fraser, Proc. Chem. Soc., 1964, 116.
19. S.J. La Placa and J.A. Ibers, J. Amer. Chem. Soc., 1965, 87, 2581.
20. R. Cramer and G.W. Parshall, J. Amer. Chem. Soc., 1965, 87, 1392.
21. M.C. Baird and G. Wilkinson, J. Chem. Soc. (A), 1967, 865.
22. F. Cariati, R. Ugo and F. Bonati, Inorg. Chem., 1966, 5, 1128.
23. A.J. Chalk and J.F. Harrod, J. Amer. Chem. Soc., 1965, 87, 116.
24. J.F. Harrod, D.F.R. Gilson and R. Charles, Can. J. Chem., 1969, 47, 2205.
25. L. Vaska, Accounts Chem. Res., 1968, 1, 335.
26. J. Chatt, J. Chem. Soc., 1950, 3201.
27. "Basic Principles of Organic Chemistry", J.D. Roberts and M.C. Caserio, Benjamin Inc., pp.175 - 178.
28. R.G. Pearson and W.R. Muir, J. Amer. Chem. Soc., 1970, 92, 5519.
29. J.A. Labinger, R.J. Barnes, D. Dolphin and J.A. Osborn, Chem. Comm., 1970, 612.

30. D. Commereuc, I. Douek and G. Wilkinson, J. Chem. Soc. (A), 1970, 1771.
31. R.J. Cross and F. Glockling, J. Chem. Soc., 1965, 5422.
32. W. Keim, J. Organometallic Chem., 1968, 14, 179.
33. H. Singer and G. Wilkinson, J. Chem. Soc. (A), 1968, 849.
34. A. Furlani, I. Collamati and G. Sartori, J. Organometallic Chem., 1969, 17, 463.
35. H.D. Kaesz and R.B. Saillant, Chem. Reviews, 1972, 72, 231.
36. A.P. Ginsberg, Transition Metal Chem., 1965, 1, 112.
37. M.L.H. Green and D.J. Jones, Advan. Inorg. Chem. Radiochem., 1965, 7, 115.
38. Yu E. Brouzntein, V. Yu Gauki, D.P. Krinkin and D.M. Radkavskii, Russ. J. Phys. Chem., 1966, 40, 802.
39. (a) F.L. Eplattenier and F. Calderazzo, Inorg. Chem., 1967, 6, 2092;
(b) ibid., 1968, 7, 1290.
40. H.D. Kaesz, S.A. Knox, J.W. Koepke and R.B. Saillant, J. Chem. Soc. (D), 1971, 477.
41. T. Ho, S. Kitazume, A. Yamamoto and S. Ikeda, J. Amer. Chem. Soc., 1970, 92, 3011.
42. L. Vaska and R.E. Rhodes, J. Amer. Chem. Soc., 1965, 87, 4970.
43. J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. (A), 1966, 1711.
44. F. Glockling and K.A. Hooton, J. Chem. Soc. (A), 1967, 1066.
45. (a) F. Glockling and M.D. Wilbey, J. Chem. Soc. (A), 1970, 1675;
(b) J. Chem. Soc. (D), 1969, 286.
46. (a) A. Socco and M. Rossi, Inorg. Chim. Acta, 1968, 2, 127.
(b) Chem. Comm., 1967, 316.
47. M. Aresta, P. Giannaccaro, M. Rossi and A. Sacco, Inorg. Chim. Acta, 1971, 5, 115.
48. W. Kruse and R.H. Atalla, Chem. Comm., 1968, 921.
49. J. Chatt, B.L. Shaw and A.E. Field, J. Chem. Soc., 1964, 3466.
50. A. Yamamoto, S. Kitazume, L.S. Pu and S. Ikeda, J. Amer. Chem. Soc., 1971, 93, 371.
51. W. Hieber and H. Duchatsch, Chem. Ber., 1965, 98, 3933.
52. W. Hieber, M. Höfler and J. Musch, Chem. Ber., 1965, 98, 311.

53. F. Ungvary and L. Markó, J. Organometallic Chem., 1969, 20, 205.
54. H.C. Clark, K.R. Dixon and D.J. Jacobs, J. Amer. Chem. Soc., 1968, 90, 2259.
55. W. Kruse and R.H. Atalla, Chem. Comm., 1968, 1223.
56. J. Chatt, R.S. Coffey, A. Gough and D.T. Thompson, J. Chem. Soc. (A), 1968, 190.
57. M.J. Mays and G. Wilkinson, J. Chem. Soc. (A), 1965, 29.
58. J.B. Wilford and F.G.A. Stone, Inorg. Chem., 1965, 4, 93.
59. M.J. Church and M.J. Mays, J. Chem. Soc. (A), 1968, 3074.
60. M.J. Church and M.J. Mays, J. Chem. Soc. (A), 1970, 1938.
61. L. Vaska, Chem. Comm., 1966, 614.
62. L. Vaska, J. Amer. Chem. Soc., 1966, 88, 4100.
63. G. Yagupsky, C.K. Brown and G. Wilkinson, J. Chem. Soc. (A), 1970, 1392.
64. C.K. Brown, W. Mowat, G. Yagupsky and G. Wilkinson, J. Chem. Soc. (A), 1971, 850.
65. C. O'Connor and G. Wilkinson, J. Chem. Soc. (A), 1968, 2665.
66. L. Vaska, Inorg. Nuclear Chem. Letters, 1965, 1, 89.
67. C.K. Brown and G. Wilkinson, J. Chem. Soc. (A), 1970, 2753.
68. W.H. Baddley and M.S. Fraser, J. Amer. Chem. Soc., 1969, 91, 3661.
69. (a) F. Kiji and J. Furakawe, Chem. Comm., 1970, 977.
(b) G. Wilke, M. Schott and P. Heimback, Angew. Chem. Internat. Ed., 1967, 6, 92.
70. I. Collamiti and A. Furlani, J. Organometal. Chem., 1969, 17, 457.
71. J.H. Nelson, H.B. Jonassen and D.M. Roundhill, Inorg. Chem., 1969, 8, 2591.
72. J.P. Collman and J.W. Kang, J. Amer. Chem. Soc., 1967, 89, 844.
73. C.E. Coates and C. Parkin, J. Chem. Soc., 1962, 3220.
74. J.T. Magee and G. Wilkinson, Inorg. Chem., 1968, 7, 542.
75. J.L. Boston, D.W.A. Sharp and G. Wilkinson, J. Chem. Soc., 1962, 3488.
76. B. Clarke, M. Green, R.B.L. Osborn and F.G.A. Stone, J. Chem. Soc. (A), 1968, 167.
77. A. Bond and M. Green, Chem. Comm., 1971, 12.
78. R.L. Hunt, D.M. Roundhill and G. Wilkinson, J. Chem. Soc. (A), 1967, 982.

80. S.J. La Placa and J.A. Ibers, Inorg. Chem., 1966, 5, 405.
81. (a) C.D. Cook and G.S. Jauhal, J. Amer. Chem. Soc., 1967, 89, 3066.
(b) J.J. Levinson and S.D. Robinson, Chem. Comm., 1967, 198.
82. J. Valentine, D. Valentine, Jr., and J.P. Collman, Inorg. Chem., 1971, 10, 219.
83. W.H. Baddley, J. Amer. Chem. Soc., 1966, 88, 4545.
84. J. Chatt, G.A. Rowe and A.A. Williams, Proc. Chem. Soc., 1957, 208.
85. B.L. Shaw and R.E. Steinbank, J. Chem. Soc. (A), 1971, 3716.
86. D.M. Roundhill, P.G. Tripathy and B.W. Renoe, Inorg. Chem., 1971, 10, 727.
87. L. Malatesta, G. Caglio and M. Angoletta, J. Chem. Soc., 1965, 6974.
88. J.P. Collman, F.D. Vastine and W.R. Roper, J. Amer. Chem. Soc., 1968, 90, 2282.
89. Pi-Chang Kong and D.M. Roundhill, Inorg. Chem., 1972, 11, 1437.
90. R.W. Mitchell, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. (A), 1971, 3224.
91. P. Legzdins, R.W. Mitchell, G.L. Rempel, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. (A), 1970, 3322.
92. J. Chatt, N.P. Johnson, B.L. Shaw, J. Chem. Soc. (A), 1967, 604.
93. D.H. Blake, M. Kubota, Inorg. Chem., 1970, 9, 989.
94. A.J. Deeming and B.L. Shaw, J. Chem. Soc. (A), 1968, 1887.
95. W.C. Drinkard, D.R. Eaton, J.P. Jesson and R.V. Lindsey, Jr., Inorg. Chem., 1970, 9, 392.
96. R.G. Pearson, J. Amer. Chem. Soc., 1963, 85, 3533.
97. B.L. Booth and A.D. Lloyd, J. Organometal. Chem., 1972, 35, 195.
98. (a) J.D. Gilbert, D. Rose and G. Wilkinson, J. Chem. Soc. (A), 1970, 2765, in the formation of $\text{Ru}(\text{pyS})_2(\text{PPh}_3)_2$, and
(b) S.R. Fletcher and A.C. Skapski, J.C.S. Dalton, 1972, 635 for crystal structure of $\text{Ru}(\text{pyS})_2(\text{PPh}_3)_2$.