

OXIDATIVE ADDITION REACTIONS OF SOME IRIDIUM(I) COMPLEXES

by

Romeo Charles

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Research School of Chemistry,  
The Australian National University,  
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b. Results and Discussion

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SOME COMPLEXES AND THEIR NUMBERED ASSIGNMENTS

$\text{IrCl}(\text{Ph}_3\text{P})_3$  1;  $\text{IrCl}(\text{Ph}_3\text{As})_3$  2;  $\text{IrCl}(\text{MePh}_2\text{P})_3$  3;  
 $\text{RhCl}(\text{Ph}_3\text{P})_3$  23; trans- $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  11;  
 $\text{IrHCl}_2(\text{Ph}_3\text{P})_3$  28.

In Chapter 2:  $\text{IrHCl}(\text{SiR}_3)(\text{Ph}_3\text{P})_2$  4;  $\text{R}_3 =$  (a)  $\text{Cl}_3$ ,  
 (b)  $\text{MeCl}_2$ , (c)  $\text{Ph}_3$ , (d)  $(\text{OEt})_3$ ,  
 $\text{IrHCl}(\text{SiR}_3)(\text{Ph}_3\text{As})_2$  5;  $\text{R}_3 =$  (a)  $\text{Cl}_3$ ,  
 (b)  $\text{MeCl}_2$ , (c)  $\text{Ph}_3$ , (d)  $(\text{OEt})_3$ ,  
 $\text{IrHCl}(\text{SiR}_3)(\text{MePh}_2\text{P})_2$  8;  $\text{R}_3 =$  (a)  $\text{Cl}_3$ ,  
 (b)  $\text{MeCl}_2$ , (c)  $(\text{OEt})_3$ .

In Chapter 4:  $\text{IrCl}_2(\text{R})(\text{CO})(\text{Ph}_3\text{P})_2$  33;  $\text{R} =$  (a) Me,  
 (b) Et, (c)  $(\text{CH}_2)_2\text{Me}$ , (d)  $(\text{CH}_2)_3\text{Me}$ ,  
 (e)  $(\text{CH}_2)_4\text{Me}$ , (f)  $(\text{CH}_2)_2\text{Ph}$ , (g) Ph,  
 (h)  $(\text{CH}_2)_6\text{Me}$ ,  
 $(\text{IrCl}_2(\text{R})(\text{CO}))_2$  39;  $\text{R} =$  (a) Me, (b) Et,  
 (c) iso-propyl, (d) Ph, (e) n-propyl,  
 (f) n-butyl, (g) 2-butyl, (h) 2-phenethyl,  
 (i) 2-phenethyl, (j) n-pentyl.

ABBREVIATIONS AND NUMBERING OF COMPLEXES

The following abbreviations are used throughout this thesis:

Me	=	CH <sub>3</sub>
Et	=	C <sub>2</sub> H <sub>5</sub>
1,5-C <sub>8</sub> H <sub>12</sub>	=	cycloocta-1,5-diene
Ph	=	C <sub>6</sub> H <sub>5</sub>
C <sub>8</sub> H <sub>14</sub>	=	cyclooctene
n.m.r.	=	nuclear magnetic resonance
<u>o</u> -, <u>m</u> -, <u>p</u> -	=	ortho-, meta-, para-

SOME COMPLEXES AND THEIR NUMBERED ASSIGNMENTS

IrCl(Ph<sub>3</sub>P)<sub>3</sub> 1; IrCl(Ph<sub>3</sub>As)<sub>3</sub> 2; IrCl(MePh<sub>2</sub>P)<sub>3</sub> 3;  
 RhCl(Ph<sub>3</sub>P)<sub>3</sub> 23; trans-IrCl(CO)(Ph<sub>3</sub>P)<sub>2</sub> 11;  
 IrHCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>3</sub> 38.

In Chapter 2: IrHCl(SiR<sub>3</sub>)(Ph<sub>3</sub>P)<sub>2</sub> 4; R<sub>3</sub> = (a) Cl<sub>3</sub>,  
 (b) MeCl<sub>2</sub>, (c) Ph<sub>3</sub>, (d) (OEt)<sub>3</sub>  
 IrHCl(SiR<sub>3</sub>)(Ph<sub>3</sub>As)<sub>2</sub> 5; R<sub>3</sub> = (a) Cl<sub>3</sub>,  
 (b) MeCl<sub>2</sub>, (c) Ph<sub>3</sub>, (d) (OEt)<sub>3</sub>  
 IrHCl(SiR<sub>3</sub>)(MePh<sub>2</sub>P)<sub>3</sub> 8; R<sub>3</sub> = (a) Cl<sub>3</sub>,  
 (b) MeCl<sub>2</sub>, (c) (OEt)<sub>3</sub>

In Chapter 4: IrCl<sub>2</sub>(R)(CO)(Ph<sub>3</sub>P)<sub>2</sub> 33; R = (a) Me,  
 (b) Et, (c) (CH<sub>2</sub>)<sub>2</sub>Me, (d) (CH<sub>2</sub>)<sub>3</sub>Me,  
 (e) (CH<sub>2</sub>)<sub>4</sub>Me, (f) (CH<sub>2</sub>)<sub>2</sub>Ph, (g) Ph,  
 (h) (CH<sub>2</sub>)<sub>6</sub>Me  
 [IrCl<sub>2</sub>(R)(CO)<sub>2</sub>]<sub>2</sub> 39; R = (a) Me, (b) Et  
 (c) iso-propyl (d) Ph (e) n-propyl  
 (f) n-butyl, (g) 2-butyl, (h) α-phenethyl  
 (i) β-phenethyl (j) n-pentyl.



In Chapter 5:  $\text{IrHCl}[(\text{C}_6\text{H}_4\text{O})(\text{PhO})_2\text{P}]_2\text{L}_2$  45;

- L = (a)  $(\text{PhO})_3\text{P}$ , (b)  $\text{Ph}_3\text{P}$ , (c)  $\text{MePh}_2\text{P}$ ,  
 (d)  $\text{Me}_2\text{PhP}$ , (e)  $\text{Ph}_3\text{As}$ .

This work is concerned with the addition reactions of iridium(I) complexes,  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ ,  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{As})_2$ ,  $\text{IrCl}(\text{CO})(\text{MePh}_2\text{P})_2$ ,  $\text{IrCl}(\text{CO})(\text{Me}_2\text{PhP})_2$ . The addition reactions of silicon hydrides, acetylenes and acyl chlorides have been studied and the products characterized by infrared and n.m.r. spectroscopy.

The products obtained from the reaction of silicon hydrides and the iridium(I) complexes are all hydride-silylium(III) complexes; the coordination number of the complexes (5 or 6), however, varies with the ligand L and the silicon hydride used. Carbonylation of these silylium(III) complexes in most cases gives stable octahedral silylium(III)-acetyl-hydride complexes.

Alkylsilylium(III) complexes of the type  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2(\text{R})$  (R-straight-chain alkyl) are obtained when acyl chlorides,  $\text{RCOCl}$ , (R-straight or branched-chain alkyl) react with the iridium(I) complex,  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ . The interesting feature of these reactions is the observed isomerization from branched-chain alkyl to straight-chain alkyl when a branched-chain acyl chloride reacts with the iridium(I) complex. This isomerization is discussed and compared with the mechanism proposed for hydroformylation. A similar isomerization occurs in the oxidative addition of acyl chlorides to the complex  $\text{IrCl}(\text{CO})(\text{C}_2\text{H}_5)_2$ , giving as the final product  $\text{IrCl}(\text{CO})_2(\text{C}_2\text{H}_5)_2$ . In this series an equilibrium exists between the branched-chain alkyl and the straight-chain alkyl complexes.



SUMMARY

This work is concerned primarily with oxidative addition reactions of the iridium(I) complexes,  $\text{IrClL}_3$  ( $\text{L}=\text{Ph}_3\text{P}, \text{Ph}_3\text{As}, \text{MePh}_2\text{P}$ ). The addition reactions of silicon hydrides, acetylenes and acyl chlorides have been studied and the products characterized by infrared and n.m.r. spectroscopies.

The products obtained from the reaction of silicon hydrides and the iridium(I) complexes are all hydrido-silyliridium(III) complexes; the coordination number of the complexes (5 or 6), however, varies with the ligand L and the silicon hydride used. Carbonylation of these silyliridium(III) complexes gives in most cases stable octahedral silyliridium(III)-carbonyl-hydride complexes.

Alkyliridium(III) complexes of the type  $\text{IrCl}_2\text{R}(\text{CO})(\text{Ph}_3\text{P})_2$  ( $\text{R}=\text{straight-chain alkyl}$ ) are obtained when acyl chlorides,  $\text{RCOCl}$ , ( $\text{R}=\text{straight- or branched-chain alkyl}$ ) react with the iridium(I) complex,  $\text{IrCl}(\text{Ph}_3\text{P})_3$ . The interesting feature of these reactions is the observed isomerization from branched-chain alkyl to straight-chain alkyl when a branched-chain acyl chloride reacts with the iridium(I) complex. This isomerization is discussed and compared with the mechanism proposed for hydroformylation. A similar isomerization occurs in the oxidative addition of acyl chlorides to the complex  $[\text{IrCl}(\text{CO})(\text{C}_8\text{H}_{14})_2]_2$  giving as the final product  $[\text{IrCl}_2\text{R}(\text{CO})_2]_2$ . In this series an equilibrium exists between the branched-chain alkyl and the straight-chain alkyl complexes.

Terminal acetylenes ( $\text{HC}\equiv\text{CR}$ ) react with the complex  $\text{IrCl}(\text{Ph}_3\text{P})_3$  to give hydridoiridium(III)-acetylide complexes. The reaction with diphenylacetylene gives a known  $\mu$ -bonded iridium-acetylene complex, and the reaction with dimethyl acetylenedicarboxylate produces a known iridocycle complex containing a dimerised acetylene moiety.

The complex  $\text{IrCl}(\text{MePh}_2\text{P})_3$  when heated in benzene isomerizes to a hydridoiridium(III) complex. The hydrogen atom is shown to originate probably from the ortho-position of a phenyl ring and not from a methyl group of a phosphine ligand.

Attempts to prepare iridium(I) triphenylphosphite complexes of type  $\text{IrCl}[(\text{PhO})_3\text{P}]_2$  [ $\text{L}=(\text{PhO})_3\text{P}, \text{Ph}_3\text{P}, \text{Ph}_3\text{As}, \text{MePh}_2\text{P}, \text{Me}_2\text{PhP}$ ] lead in all cases to the formation of iridium(III)-hydride complexes,  $\text{IrHCl}[(\text{o-C}_6\text{H}_4\text{O})(\text{PhO})_2\text{P}]_2$ . When these new complexes are heated in an inert solvent, complexes possessing two metal-ortho-carbon bonds are obtained. These bonds are shown to be formed by the interaction of the metal and the ortho-carbon atoms of two of the phenyl rings of the triphenylphosphite ligand and not from the ligand L.

## CHAPTER 1

### GENERAL INTRODUCTION

Oxidative addition reactions of transition metal complexes have been reviewed in detail by several authors.<sup>1,2,3,4</sup> This chapter will only summarize the more important results contained in those reviews with special emphasis on the reactions of  $d^8$  complexes.

Complexes of transition metals having a  $d^8$  configuration may either be (i) four-coordinated and possess a square-planar configuration or (ii) five-coordinated. The latter complexes are coordinatively saturated, since there are 18 electrons in the valence shell, and usually have a trigonal bipyramidal configuration, whereas the former complexes are coordinatively unsaturated, with 16 electrons in the valence shell, e.g.,

four-coordinate  $d^8$  complexes :  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ ,  $\text{RhCl}(\text{Ph}_3\text{P})_3$ ,  
 $\text{PtHCl}(\text{Et}_3\text{P})_2$

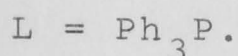
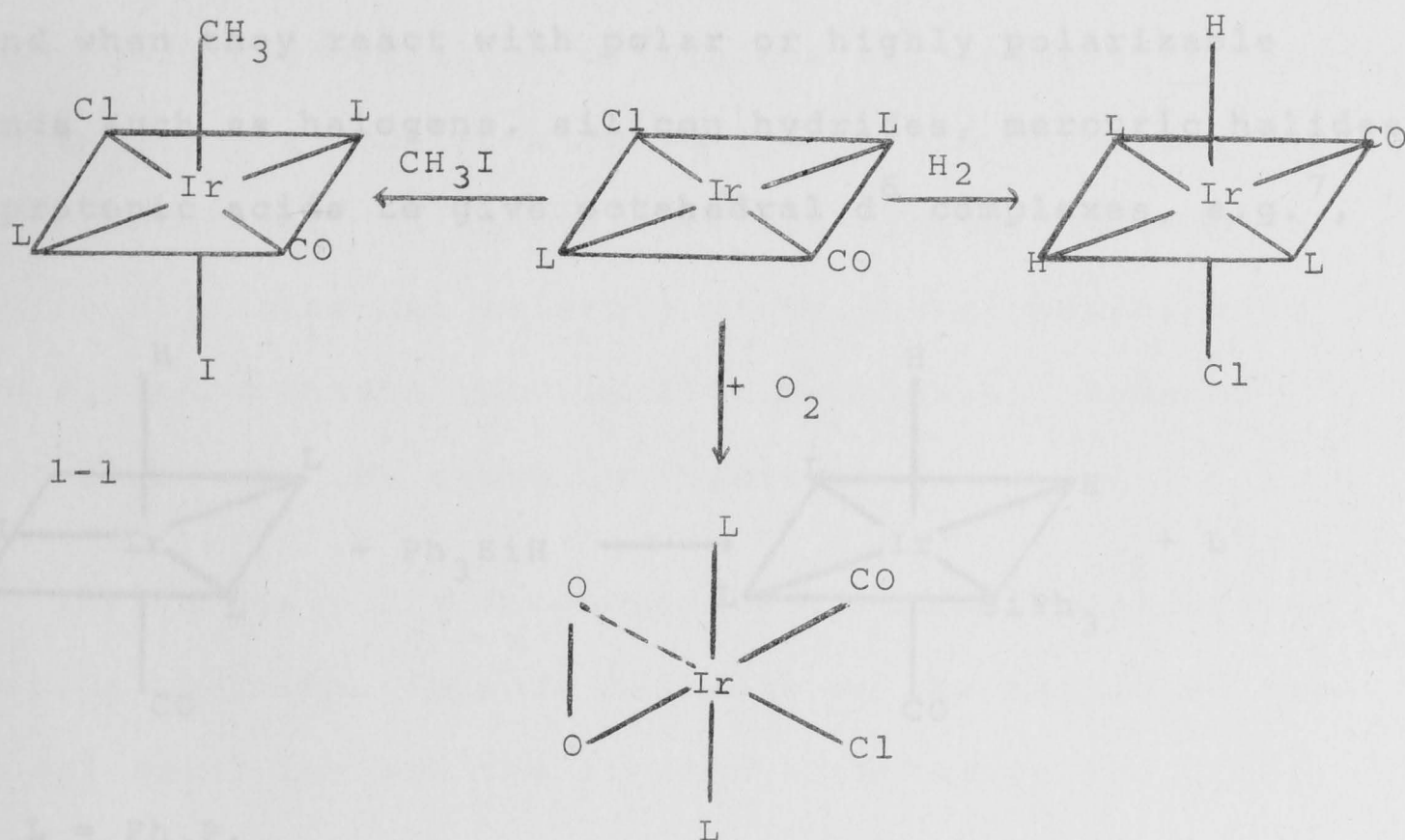
five-coordinate  $d^8$  complexes :  $\text{IrH}(\text{CO})(\text{Ph}_3\text{P})_3$ ,  $\text{Os}(\text{CO})_5$ ,  
 $\text{Ru}(\text{CO})_3(\text{Ph}_3\text{P})_2$

Nyholm<sup>5</sup> has pointed out that in general the tendency for an element having a  $d^8$  configuration to become five-coordinate increases as one ascends a triad and as one passes from right to left in Group VIII.

Planar complexes having a  $d^8$  configuration are often converted into octahedral  $d^6$  complexes by the addition of a covalent molecule to the coordination sphere. The most extensive studies on the oxidative addition reactions of  $d^8$  complexes have been made on square-planar iridium(I) complexes



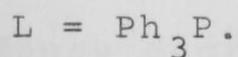
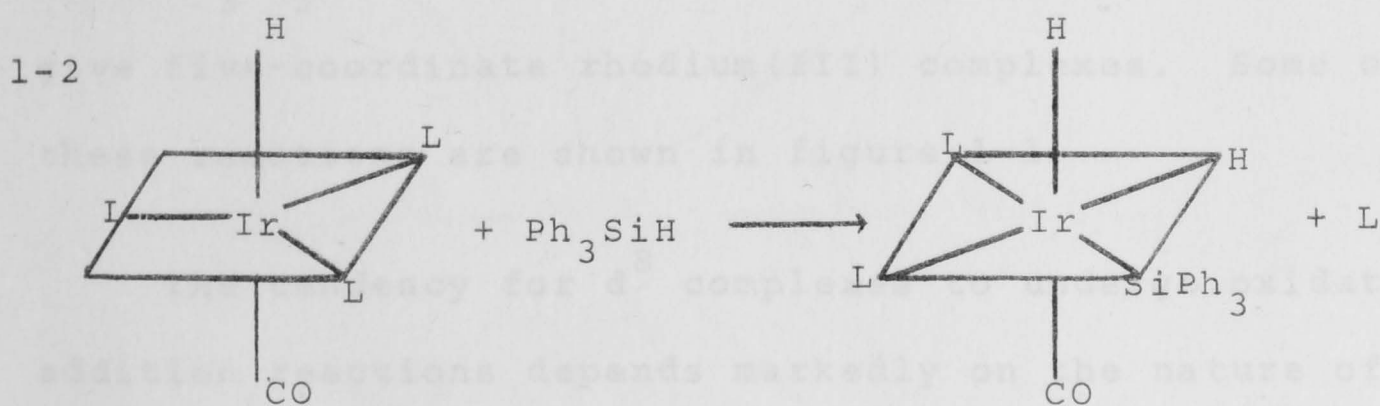
of the type  $\text{IrY}(\text{CO})\text{L}_2$  [Y=halogen, L=tertiary phosphines]. These complexes undergo a number of oxidative addition reactions with molecules such as acyl halides, halogens, silicon hydrides, acetylene, olefins and alkyl halides. In most cases there is complete cleavage of the addendum bond but in certain cases, addition takes place so that the two parts of the addendum remain joined by a bond, e.g.,



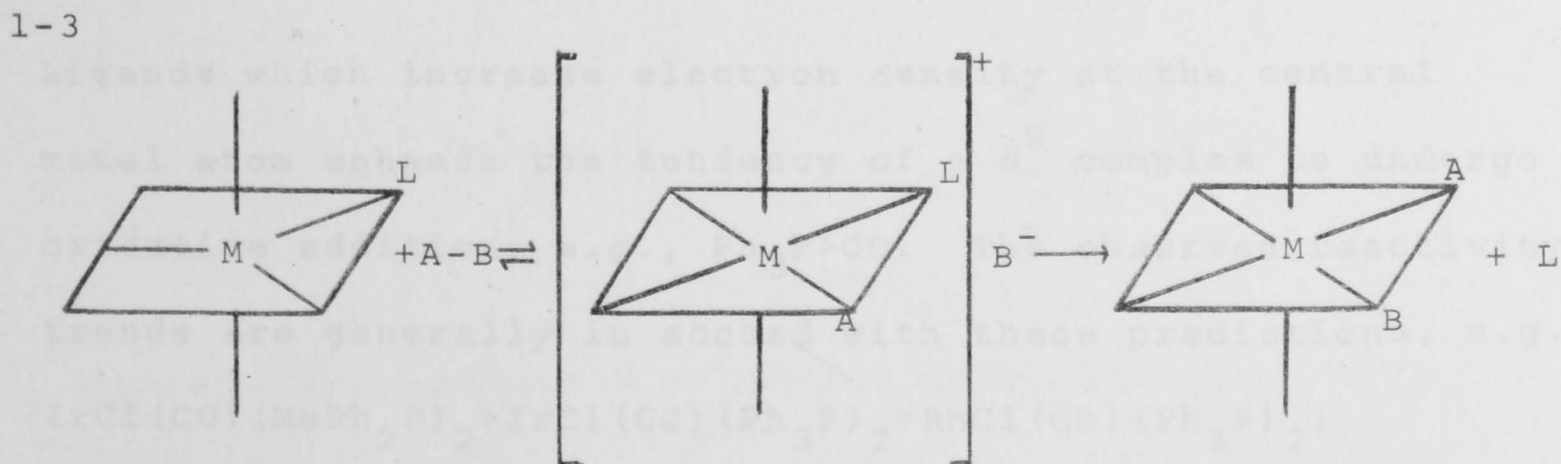
These additions often occur in a stereospecific manner; both cis and trans modes of addition have been observed depending on the reagent and the medium. Chock and Halpern<sup>6</sup> have performed kinetic studies of the addition of alkyl halides and hydrogen to the iridium(I) complex, trans- $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ . They interpreted their results in terms of two different limiting mechanisms. The addition of hydrogen appears to be a concerted process, involving a relatively nonpolar transition state which leads to a cis adduct (eqn. 1-1). The oxidative addition of alkyl halides,

on the other hand, is believed to entail an  $S_N2$  type of attack, with at least partial halide displacement, through a highly unsymmetrical transition state (see also Chapter 2, section d). This mechanism is supported by the fact that the stereochemistry of oxidative addition of alkyl halides is trans.

Coordinatively saturated  $d^8$  complexes lose a neutral ligand when they react with polar or highly polarizable addenda such as halogens, silicon hydrides, mercuric halides and protonic acids to give octahedral  $d^6$  complexes, e.g. <sup>7</sup>,



Collman and Roper<sup>2</sup> have suggested a two-step mechanism, in which the electrophile forms a bond with the central metal in the trigonal plane as an intermediate, with the second step being the irreversible loss of a neutral ligand:

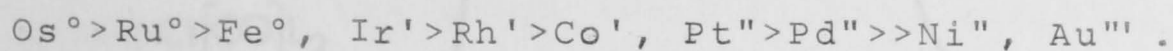




Alternatively five-coordinate  $d^8$  complexes can react through dissociation prior to oxidative addition.<sup>8</sup> The final products of oxidative addition to saturated  $d^8$  complexes are those resulting from overall cis addition.

Oxidative addition reactions to the planar  $d^8$  complex,  $\text{RhCl}(\text{Ph}_3\text{P})_3$  have also been extensively studied.<sup>9,10</sup> This is mainly due to the ability of this complex to catalyse homogeneous hydrogenation of olefins and acetylenes, and to decarbonylate alcohols, aldehydes and acid chlorides (see also Chapter 4). In many of its additions, the complex  $\text{RhCl}(\text{Ph}_3\text{P})_3$  loses one molecule of triphenylphosphine to give five-coordinate rhodium(III) complexes. Some of these reactions are shown in figure 1-1.

The tendency for  $d^8$  complexes to undergo oxidative addition reactions depends markedly on the nature of the central metal ion and the ligands attached to it. This tendency decreases in going from left to right across the transition series and increases in going down a given group. The resultant reactivity towards oxidative addition is therefore expected to decrease roughly in the following order:



Ligands which increase electron density at the central metal atom enhance the tendency of a  $d^8$  complex to undergo oxidative addition, e.g.,  $\text{Ph}_3\text{P} > \text{CO}$ . The observed reactivity trends are generally in accord with these predictions, e.g.

$$\text{IrCl}(\text{CO})(\text{MePh}_2\text{P})_2 > \text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2 > \text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2;$$

$$\text{IrCl}(\text{Ph}_3\text{P})_3 > \text{RhCl}(\text{Ph}_3\text{P})_3 > \text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2.$$

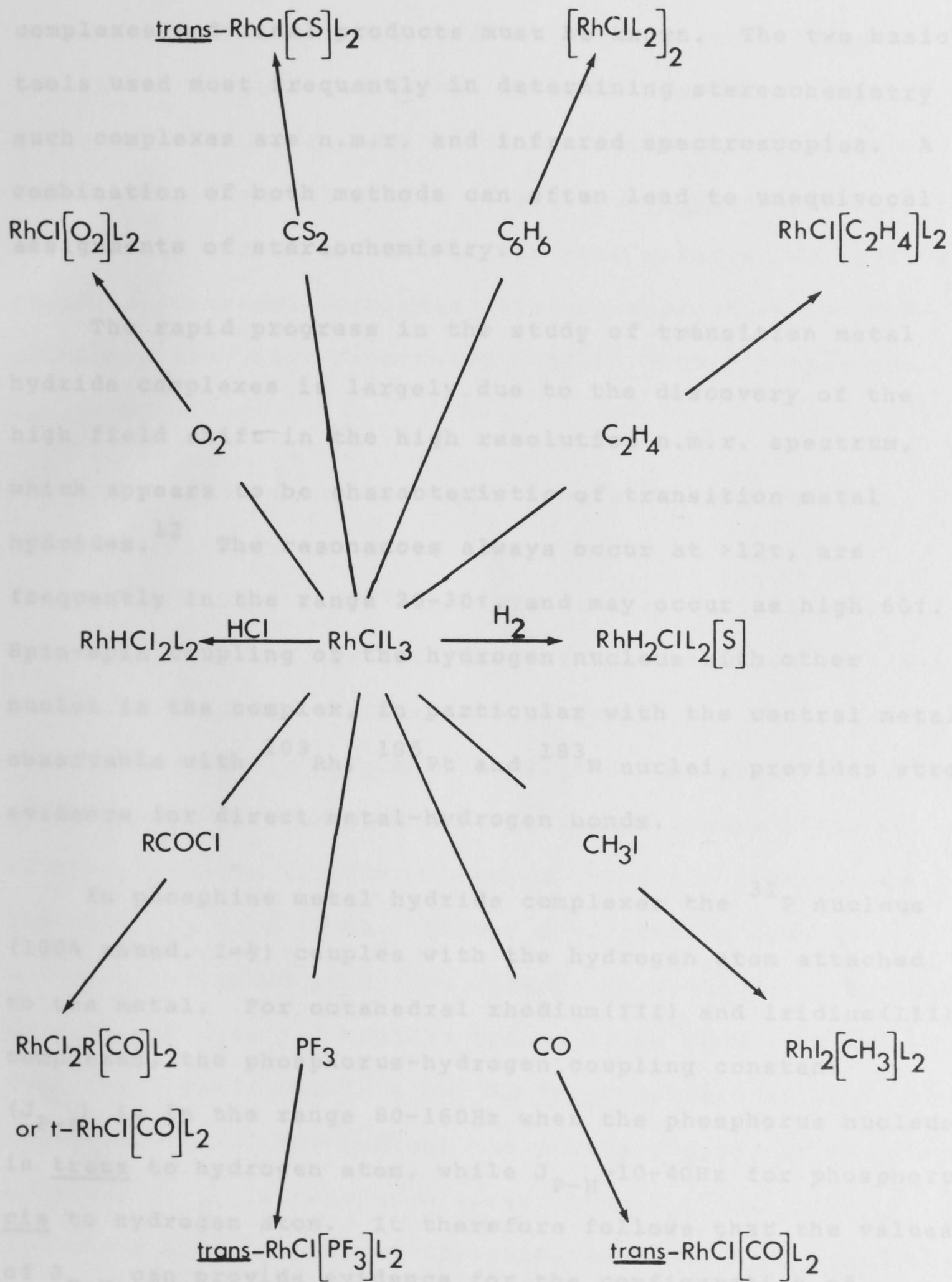


Figure 1-1. Some reactions of the complex  $\text{RhClL}_3$ ;  $\text{L} = \text{Ph}_3\text{P}$ .

In order that mechanisms may be proposed for oxidative addition reactions, the stereochemistry of both starting complexes and final products must be known. The two basic tools used most frequently in determining stereochemistry of such complexes are n.m.r. and infrared spectroscopies. A combination of both methods can often lead to unequivocal assignments of stereochemistry.

The rapid progress in the study of transition metal hydride complexes is largely due to the discovery of the high field shift in the high resolution n.m.r. spectrum, which appears to be characteristic of transition metal hydrides.<sup>12</sup> The resonances always occur at  $>12\tau$ , are frequently in the range 20-30 $\tau$ , and may occur as high 60 $\tau$ . Spin-spin coupling of the hydrogen nucleus with other nuclei in the complex, in particular with the central metal, observable with  $^{103}\text{Rh}$ ,  $^{195}\text{Pt}$  and  $^{183}\text{W}$  nuclei, provides strong evidence for direct metal-hydrogen bonds.

In phosphine metal hydride complexes the  $^{31}\text{P}$  nucleus (100% abund.  $I=\frac{1}{2}$ ) couples with the hydrogen atom attached to the metal. For octahedral rhodium(III) and iridium(III) complexes, the phosphorus-hydrogen coupling constant ( $J_{\text{P-H}}$ ) is in the range 80-160Hz when the phosphorus nucleus is trans to hydrogen atom, while  $J_{\text{P-H}}=10-40\text{Hz}$  for phosphorus cis to hydrogen atom. It therefore follows that the values of  $J_{\text{P-H}}$  can provide evidence for the configuration of various phosphine complexes. Table 1-1 lists chemical shifts and coupling constants for several phosphine iridium(III) complexes. In some dihydrido-complexes coupling between the non-equivalent hydrogen atoms is observed;  $J_{\text{H1-H2}}=4-8\text{Hz}$ .



From a survey of octahedral iridium(III) hydride complexes it is evident that protons trans to halogens have much higher chemical shifts ( $\sim 30\tau$ ) than protons trans to phosphorus nucleus and carbon monoxide (19-24 $\tau$ ). On the other hand, there appears to be no characteristic difference between the chemical shifts of protons trans to phosphorus nucleus and carbon monoxide. Not many examples of hydrido-phosphine-carbonyl complexes with the appropriate stereochemistry are known from which a satisfactory comparison may be made.

In octahedral iridium(III) complexes in which the phosphine ligands are methyl substituted (e.g.  $\text{MePh}_2\text{P}$ ), Jenkins and Shaw<sup>11</sup> have demonstrated that it is possible to determine the relative positions of the methyl substituted phosphine ligands by n.m.r. spectroscopy. In complexes having mutually trans phosphine ligands the proton n.m.r. spectra exhibit a triplet for the methyl groups attached to the phosphine ligands. However, when the ligands are mutually cis, the (P- $\text{CH}_3$ ) groups give rise to doublets. Methyl substituted phosphine ligands (e.g.  $\text{MePh}_2\text{P}$ ) represent examples of  $X_n\text{AA}'X_n$  nuclear spin systems [ $X=\text{H}$ ,  $A=\text{P}$ ]. When the ligands are in a mutual trans-configuration in the metal complexes, the geminal phosphorus-phosphorus coupling constant  $J_{A-A'}$  is very much larger than  $L_{AX}$ , [ $L_{AX} = |^2J_{AX} - ^4J_{AX}'|$ ] and the  $X_n\text{AA}'X_n$  spectrum approximates to an  $A_nX_{2n}$  system with the central line of the triplet resulting from overlap of lines. In analogous cis complexes, however,  $J_{AA'}$  and  $J_{AX}$  are both small and the proton n.m.r. spectrum therefore usually appears as a doublet.

The infrared spectra of most iridium hydride complexes show bands in the region  $1700-2200\text{cm}^{-1}$ , which are assigned to the iridium-hydrogen stretching modes.<sup>12</sup> Table 1-1 lists the iridium-hydrogen stretching frequencies of several iridium(III) hydride complexes. A similar trend is observed for  $\nu(\text{Ir-H})$  depending on the ligand trans to the hydrogen atom as is observed for  $\nu(\text{Ir-H})$ . For octahedral iridium(III) hydrides, hydrogen atoms trans to halogens have much higher iridium-hydrogen stretching frequencies than do hydrogen atoms trans to phosphine or carbonyl groups. Most iridium-hydrogen stretching frequencies are observed between  $2000\text{cm}^{-1}$  and  $2200\text{cm}^{-1}$  but frequencies as low as  $1700\text{cm}^{-1}$  have been recorded and several authors have associated these frequencies with vibrations involving two hydrogen atoms in mutually trans positions.

The carbonyl stretching vibrations in iridium-carbonyl complexes are very sensitive to the charge of the central metal ion, moving to higher frequencies as the positive charge on the metal ion increases, viz.  $\nu(\text{C}\equiv\text{O})$  for  $\text{Ir(III)} > \nu(\text{C}\equiv\text{O})$  for  $\text{Ir(I)}$ . Such a strengthening of the CO bonding is expected since positive charge on the metal tends to reduce donation by the metal into the antibonding  $\pi(\text{II})$  orbital of the carbonyl group.

Jenkins and Shaw have studied the far-infrared absorption spectra of a series of halogeno-iridium(III) complexes.<sup>13</sup> They observed that the iridium-chlorine frequency is sensitive to the ligand trans to the chlorine atom and is insensitive to the cis ligands. The general range observed for the values of the  $\nu(\text{Ir-Cl})$  is  $320-330\text{cm}^{-1}$



[Cl trans to halogen],  $300-320\text{cm}^{-1}$  [Cl trans to carbonyl],  $275-290\text{cm}^{-1}$  [Cl trans to phosphine] and  $250-265\text{cm}^{-1}$  [Cl trans to H or alkyl group].

The preparation and some reactions of the iridium(I) complexes  $\text{IrClL}_3$  [L=tertiary phosphine, arsine, stibine] have been studied previously.<sup>36</sup> The work presented in this thesis follows on from the previous work with more emphasis on oxidative addition reactions of complexes  $\text{IrClL}_3$  [L= $\text{Ph}_3\text{P}$ ,  $\text{Ph}_3\text{As}$ ,  $\text{MePh}_2\text{P}$ ]. Chapter 2 deals with the addition of silicon hydrides to complexes of type  $\text{IrClL}_3$  [1 L= $\text{Ph}_3\text{P}$ ; 2 L= $\text{Ph}_3\text{As}$ ; 3 L= $\text{MePh}_2\text{P}$ ]. The oxidative addition reactions of acetylenes and acyl chlorides to the iridium(I) complexes 1 and 3 are presented in Chapters 3 and 4 respectively. Chapter 5 is concerned with the reactions and behaviour of some triphenylphosphite iridium complexes containing tertiary phosphines and triphenylarsine. Finally in Chapter 6 a general discussion on the results obtained is presented and comparisons of the reactivities towards oxidative additions with the complexes  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ ,  $\text{RhCl}(\text{Ph}_3\text{P})_3$  and  $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$  are made and discussed.

TABLE 1-1

N.m.r. and infrared data for some iridium(III)-hydride complexes.<sup>a</sup>

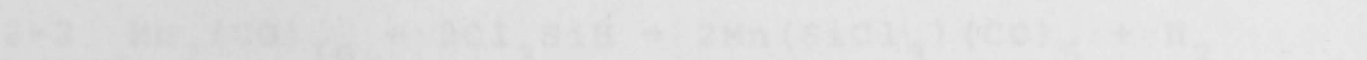
Complex	H trans to $\tau$	$\tau$ (Ir-H)	$J_{P-H}$ Hz	$\nu$ (Ir-H) $cm^{-1}$
$IrHCl_2(Ph_3P)_3^b$	Cl	29.2	15	2228
$IrH_2Cl(CO)(Ph_3P)_2$	Cl	28.4	15	2222
$IrHCl_2(CO)(Et_2PhP)_2^b$	Cl	26.1	12	2189
$IrHCl_2(Ph_3P)_3^b$	$Ph_3P$	23.8	164	2193
$IrH_2Cl(Ph_3P)_3$	$Ph_3P$	21.1	136	2120
$IrHCl_2(Et_2PhP)_3$	$Et_2PhP$	22.6	158	2090
$IrH_2Cl(CO)(Ph_3P)_2^b$	CO	17.3	15	2090
$IrHCl_2(CO)(Et_2PhP)_2$	CO	19.0	16	2008
$IrHCl(SnCl_3)(CO)(Ph_3P)_2^b$	$SnCl_3$	19.9	10	2148

a..... these data were obtained from reference 12 unless otherwise stated.

b..... from reference 27.



nickel,<sup>20</sup> molybdenum<sup>22</sup> and platinum<sup>19</sup> have been prepared by the direct reaction of silicon hydrides and the corresponding transition metal complexes, e.g.,



The reaction of ethoxyallyl-lithium and chloro-transition metal complexes has produced allyl derivatives of zirconium,<sup>21</sup> molybdenum,<sup>23</sup> tungsten,<sup>23</sup> gold<sup>24</sup> and platinum.<sup>24</sup> e.g.,



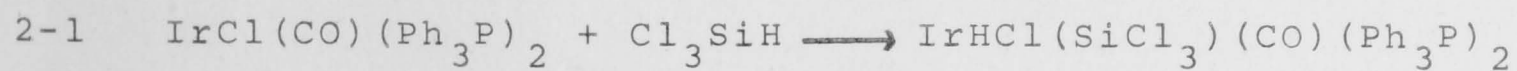
## CHAPTER 2

THE ADDITION OF SILICON HYDRIDES

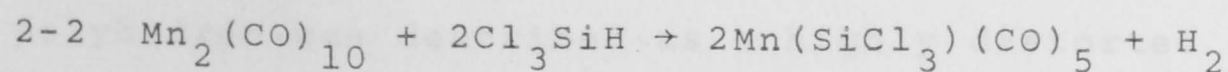
Although the first compound containing a silicon-transition metal bond was prepared in 1956,<sup>14</sup> the field has attracted wide attention only in the past five years<sup>15</sup> and many such compounds are now known.

This sudden interest stems from the fact that oxidative addition reactions have received a great deal of attention both as an interesting class of reaction of transition metal complexes and as an important step in several homogeneous catalytic reactions.<sup>2,4</sup> In 1965 Harrod and Chalk postulated that oxidative addition of silicon hydrides to certain d<sup>8</sup> complexes was a key factor in the ability of the latter to catalyze the hydrosilation of unsaturated organic compounds.<sup>16</sup>

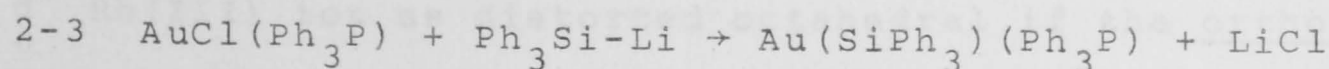
Since then oxidative addition reactions involving cleavage of the silicon-hydrogen bond have afforded silyl hydrides of rhodium,<sup>17,18,25</sup> iridium,<sup>7,16</sup> chromium,<sup>17</sup> manganese,<sup>17</sup> iron,<sup>17</sup> cobalt<sup>17</sup> and platinum,<sup>19</sup> e.g.,



Silyl derivatives of manganese,<sup>20</sup> rhenium,<sup>20</sup> ruthenium,<sup>21</sup> nickel,<sup>22</sup> molybdenum<sup>22</sup> and platinum<sup>19</sup> have been prepared by the direct reaction of silicon hydrides and the corresponding transition metal complexes, e.g.,



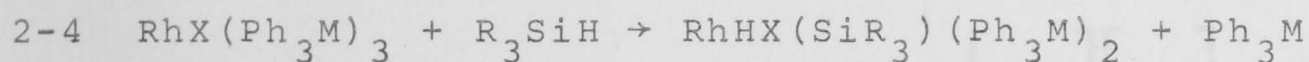
The reaction of triorganosilyl-lithiums and chloro-transition metal complexes has produced silyl derivatives of zirconium,<sup>23</sup> molybdenum,<sup>23</sup> tungsten,<sup>23</sup> gold<sup>24</sup> and platinum,<sup>24</sup> e.g.,





Many transition metal complexes possessing covalent metal-tin, germanium or lead bonds have been prepared by routes which are similar to those used for silyl-transition metal complexes.<sup>15,37</sup>

The reaction of silicon hydrides with the complexes  $\text{RhCl}(\text{Ph}_3\text{M})_3$  [M=P,As,Sb] at room temperature gives five-coordinate silylrhodium(III) complexes, as shown independently by two groups:<sup>18,25</sup>



M = P,As,Sb

X = Cl,Br,I

$\text{R}_3 = \text{Cl}_3, \text{MeCl}_2, \text{EtCl}_2, \text{Me}_2\text{Cl}, \text{Et}_2\text{Cl}, \text{Me}_3, \text{Et}_3, \text{Ph}_3, (\text{OEt})_3$

Carbonylation of the silylrhodium(III) derivatives results in loss of silane and formation of the rhodium(I) complexes of type  $\text{RhX}(\text{CO})(\text{Ph}_3\text{M})_2$ . There is some infrared spectroscopic evidence for intermediate six-coordinate complexes,  $\text{RhHX}(\text{SiR}_3)(\text{CO})(\text{Ph}_3\text{M})_2$  but these are too unstable at room temperature for detailed study.

The crystal structure of one of the silylrhodium(III) adducts,  $\text{RhHCl}(\text{SiCl}_3)(\text{Ph}_3\text{P})_2$  has been studied.<sup>26</sup> Figure 2-1 shows a perspective view of the coordination polyhedron around the rhodium atom and table 2-1 lists some selected interatomic distances and angles. The rhodium coordination polyhedron was described as a highly distorted trigonal bipyramid, with trans phosphines at the apices and H, Cl and  $\text{SiCl}_3$  in the trigonal plane. Alternatively the authors described the coordination about the formally  $d^6$  Rh(III) ion as distorted octahedral if the ortho-hydrogen

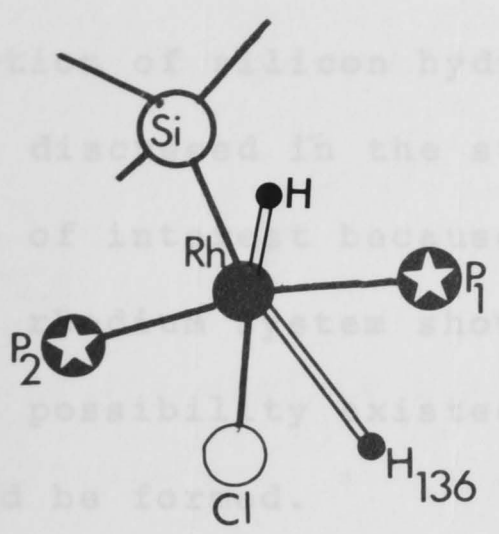
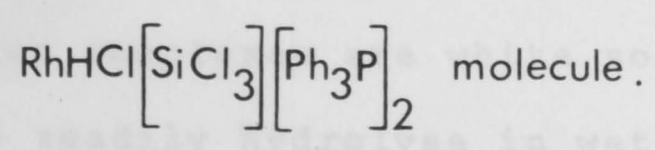


Figure 2-1. Perspective view of the  $\text{RhHCl}[\text{SiCl}_3][\text{Ph}_3\text{P}]_2$  molecule.

Distances	Value, Å	Angles	Value, deg.
Rh-Si	2.203	Si-Rh-Cl	115.9
Rh-Cl	2.387	Si-Rh-P <sub>1</sub>	98.3
Rh-P <sub>1</sub>	2.344	Si-Rh-P <sub>2</sub>	98.4
Rh-P <sub>2</sub>	2.332	Si-Rh-H	69
Rh-H	1.48	Si-Rh-H <sub>136</sub>	166
Rh-H <sub>136</sub>	2.79	Cl-Rh-H	174
		P <sub>1</sub> -Rh-P <sub>2</sub>	161.7

Table 2-1. Some interatomic distances and angles of the





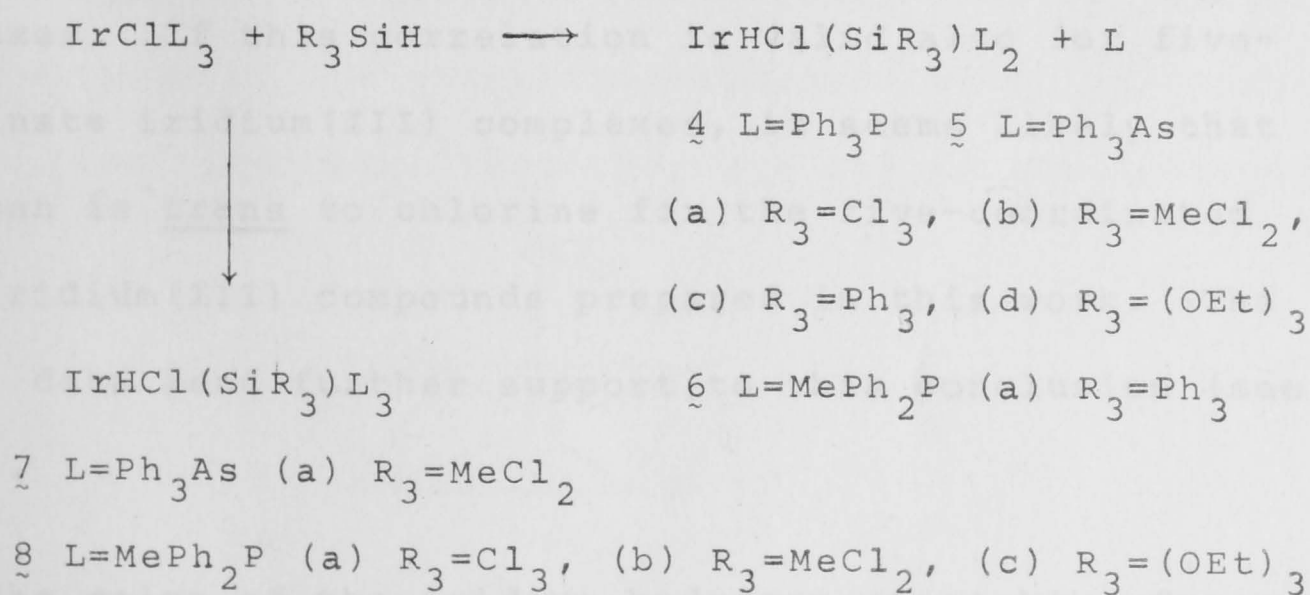
atom on a phenyl ring of a triphenylphosphine group is included at the sixth coordination site.

The reaction of silicon hydrides with complexes 1, 2 and 3 will be discussed in the subsequent section. These reactions are of interest because firstly, comparisons with the analogous rhodium system should be possible and secondly, the possibility existed that stable carbonylation products would be formed.

#### b. Results and Discussion

A variety of silicon hydrides reacts readily with the complexes  $\text{IrClL}_3$  [1  $\text{L}=\text{Ph}_3\text{P}$ , 2  $\text{L}=\text{Ph}_3\text{As}$ , 3  $\text{L}=\text{MePh}_2\text{P}$ ] to yield adducts according to scheme 2-5:

2-5



The five-coordinated iridium(III) products are air stable, yellow or orange-yellow solids, whereas the six-coordinated complexes are white solids. The chlorosilyl complexes readily hydrolyse in wet solvents giving off hydrogen chloride. The thermal stability of all the complexes is reasonably high, the decomposition points being in the range 95-200°C. The compounds are generally stable in

chlorine atom in these compounds. However, the low value solution in the presence of air but the chlorosilylmethyl-diphenylphosphine complexes undergo slow decomposition. Table 2-6 list the analyses of the silyliridium(III) complexes. suggests that hydrogen is probably trans to triphenylarsine or methyl-diphenylphosphine respectively.

### Infrared Spectra

All the adducts exhibit a strong bond in the region  $2130-2225\text{cm}^{-1}$  (table 2-2) which is distinctly different from the silicon-hydrogen stretching frequency of the free silane.<sup>29</sup> This bond is assigned to the iridium-hydrogen stretching mode and it lies in the range observed for other iridium(III)-hydride complexes.<sup>16,27,28</sup> The values of the iridium-hydrogen stretching frequencies for most of the silyliridium(III) adducts are characteristic of hydrogen trans to chlorine (ca.  $2200\text{cm}^{-1}$ ) in octahedral iridium(III) complexes. If this correlation is valid also for five-coordinate iridium(III) complexes, it seems likely that hydrogen is trans to chlorine for the five-coordinated silyliridium(III) compounds prepared in this work. The n.m.r. data lend further support to this conclusion (see below).

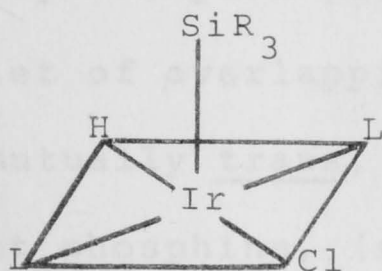
The value of the iridium-hydrogen stretching frequency ( $2130\text{cm}^{-1}$ ) for the five-coordinate complex,  $\text{IrHCl}(\text{SiCl}_3)(\text{Ph}_3\text{As})_2$  (5a) suggests that hydrogen is not trans to chlorine atom.

From the values of the iridium-hydrogen stretching frequencies  $2175\text{cm}^{-1}$ , for the octahedral silyliridium(III) complexes,  $\text{IrHCl}(\text{SiR}_3)(\text{MePh}_2\text{P})_3$ ,  $\text{R}_3 = \text{Cl}_3, \text{MeCl}_2$  (8a and 8b) it would be reasonable to assume that hydrogen is trans to

chlorine atom in these compounds. However, the low value ( $2150\text{cm}^{-1}$ ) of  $\nu(\text{Ir-H})$  for the complex  $\text{IrHCl}(\text{SiMeCl}_2)(\text{Ph}_3\text{As})_3$  (7a) and for  $\text{IrHCl}[\text{Si}(\text{OEt})_3](\text{MePh}_2\text{P})_3$  (8c) ( $2160\text{cm}^{-1}$ ) suggests that hydrogen is probably trans to triphenylarsine or methyldiphenylphosphine respectively.

### $^1\text{H-N.M.R. Spectra}$

In addition to the resonances due to the ligands  $\text{Ph}_3\text{P}$ ,  $\text{Ph}_3\text{As}$ ,  $\text{MePh}_2\text{P}$  and the silyl groups, the n.m.r. spectra also show signals in the high field region,  $20-30\tau$ , which is characteristic of hydrogen bound to transition metal. Table 2-3 lists the  $^1\text{H-n.m.r.}$  data for the silyliridium(III) complexes. For the five-coordinated complexes 4a, 4b, 4c, 4d and 6a a single triplet at about  $28\tau$  is observed, (see figure 2-2). This suggests that the two phosphine ligands must be in equivalent or closely similar positions and the value of the phosphorus-hydrogen coupling constant [ $J_{\text{PH}} \approx 15\text{Hz}$ ] indicates that they are cis to the hydrogen atom.<sup>28</sup>



4 L =  $\text{Ph}_3\text{P}$ , (a)  $\text{R}_3 = \text{Cl}_3$ , (b)  $\text{R}_3 = \text{MeCl}_2$ , (c)  $\text{R}_3 = \text{Ph}_3$ ,  
(d)  $\text{R}_3 = (\text{OEt})_3$

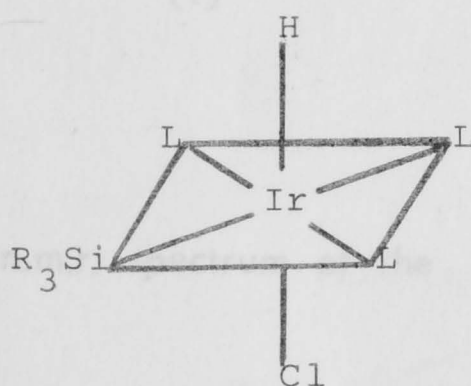
6 L =  $\text{MePh}_2\text{P}$ , (a)  $\text{R}_3 = \text{Ph}_3$

The high field n.m.r. spectra of the triphenylarsine analogues show only a singlet. Presumably the expected coupling with  $^{75}\text{As}(I=3/2)$  is not observed because this nucleus



possesses an electric quadrupole moment.

The stereochemistry of octahedral iridium(III)-hydride complexes containing tertiary phosphines can be determined from the position and multiplicity of the high field lines,<sup>28</sup> (see chapter 1). Thus, the position of the high field signal ( $29\tau$ ) in the n.m.r. spectra of the complexes  $\underline{8a}$  and  $\underline{8b}$  and the small coupling constants (table 2-3) indicate that hydrogen is trans to the chlorine atom and is mutually cis to three phosphorus atoms:



$\underline{8}$  L =  $\text{MePh}_2\text{P}$ , (a)  $\text{R}_3 = \text{Cl}_3$ , (b)  $\text{R}_3 = \text{MeCl}_2$

For the trichlorosilyl complex  $\underline{8a}$ , the hydride resonance consists of a doublet of overlapping triplets arising from coupling with two mutually trans, equivalent phosphines and a third inequivalent phosphine, (see figure 2-4).

In the case of the dichloromethylsilyl complex  $\underline{8b}$ , the hydride resonance consists of a 1:3:3:1 quartet (see figure 2-3); this suggests that the three phosphines, although not chemically equivalent, are magnetically equivalent,

$$J_{\text{P-H}} = 10.5\text{Hz.}$$

The hydrogen chemical shift ( $20.1\tau$ ) and the large coupling constant [ $J_{\text{P-H}} = 129\text{Hz}$ ] for the complex  $\text{IrHCl}[\text{Si}(\text{OEt})_3](\text{MePh}_2\text{P})_3$  ( $\underline{8c}$ ) clearly indicate that the



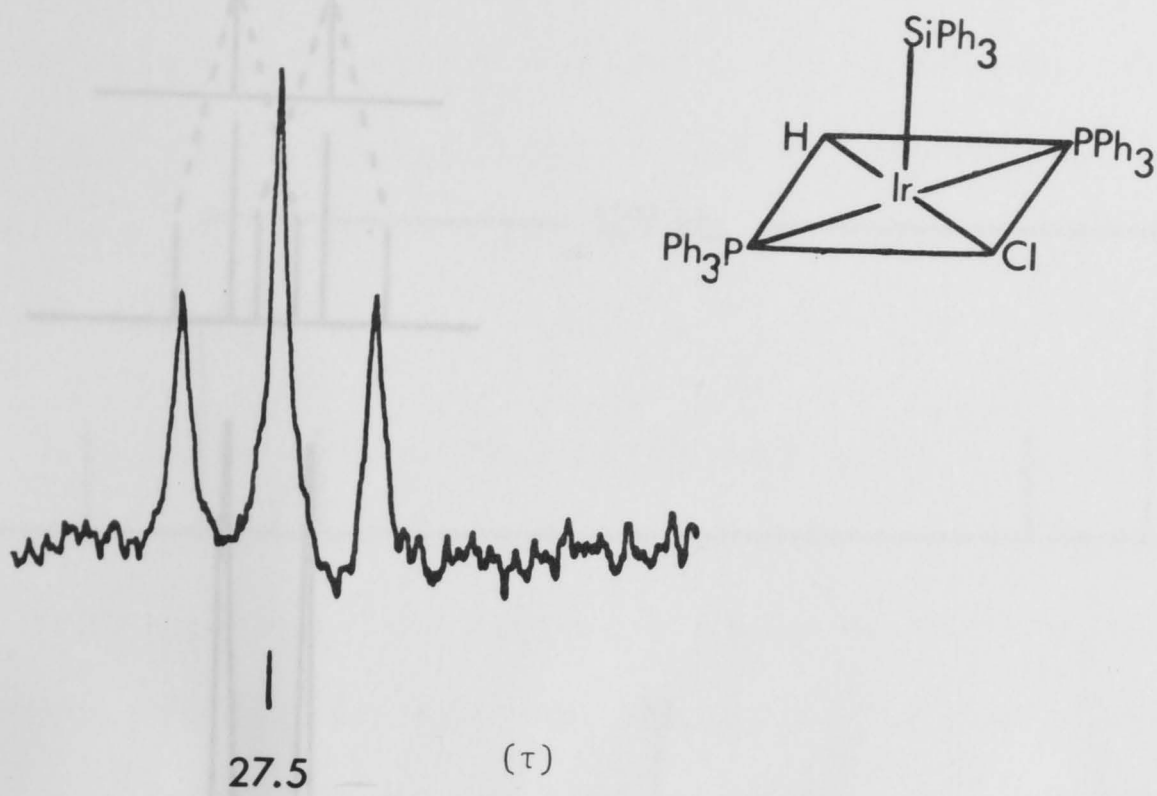


Figure 2-2. High field n.m.r. spectrum of the complex  $\text{IrHCl}[\text{SiPh}_3][\text{Ph}_3\text{P}]_2$ .

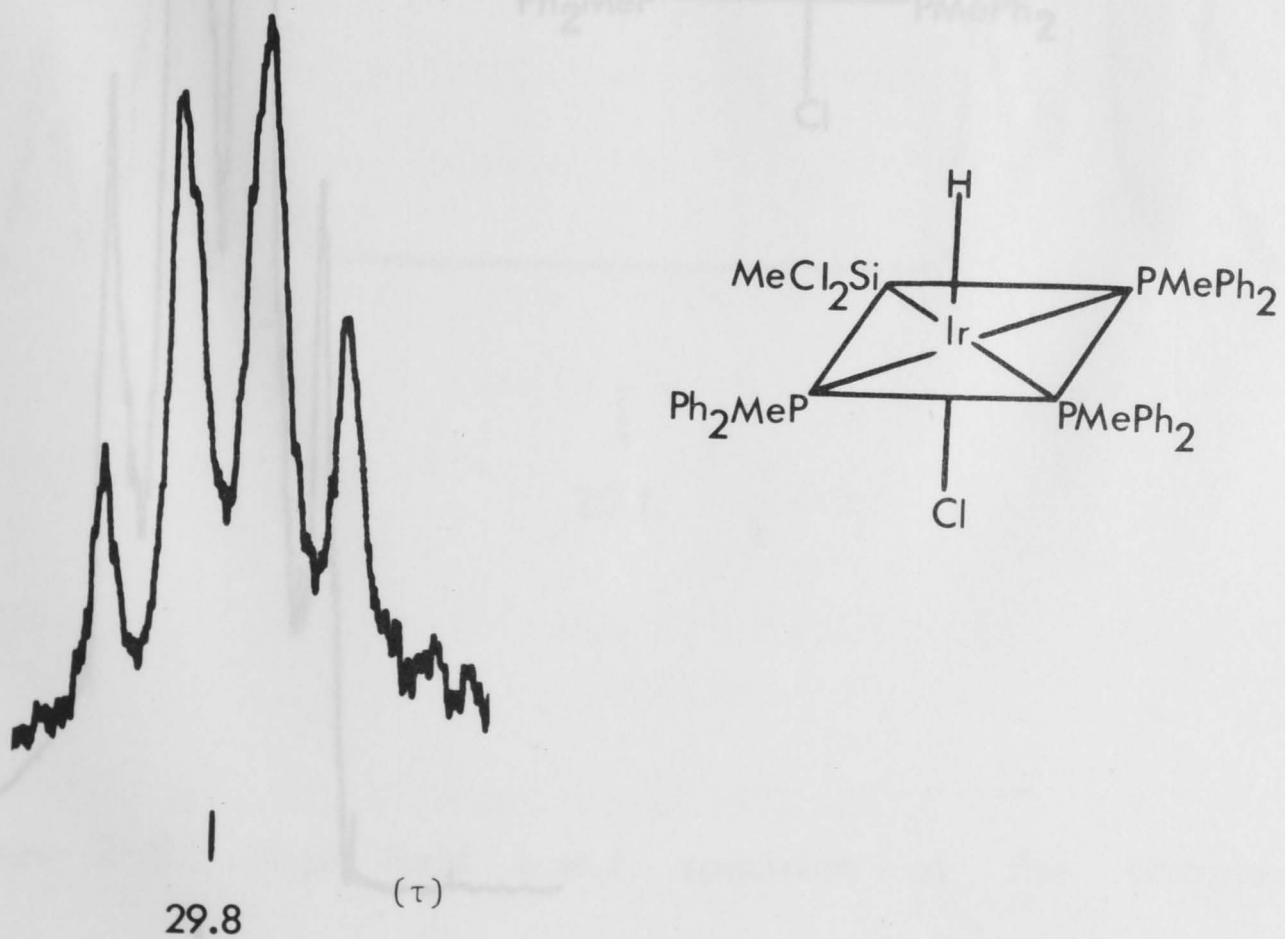


Figure 2-3. High field n.m.r. spectrum of complex  $\text{IrHCl}[\text{SiMeCl}_2][\text{MePh}_2\text{P}]_3$ .

Figure 2-4. High field n.m.r. spectrum of complex  $\text{IrHCl}[\text{SiCl}_3][\text{MePh}_2\text{P}]_3$ .

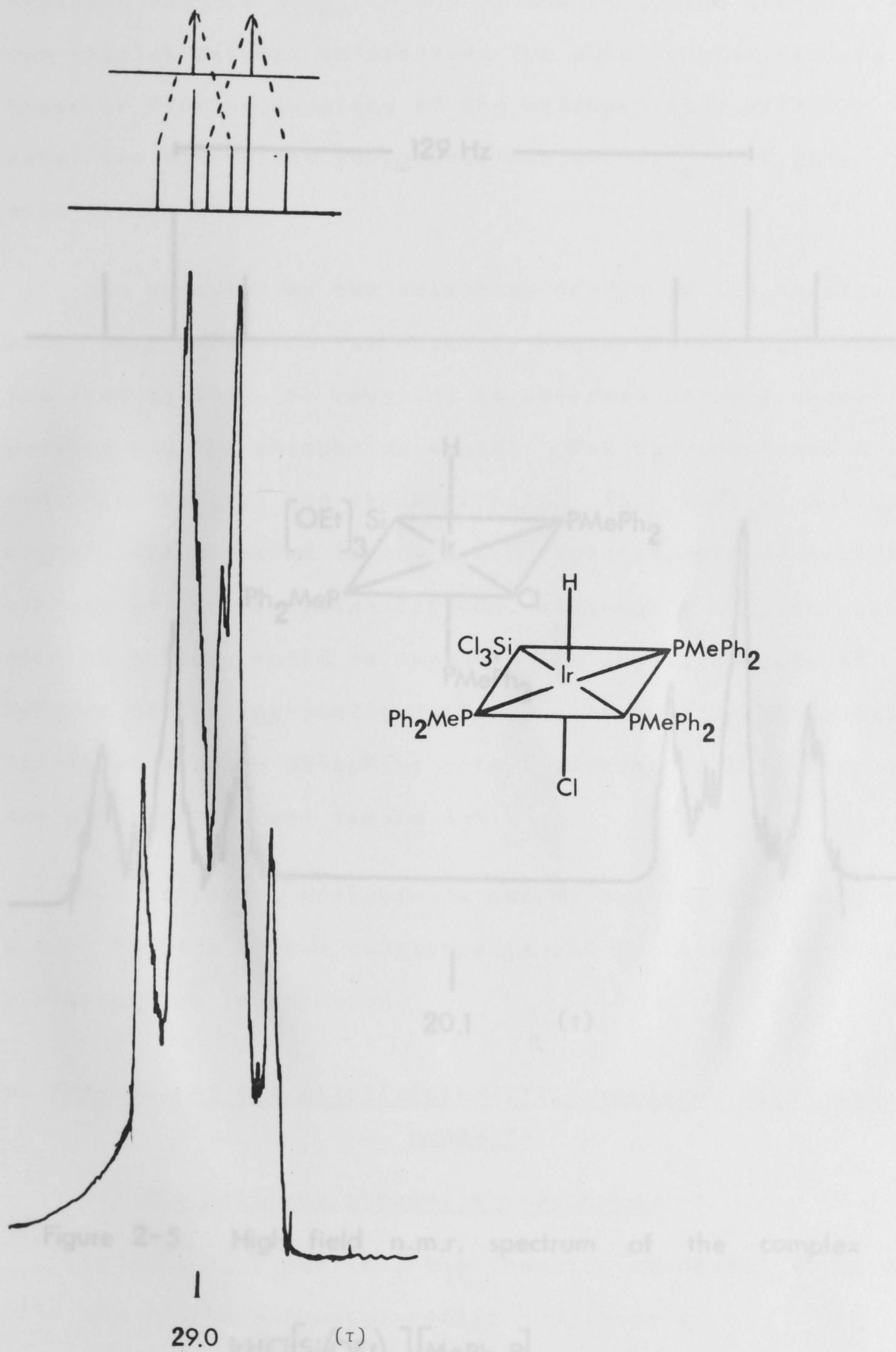


Figure 2-4. High field n.m.r. spectrum of complex  $\text{IrHCl}[\text{SiCl}_3][\text{MePh}_2\text{P}]_3$ .

hydrogen atom is trans to one of the phosphine groups. The two triplet pattern is observed for this complex because there is further coupling of the hydrogen atom with the other two equivalent phosphorus atoms.  $J_{H-P} = 129$  Hz,  $J_{P-P} = 6.5$  Hz, (see figure 2-5).

The signal for the triethoxy groups of the triethoxy-

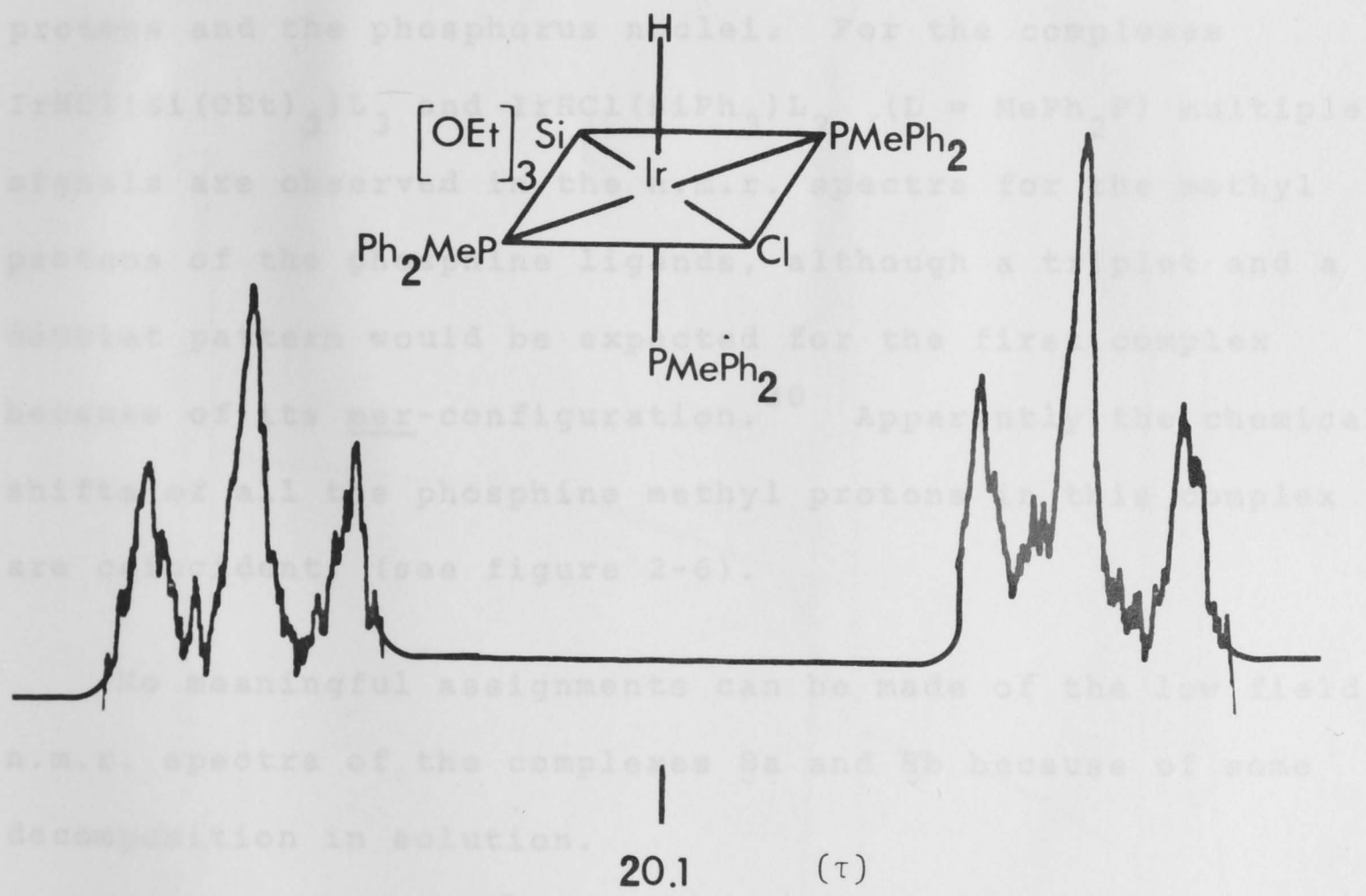
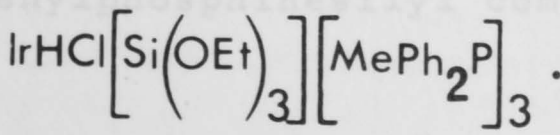


Figure 2-5. High field n.m.r. spectrum of the complex





hydrogen atom is trans to one of the phosphine groups. The two triplet pattern is observed for this complex because there is further coupling of the hydrogen atom with the other two equivalent phosphorus nuclei,  $J_{P-H} = 16.5\text{Hz}$ , (see figure 2-5).

The signals for the triethoxy groups of the triethoxysilyl complexes occur at slightly higher field than those for the free silane. No coupling is observed between these protons and the phosphorus nuclei. For the complexes  $\text{IrHCl}[\text{Si}(\text{OEt})_3]_3\text{L}_3$  and  $\text{IrHCl}(\text{SiPh}_3)_2\text{L}_2$  ( $\text{L} = \text{MePh}_2\text{P}$ ) multiplet signals are observed in the n.m.r. spectra for the methyl protons of the phosphine ligands, although a triplet and a doublet pattern would be expected for the first complex because of its mer-configuration.<sup>30</sup> Apparently the chemical shifts of all the phosphine methyl protons in this complex are coincident, (see figure 2-6).

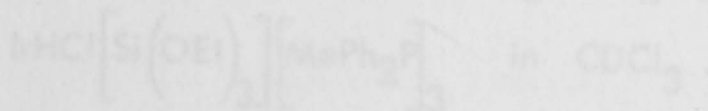
No meaningful assignments can be made of the low field n.m.r. spectra of the complexes  $\text{8a}$  and  $\text{8b}$  because of some decomposition in solution.

c. Reaction of the silyliridium(III)-complexes with carbon monoxide

(i) The triphenylphosphine complexes

Equation 2-6 outlines the reaction of carbon monoxide with the triphenylphosphinesilyl complexes  $\text{4}$ :

Figure 2-5. Low field n.m.r. spectrum [0-9] of the complex



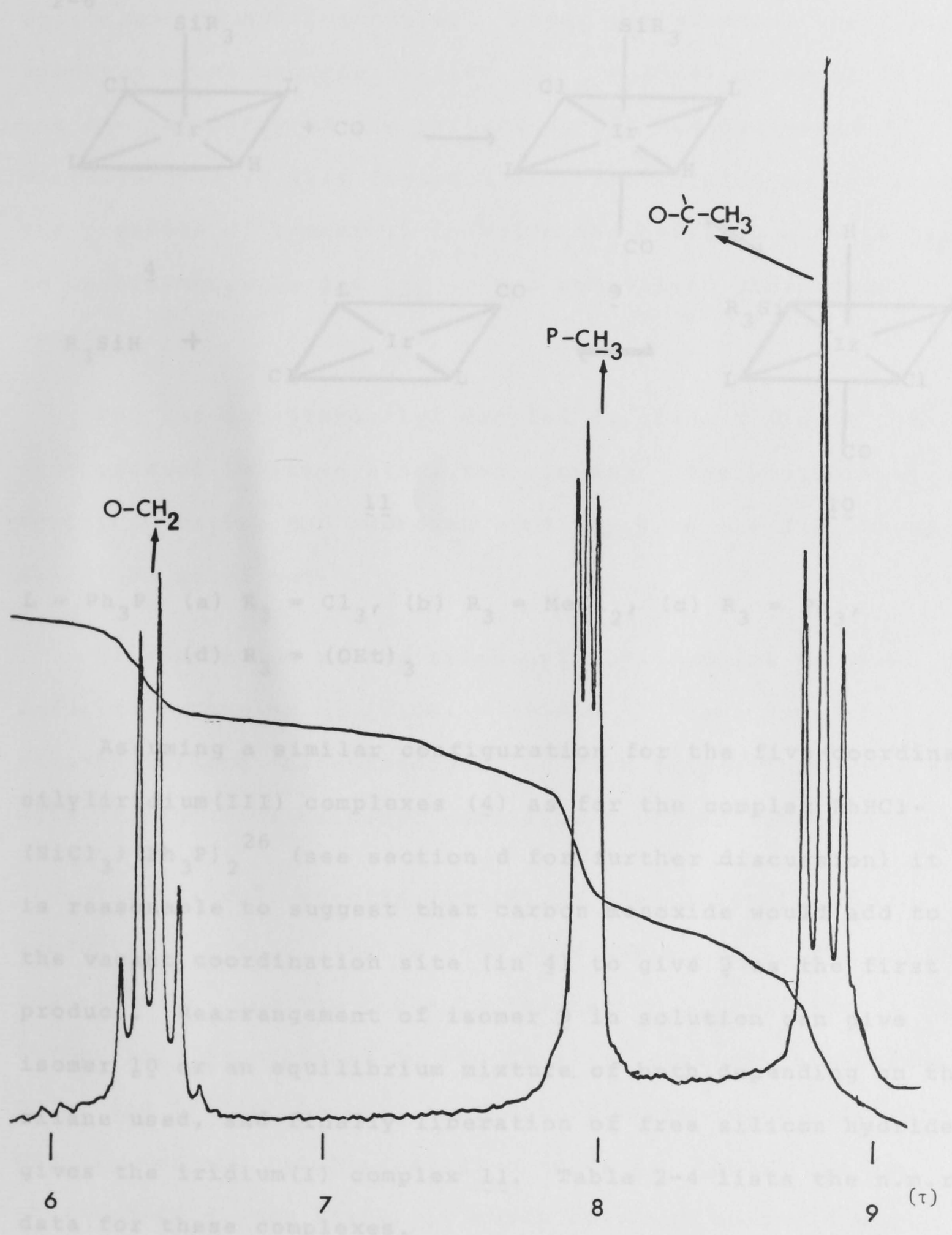
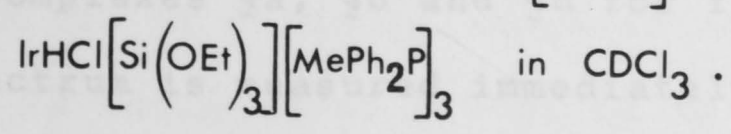


Figure 2-6. Low field n.m.r. spectrum [6-9  $\tau$ ] of the complex



If carbon monoxide is bubbled through freshly prepared solutions of complexes (a), (b) and (c) for five minutes and the n.m.r. spectra are immediately afterwards, a single triplet ( $J_{P-H} = 12\text{Hz}$ ) at about 27 $\tau$  for  $\tau(Ir-H)$  is observed; this suggests the presence of complex 9 in which





the hydrogen atom is trans to chlorine atom and cis to two equivalent phosphorus nuclei. After ten minutes, the n.m.r. spectrum shows another triplet ( $J_{P-H} = 15\text{Hz}$ ) at about  $16\tau$  and the intensity of the triplet at  $27\tau$  has decreased correspondingly, (see figure 2-7). The triplet at  $16\tau$  suggests the presence of isomer 10 in which the hydrogen atom is trans to carbon monoxide and cis to two equivalent phosphorus nuclei.

For the trichlorosilyl complex 4a, isomer 10a is the sole product isolated after ten minutes. The possibility of isomer 10 having the hydrogen atom trans to the  $\text{SiR}_3$  group cannot be ruled out.

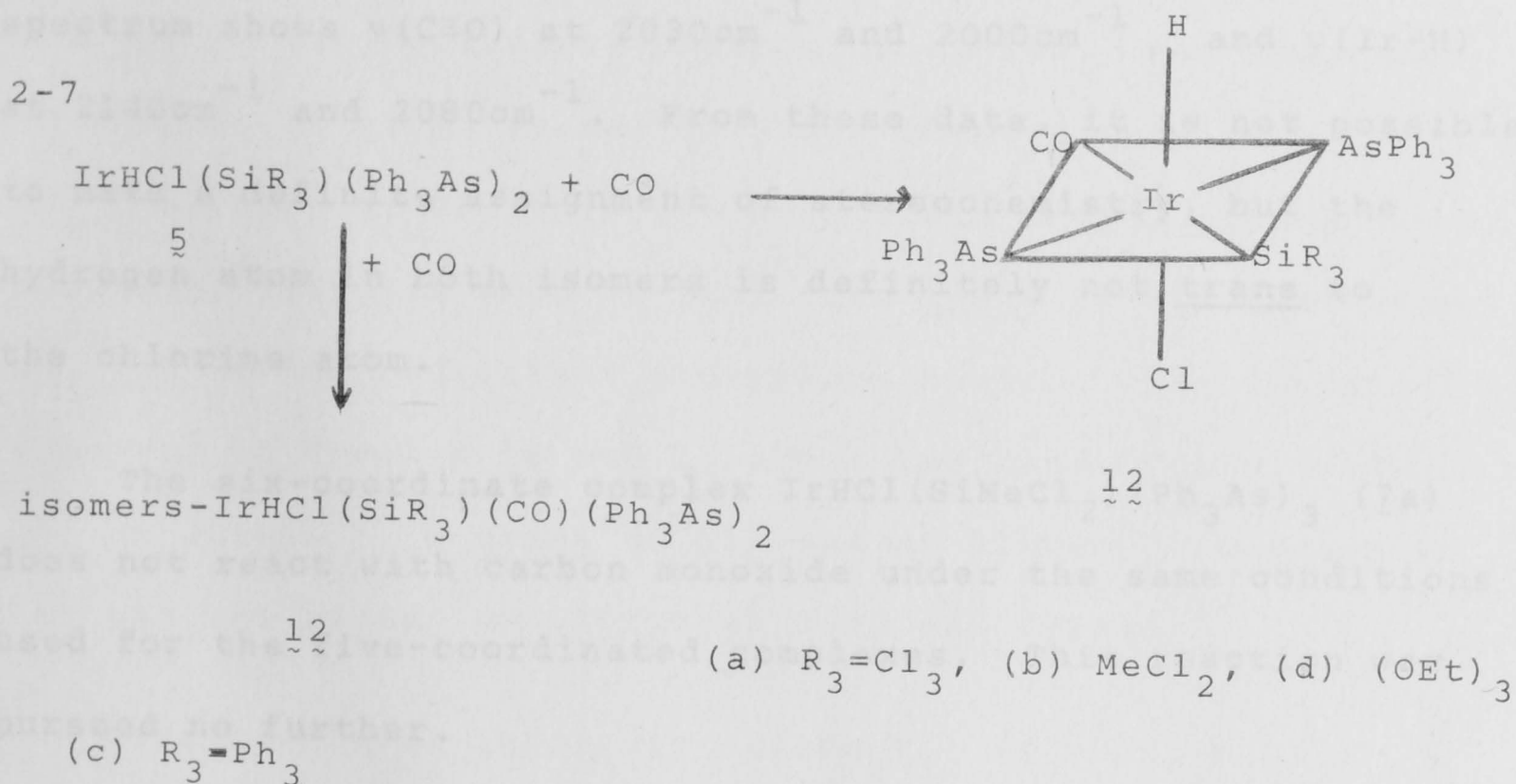
Carbonylation of the triphenylsilyl complex 4c gives the iridium(I) complex 11 [ $\nu(\text{CO}) = 1950\text{cm}^{-1}$ ]<sup>31</sup> and free triphenylsilane instantaneously at room temperature; no silyliridium(III) carbonyl complexes could be detected.

The infrared spectra (solid) of the carbonylated products, 9 and 10, (table 2-5) show two bands in the region  $2000-2050\text{cm}^{-1}$  and two bands in the region  $2100-2235\text{cm}^{-1}$ . The former pair is assigned to the terminal carbonyl stretching modes and the latter pair to the iridium-hydrogen stretching modes. For the trichlorosilyl complex 4a, isomer 10a is obtained in a pure state; it shows only two bands in the infrared spectrum (solid),  $\nu(\text{C}\equiv\text{O})$  at  $2025\text{cm}^{-1}$  and  $\nu(\text{Ir-H})$  at  $2118\text{cm}^{-1}$ . After ten minutes the infrared spectrum in chloroform solution of 9 and 10 shows an additional band at  $1950\text{cm}^{-1}$  which is assigned to  $\nu(\text{C}\equiv\text{O})$  of the iridium(I) complex 11.



(ii) The triphenylarsine complexes

All the five-coordinate triphenylarsine-silyliridium(III) complexes (5) add carbon monoxide to give the corresponding octahedral iridium(III) carbonyl derivatives:



The products 12(a), 12(b) and 12(d) are assigned the above stereochemistry (eqn. 2-7) from infrared and high field n.m.r. data (tables 2-4 and 2-5). For each of the silyl complexes 12a, 12b and 12d a singlet is obtained in the high field region ( $\sim 28\tau$ ) of the n.m.r. spectra. The  $\tau$ -value is characteristic of hydrogen atom trans to a chlorine atom. The infrared spectrum of complexes 12a, 12b and 12d gives a band at  $2200\text{cm}^{-1}$  for  $\nu(\text{Ir-H})$  [H trans to Cl] and another band at  $2050\text{cm}^{-1}$  [ $\nu(\text{C}\equiv\text{O})$ ]. It is assumed that the triphenylarsine ligands are mutually trans in 12a, 12b and 12d because the spectroscopic data of 12a, 12b and 12d are similar to those of product 9 (eqn. 2-6), in which the triphenylphosphine ligands are considered to be mutually trans.





The first product apparently results from the displacement of the phosphine ligand trans to hydrogen atom to yield isomer 14. This isomer gives a triplet ( $J_{P-H} = 16.5\text{Hz}$ ) in the high field region of the n.m.r. spectrum at  $17.0\tau$  for  $\tau(\text{Ir-H})$ ; hydrogen atom is therefore trans to carbon monoxide and cis to two equivalent phosphorus nuclei. Rearrangement of complex 14 gives isomer 15 which shows a triplet ( $J_{P-H} = 12\text{Hz}$ ) at  $28.5\tau$  in the high field region of the n.m.r. spectrum; hydrogen atom is therefore trans to chlorine atom and cis to two equivalent phosphorus nuclei. The infrared spectrum of complex 14 and 15 shows two bands for  $\nu(\text{Ir-H})$ , one at  $2200\text{cm}^{-1}$  (H trans to Cl) and at  $2100\text{cm}^{-1}$  (H trans to CO) and two bands for  $\nu(\text{C}\equiv\text{O})$  at  $2050$  and  $1980\text{cm}^{-1}$ .

The complexes  $\text{IrHCl}(\text{SiR}_3)(\text{MePh}_2\text{P})_3$  ( $\text{R}_3 = \text{Cl}_3, \text{MeCl}_2$ ) (8a and 8b) react with carbon monoxide to give complexes of the type  $\text{IrHCl}(\text{SiR}_3)(\text{CO})(\text{MePh}_2\text{P})$  [16 (a)  $\text{R}_3 = \text{Cl}_3$ , (b)  $\text{MeCl}_2$ ] with the same stereochemistry as complex 15 above (eqn 2-8). A triplet ( $J_{P-H} = 12\text{Hz}$ ) at  $26.9\tau$  is observed in the high field n.m.r. spectrum and two bands, one at  $2200\text{cm}^{-1}$ ,  $\nu(\text{Ir-H})$ , and at  $2060\text{cm}^{-1}$ ,  $\nu(\text{C}\equiv\text{O})$ , in the infrared spectrum, of 16a and 16b.

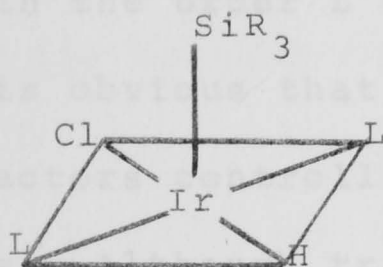
The complex  $\text{IrHCl}(\text{SiPh}_3)(\text{MePh}_2\text{P})_2$  (6a) gives trans- $\text{IrCl}(\text{CO})(\text{MePh}_2\text{P})_2$  [ $\nu(\text{CO}) = 1960\text{cm}^{-1}$ ]<sup>32</sup> and triphenylsilane when it is reacted with carbon monoxide. No intermediate silyridium(III) carbonyl complexes could be detected.

#### d. Summary of results and discussion

The reactions of silicon hydrides with the iridium(I) complexes 1, 2 and 3 are very similar to those with the complex  $\text{RhCl}(\text{Ph}_3\text{P})_3$ . It is reasonable to assume that most



of the five-coordinated silyliridium(III) complexes possess the same square pyramidal stereochemistry as that of the rhodium complex  $\text{RhHCl}(\text{SiCl}_3)(\text{Ph}_3\text{P})_2$ <sup>26</sup> (p.10), the hydrogen being trans to chlorine atom:



4 L =  $\text{Ph}_3\text{P}$ ,  $\text{R}_3$  = (a)  $\text{Cl}_3$ , (b)  $\text{MeCl}_2$ , (c)  $\text{Ph}_3$ , (d)  $(\text{OEt})_3$ .

5 L =  $\text{Ph}_3\text{As}$ ,  $\text{R}_3$  = (b)  $\text{MeCl}_2$ , (c)  $\text{Ph}_3$ , (d)  $(\text{OEt})_3$ .

6 L =  $\text{MePh}_2\text{P}$ ,  $\text{R}_3$  = (a)  $\text{Ph}_3$ .

The infrared and n.m.r. data for the complex  $\text{IrHCl}(\text{SiCl}_3)(\text{Ph}_3\text{As})_2$  (5a) suggest that hydrogen atom is not trans to chlorine atom, but the exact stereochemistry is unknown.

The reaction of methyldichlorosilane and  $\text{IrCl}(\text{Ph}_3\text{As})_3$  (2) gives both a five-coordinate and a six-coordinate adduct. The five-coordinate product (5b) has the stereochemistry shown above but it is difficult to assign any stereochemistry to the six-coordinate product based merely on spectroscopic data. It is not obvious why methyldichlorosilane should be unique among the silanes studied in yielding two adducts of different coordination number.

The stereochemistries of the products which result from the reaction of the silanes and the complex  $\text{IrCl}(\text{MePh}_2\text{P})_3$  (3) vary with the silane used. The complexes 8a, 8b and 8c (eqn 2-5) all have the phosphine ligands in a mer-configuration but have hydrogen trans to chlorine atom in complexes 8a and 8b and hydrogen trans to a phosphine ligand

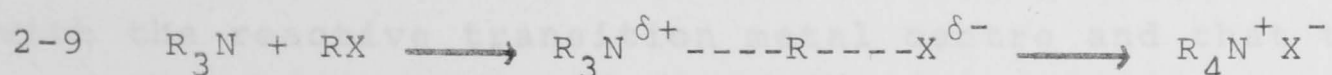


in the triethoxysilyl product 8c. The complex  $\text{IrHCl}(\text{SiPh}_3) - (\text{MePh}_2\text{P})_2$  (6a) is assigned the stereochemistry shown above.

The tendency for the products  $\text{IrHCl}(\text{SiR}_3)\text{L}_n$  to be octahedral is in the order  $\text{L} = \text{MePh}_2\text{P} > \text{Ph}_3\text{As} > \text{Ph}_3\text{P}$ . From this order it is obvious that basicity and steric factors are the main factors controlling the coordination number in the products. Although triphenylarsine and triphenylphosphine are generally similar as ligands, coordinated triphenylarsine probably causes less steric hindrance to an addend molecule than does triphenylphosphine because of the larger atomic radius of arsenic; this causes the bulky phenyl rings of the triphenylarsine to be further away from the iridium nucleus than in the case of triphenylphosphine.

Similar steric factors probably account for the observation that all the triphenylsilyliridium(III) adducts obtained from triphenylsilane and complexes 1, 2 and 3 are five-coordinate, since the coordinated triphenylsilyl group is geometrically similar to coordinated triphenylphosphine.

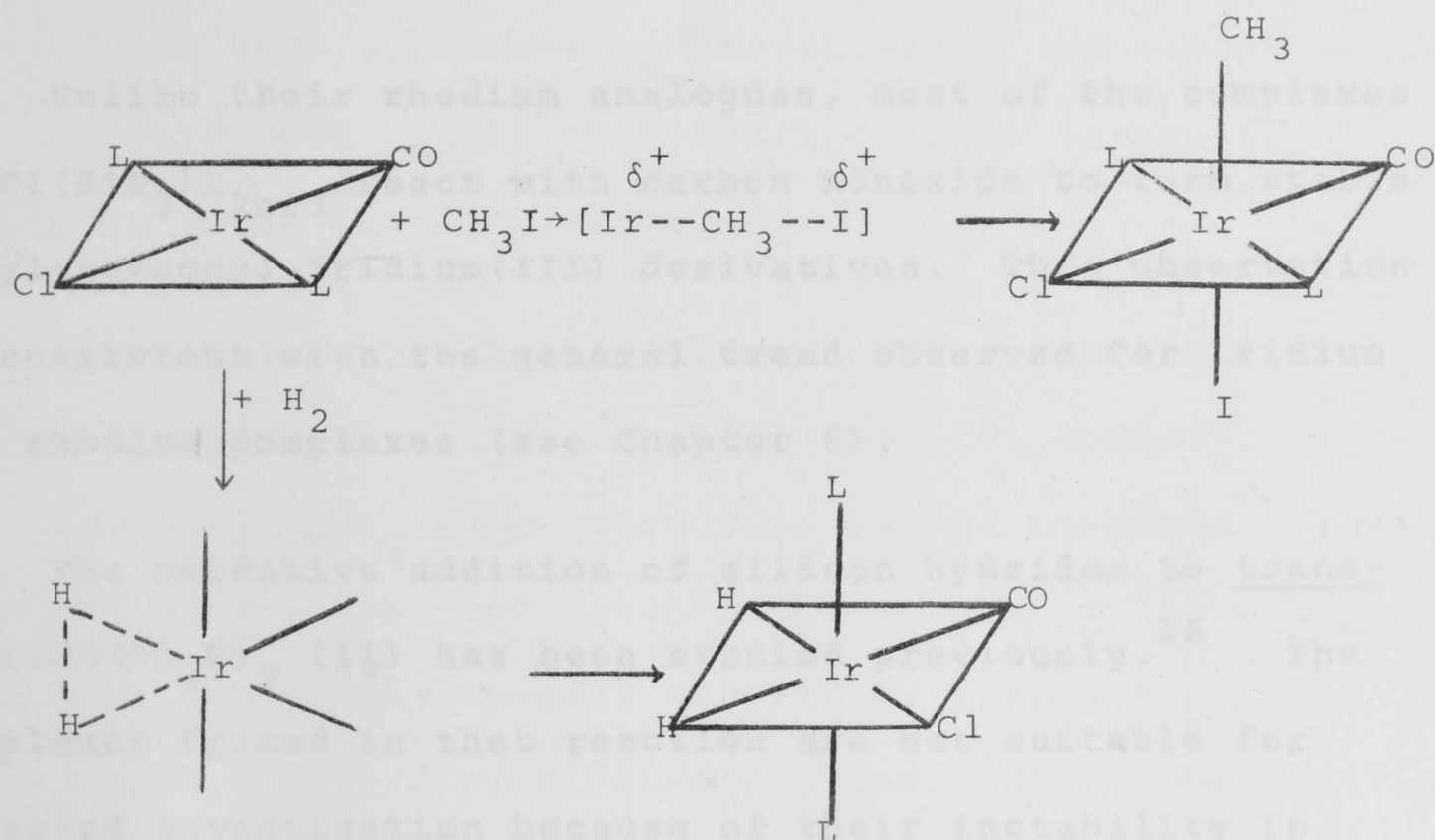
The overriding question in oxidative addition reactions, from a mechanistic point of view, is whether the addition proceeds via a concerted three-centre transition state,<sup>3,6</sup> or by a transition state analogous to that proposed for the Menschutkin reaction:<sup>6</sup>



The addition of methyl iodide to trans- $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  (11) is believed to involve a highly polar transition state to that proposed for the Menschutkin reaction,<sup>6</sup> and a trans

mode of addition results. On the other hand the activation parameters for the hydrogen addition are consistent with a three-centre transition state in which both addend atoms interact simultaneously with the metal ion, with hydrogen atoms ending up cis to each other:

2-10



L = Ph<sub>3</sub>P.

Sommer and co-workers have studied<sup>34</sup> a number of reactions involving optically active,  $\alpha$ -naphthylphenylmethylsilane in the presence of reactive transition metal centres e.g. IrCl(CO)(Ph<sub>3</sub>P)<sub>2</sub>. The bulk of their evidence obtained indicates that the initial process in these reactions may be a stereospecific interaction of the silicon-hydrogen bond with the reactive transition metal centre and that this reaction occurs with an exceedingly high degree of retention of configuration at the silicon atom. These results are inconsistent with an S<sub>N</sub>2 mechanism but support a three-centre mechanism for silicon hydride addition to transition metal complexes.

Based on the observations discussed above, it seems very likely that silicon hydride addition to the iridium(I) complexes 1, 2 and 3 proceeds through a three-centre mechanism. This conclusion is supported but not proved by the observation that the ligand atoms silicon and hydrogen are always cis in the adducts isolated. However, no work which would define the mechanism has been carried out.

Unlike their rhodium analogues, most of the complexes  $\text{IrHCl}(\text{SiR}_3)\text{L}_{2\text{or}3}$  react with carbon monoxide to form stable silyl-carbonyl-iridium(III) derivatives. This observation is consistent with the general trend observed for iridium and rhodium complexes (see Chapter 6).

The oxidative addition of silicon hydrides to trans- $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  (11) has been studied previously.<sup>16</sup> The complexes formed in that reaction are not suitable for detailed investigation because of their instability in solution and because the reaction is limited to silicon hydrides bearing electronegative substituents. The products from the reaction of carbon monoxide with the triphenylphosphine-silyliridium(III) complexes 4a, 4b and 4d are generally identical with or are isomeric with those prepared by Chalk and Harrod<sup>16</sup> as shown by comparison of infrared spectra. A recent re-examination of the n.m.r. spectrum of the adduct from the reaction of triethoxysilane with complex 11 has shown the presence of a triplet ( $J_{\text{P-H}} = 14\text{Hz}$ ) at  $16.1\tau$  due to Ir-H.<sup>33</sup> This result is in fair agreement with that obtained for one of the isomers (10d) of the complex  $\text{IrHCl}[\text{Si}(\text{OEt})_3](\text{CO})(\text{Ph}_3\text{P})_2$  obtained by addition of triethoxysilane to the complex 1 and subsequent carbonylation;



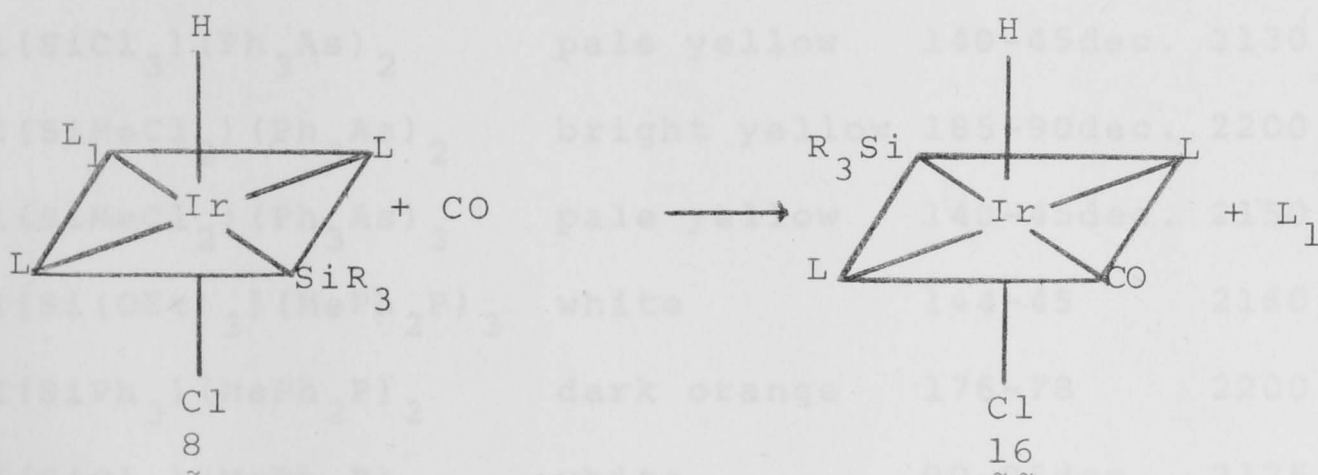
the n.m.r. spectrum also shows a triplet ( $J_{P-H} = 15\text{Hz}$ ) at  $16.0\tau$  for  $\tau(\text{Ir-H})$ . The author<sup>33</sup> indicated that such a low chemical shift suggests that hydrogen is trans to a group with an extremely large trans-effect such as  $\text{Si}(\text{OEt})_3$ . This suggestion would imply a trans mode of addition for triethoxysilane, and this in turn would favour an  $S_N2$  mechanism for the addition. This seems highly unlikely in view of the work by Sommer and co-workers<sup>35</sup> mentioned above, and it seems more likely that hydrogen atom is trans to carbon monoxide in this isomer.

It is not surprising to observe the formation of the complex trans- $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  (11) when the complex  $\text{IrHCl}(\text{SiPh}_3)(\text{Ph}_3\text{P})_2$  is reacted with carbon monoxide, since triphenylsilane does not react with complex 11.<sup>16</sup> Similarly, carbonylation of the complex  $\text{IrHCl}(\text{SiPh}_3)(\text{MePh}_2\text{P})_2$  forms the complex trans- $\text{IrCl}(\text{CO})(\text{MePh}_2\text{P})_2$  and free triphenylsilane. Presumably octahedral silyliridium(III)-carbonyl complexes are formed initially which rapidly decompose to form the complexes trans- $\text{IrCl}(\text{CO})\text{L}_2$  ( $\text{L} = \text{Ph}_3\text{P}, \text{MePh}_2\text{P}$ ) and free triphenylsilane. However the complex  $\text{IrHCl}(\text{SiPh}_3)(\text{Ph}_3\text{As})_2$  reacts with carbon monoxide to give stable silyliridium(III)-carbonyl products. These observations therefore suggest that the reactivity of complexes of type trans- $\text{IrCl}(\text{CO})\text{L}_2$  ( $\text{L} = \text{Ph}_3\text{P}, \text{Ph}_3\text{As}, \text{MePh}_2\text{P}$ ) to undergo oxidative addition with triphenylsilane may be in the order  $\text{L} = \text{Ph}_3\text{As} > \text{MePh}_2\text{P} = \text{Ph}_3\text{P}$ . Since it has been shown that ligands which increase electron density at the central metal enhance the tendency of the metal to undergo oxidative addition,<sup>2</sup> the order of L should be  $\text{MePh}_2\text{P} > \text{Ph}_3\text{P} > \text{Ph}_3\text{As}$ . Apparently steric factors must be the

deciding force in the reactions of these complexes with triphenylsilane.

The six-coordinated complexes  $\underline{8a}$ ,  $\underline{8b}$  and  $\underline{8c}$  (eqn 2-5) react with carbon monoxide by displacing one of the phosphine groups to give stable silyliridium(III)-carbonyl complexes. It seems likely that the phosphine ligand ( $L_1$ ) trans to the silyl group in complexes  $\underline{8a}$  and  $\underline{8b}$  (eqn 2-11) would be more labile than any of the mutually trans phosphine ligands since the  $SiR_3$  group has an extremely high trans-effect;<sup>35</sup> thus, carbon monoxide should displace  $L_1$  and give complex  $\underline{16}$ :

2-11



$L = L_1 = MePh_2P$ ,  $R_3 = (a) Cl_3$ , (b)  $MeCl_2$ .

However for the complex  $\underline{8c}$  the phosphine ligand trans to hydrogen is displaced when the complex reacts with carbon monoxide (eqn 2-8). It is assumed that complex  $\underline{14}$  (eqn 2-8) is the first product formed and that no re-arrangement has occurred prior to its formation.

TABLE 2-2

Physical properties of silyliridium(III)-complexes<sup>a</sup>.

Compound	Colour	M.P. <sup>b</sup> °C	$\nu$ (Ir-H) cm <sup>-1</sup>
$\text{IrHCl}[\text{Si}(\text{OEt})_3](\text{Ph}_3\text{P})_2$	orange-yellow	187-89	2185
$\text{IrHCl}(\text{SiPh}_3)(\text{Ph}_3\text{P})_2$	dark orange	179-80	2225
$\text{IrHCl}(\text{SiCl}_3)(\text{Ph}_3\text{P})_2$	orange	190-95dec.	2182
$\text{IrHCl}(\text{SiMeCl}_2)(\text{Ph}_3\text{P})_2$	orange	210-15dec.	2182
$\text{IrHBr}[\text{Si}(\text{OEt})_3](\text{Ph}_3\text{P})_2$	yellow	135-40	2200
$\text{IrHCl}[\text{Si}(\text{OEt})_3](\text{Ph}_3\text{As})_2$	yellow	164-66	2170
$\text{IrHCl}(\text{SiPh}_3)(\text{Ph}_3\text{As})_2$	dark orange	169-70	2200
$\text{IrHCl}(\text{SiCl}_3)(\text{Ph}_3\text{As})_2$	pale yellow	140-45dec.	2130
$\text{IrHCl}(\text{SiMeCl}_2)(\text{Ph}_3\text{As})_2$	bright yellow	185-90dec.	2200
$\text{IrHCl}(\text{SiMeCl}_2)(\text{Ph}_3\text{As})_3$	pale yellow	140-45dec.	2150
$\text{IrHCl}[\text{Si}(\text{OEt})_3](\text{MePh}_2\text{P})_3$	white	144-45	2160
$\text{IrHCl}(\text{SiPh}_3)(\text{MePh}_2\text{P})_2$	dark orange	176-78	2200
$\text{IrHCl}(\text{SiCl}_3)(\text{MePh}_2\text{P})_3$	white	90-95dec.	2175
$\text{IrHCl}(\text{SiMeCl}_2)(\text{MePh}_2\text{P})_3$	white	175-80dec.	2175

a.....all infrared data refer to the solid state

b.....dec. represents decomposition point.



TABLE 2-3

<sup>1</sup>H-NMR data for the silyliridium(III)-complexes. <sup>a, b</sup>

Complex	$\tau$ (Ir-H)	( $J_{P-H}$ )	$\tau$ (CH <sub>3</sub> )	$\tau$ (CH <sub>2</sub> )	$J_{H-H}$	$\tau$ (P-CH <sub>3</sub> )
	$\tau$	Hz	$\tau$	$\tau$	Hz	$\tau$
IrHCl[Si(OEt) <sub>3</sub> ](Ph <sub>3</sub> P) <sub>2</sub>	27.5 (t)	15.0	9.27 (t)	6.76 (q)	7.0	
IrHCl(SiPh <sub>3</sub> )(Ph <sub>3</sub> P) <sub>2</sub>	27.5 (t)	16.5				
IrHCl(SiCl <sub>3</sub> )(Ph <sub>3</sub> P) <sub>2</sub>	28.5 (t)	13.5				
IrHCl(SiMeCl <sub>2</sub> )(Ph <sub>3</sub> P) <sub>2</sub>	27.7 (t)	13.0				
IrHCl[Si(OEt) <sub>3</sub> ](Ph <sub>3</sub> As) <sub>2</sub>	29.5 (s)		9.30 (t)	6.80 (q)	7.0	
IrHCl(SiPh <sub>3</sub> )(Ph <sub>3</sub> As) <sub>2</sub>	29.5 (s)					
IrHCl(SiCl <sub>3</sub> )(Ph <sub>3</sub> As) <sub>2</sub>	19.8 (s)					
IrHCl(SiMeCl <sub>2</sub> )(Ph <sub>3</sub> As) <sub>2</sub>	30.8 (s)					
IrHCl(SiMeCl <sub>2</sub> )(Ph <sub>3</sub> As) <sub>3</sub>	23.5 (s)					
IrHBr[Si(OEt) <sub>3</sub> ](Ph <sub>3</sub> P) <sub>2</sub>	27.0 (t)	15.0	9.27 (t)	6.80 (q)	7.0	
IrHCl[Si(OEt) <sub>3</sub> ](MePh <sub>2</sub> P) <sub>3</sub> <sup>c</sup>	20.1 (2t)	129.0 16.5	8.86 (t)	6.38 (q)	7.0	7.95 (m)

TABLE 2-3 (cont'd)

Complex	$\tau(\text{Ir-H})$	$(J_{\text{P-H}})$	$\tau(\text{CH}_3)$	$\tau(\text{CH}_2)$	$J_{\text{H-H}}$	$\tau(\text{P-CH}_3)$
	$\tau$	Hz	$\tau$	$\tau$	Hz	$\tau$
$\text{IrHCl}(\text{SiPh}_3)(\text{MePh}_2\text{P})_2$	27.5 (t)	16.5				8.5 (m)
$\text{IrHCl}(\text{SiCl}_3)(\text{MePh}_2\text{P})_3^{\text{d}}$	29.0 (m)	10.5 12.0				
$\text{IrHCl}(\text{SiMeCl}_2)(\text{MePh}_2\text{P})_3$	29.8 (q)	10.5				

a....all spectra measured in  $\text{CDCl}_3$ .

b....s=singlet, t=triplet, q=quartet, m=multiplet.

c....2t represents two triplets centred at  $20.1\tau$  separated by 129.0Hz (see Figure 2-5)

d....m represents two overlapping triplets (see Figure 2-4).

TABLE 2-4

<sup>1</sup>H-n.m.r. data for the carbonyl-silyliridium(III) complexes. <sup>a,b</sup>

Complexes	$\tau$ (Ir-H)	$J_{P-H}$	$\tau$ (CH <sub>3</sub> )	$\tau$ (CH <sub>2</sub> )	$J_{H-H}$
	$\tau$	Hz	$\tau$	$\tau$	Hz
IrHCl[Si(OEt) <sub>3</sub> ](CO)(Ph <sub>3</sub> P) <sub>2</sub>	27.5 (t)	12	9.25 (t)	6.93 (q)	7
	16.0 (t)	15	8.78 (t)	6.18 (q)	7
IrHCl(SiCl <sub>3</sub> )(CO)(Ph <sub>3</sub> P) <sub>2</sub>	26.2 (t)	10			
	17.0 (t)	14.3			
IrHCl(SiMeCl <sub>2</sub> )(CO)(Ph <sub>3</sub> P) <sub>2</sub>	26.4 (t)	11.3			
	16.6 (t)	15.0			
IrHCl[Si(OEt) <sub>3</sub> ](CO)(Ph <sub>3</sub> As) <sub>2</sub>	28.0 (s)		9.45 (t)	6.90 (q)	7
	19.3 (s)				
IrHCl(SiPh <sub>3</sub> )(CO)(Ph <sub>3</sub> As) <sub>2</sub>	19.3 (s)				
	16.3 (s)				
IrHCl(SiMeCl <sub>2</sub> )(CO)(Ph <sub>3</sub> As) <sub>2</sub>	27.8 (s)				
	28.1 (s)				
IrHCl(SiCl <sub>3</sub> )(CO)(Ph <sub>3</sub> As) <sub>2</sub>	28.1 (s)				
	26.8 (t)	12			



TABLE 2-4 (cont.)

Complexes	$\tau(\text{Ir-H})$	$J_{\text{P-H}}$	$\tau(\text{CH}_2)$	$\tau(\text{CH}_3)$	$J_{\text{H-H}}$
	$\tau$	Hz	$\tau$	$\tau$	Hz
$\text{IrHCl}(\text{SiMeCl}_2)(\text{CO})(\text{MePh}_2\text{P})_2$	26.9 (t)	12			
$\text{IrHCl}[\text{Si}(\text{OEt})_3](\text{CO})(\text{MePh}_2\text{P})_2$	28.5 (t)	12			
	17.0 (t)	16.5			

a....all spectra were measured in  $\text{CH}_2\text{Cl}_2$  solutions.

b....s=singlet, t=triplet, q=quartet.

TABLE 2-5

Infrared data for the carbonyl-silyliridium(III) complexes.<sup>a</sup>

Complexes	$\nu(\text{Ir-H})$ $\text{cm}^{-1}$	$\nu(\text{C}\equiv\text{O})$ $\text{cm}^{-1}$
$\text{IrHCl}[\text{Si}(\text{OEt})_3](\text{CO})(\text{Ph}_3\text{P})_2$	2200, 2100	2050, 2000
$\text{IrHCl}(\text{SiCl}_3)(\text{CO})(\text{Ph}_3\text{P})_2$	2118	2025
$\text{IrHCl}(\text{SiMeCl}_2)(\text{CO})(\text{Ph}_3\text{P})_2$	2235, 2165	2020, 2000
$\text{IrHCl}[\text{Si}(\text{OEt})_3](\text{CO})(\text{Ph}_3\text{As})_2$	2185	2050
$\text{IrHCl}(\text{SiPh}_3)(\text{CO})(\text{Ph}_3\text{As})_2$	2140, 2080	2030, 2000
$\text{IrHCl}(\text{SiCl}_3)(\text{CO})(\text{Ph}_3\text{As})_2$	2200	2060
$\text{IrHCl}(\text{SiMeCl}_2)(\text{CO})(\text{Ph}_3\text{As})_2$	2200	2045
$\text{IrHCl}(\text{SiMeCl}_2)(\text{MePh}_2\text{P})_2$	2200	2060
$\text{IrHCl}[\text{Si}(\text{OEt})_3](\text{CO})(\text{MePh}_2\text{P})_2$	2200, 2100	2050, 1980
$\text{IrHCl}(\text{SiCl}_3)(\text{CO})(\text{MePh}_2\text{P})_2$	2200	2060

a.....all spectra were measured in the solid state as nujol mulls.

TABLE 2-6.

Analyses of the silyliridium(III)-complexes

Complexes	%C	%H	%Cl	%P	Mol.Wt.
IrHCl[Si(OEt) <sub>3</sub> ](Ph <sub>3</sub> P) <sub>2</sub>	c.55.05	5.06	3.87	6.76	915
	f.55.97	5.21	4.04	6.73	963
IrHCl(SiPh <sub>3</sub> )(Ph <sub>3</sub> P) <sub>2</sub> <sup>2</sup> C <sub>6</sub> H <sub>6</sub>	c.66.40	4.88	2.97	5.19	1165
	f.66.46	4.90	3.09	5.19	1160
IrHCl(SiCl <sub>3</sub> )(Ph <sub>3</sub> P) <sub>2</sub>	c.48.71	3.52	15.97	6.98	
	f.48.08	3.72	15.62	6.68	
IrHCl(SiMeCl <sub>2</sub> )(Ph <sub>3</sub> P) <sub>2</sub>	c.51.25	3.95	12.26	7.13	
	f.51.01	4.15	11.82	6.89	
IrHCl[Si(OEt) <sub>3</sub> ](Ph <sub>3</sub> As) <sub>2</sub>	c.50.22	4.62	3.53		
	f.50.27	4.68	3.73		
IrHCl(SiPh <sub>3</sub> )(Ph <sub>3</sub> As) <sub>2</sub>	c.58.93	4.21	3.22		
	f.60.51	4.39	3.06		
IrHCl(SiCl <sub>3</sub> )(Ph <sub>3</sub> As) <sub>2</sub>	c.44.32	3.20	14.51		
	f.45.22	3.41	13.65		
IrHCl(SiMeCl <sub>2</sub> )(Ph <sub>3</sub> As) <sub>2</sub>	c.46.50	3.56	11.15		954
	f.47.02	3.61	10.88		878



TABLE 2-6 (cont'd)

Complexes	%C	%H	%Cl	%P	Mol.Wt.
IrHCl(SiMeCl <sub>2</sub> )(Ph <sub>3</sub> As) <sub>3</sub>	c.52.30	3.89	8.45		1260
	f.52.80	4.19	8.05		942
IrHCl[Si(OEt) <sub>3</sub> ](MePh <sub>2</sub> P) <sub>3</sub>	c.54.45	5.58	3.57	9.36	991
	f.54.76	5.42	3.71	8.96	813
IrHCl(SiPh <sub>3</sub> )(MePh <sub>2</sub> P) <sub>2</sub>	c.59.48	4.76	3.99	6.97	887
	f.58.98	4.83	3.95	7.31	763
IrHCl(SiMeCl <sub>2</sub> )(MePh <sub>2</sub> P) <sub>3</sub>	c.50.93	4.59	11.30	9.85	
	f.51.07	4.66	10.98	8.93	
IrHCl(SiCl <sub>3</sub> )(MePh <sub>2</sub> P) <sub>3</sub>	c.48.60	4.18	14.74		
	f.48.74	4.41	14.59		
IrHCl(SiMeCl <sub>2</sub> )(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c.50.98	3.83		6.92	
	f.51.18	4.03		6.94	
IrHCl(SiCl <sub>3</sub> )(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c.48.53	3.41			
	f.48.63	3.53			
IrHCl[Si(OEt) <sub>3</sub> ](CO)(Ph <sub>3</sub> AS) <sub>2</sub>	c.50.03	4.49	3.73		
	f.49.78	4.62	3.73		

e. Experimental

Physical Measurements and Chemical Analyses

Materials

Iridium salts were obtained from Johnson and Matthey Co., Wembley, England.

Silicon hydrides were obtained from the Pierce Chemical Company.

Benzene was dried by heating at reflux with calcium hydride for 24 hours, distilling and storing over molecular sieves. All other solvents were stored over sodium wire or molecular sieves.

Infrared Spectra

4000-400cm<sup>-1</sup>

The samples were measured as hydrocarbon mulls (nujol) between KBr windows or as KBr pellets or in solutions on the following instruments:

Perkin Elmer 457 and Perkin Elmer 225 spectrophotometers.

450-200cm<sup>-1</sup>

The samples were measured as hydrocarbon mulls (nujol) between high density polyethylene windows or CsI plates on a Perkin Elmer 225 spectrophotometer.

Nuclear Magnetic Resonance Spectra

The proton magnetic resonance spectra (0-10 $\tau$ ) were recorded on a Varian Associates H.A. 100 instrument at 100 MHz. The high field spectra (10-40 $\tau$ ) were recorded at 60 MHz on a JEOL C60 H.L. instrument.

Phosphorus decouplings were performed on the Varian Associates H.A. 100 instrument equipped with a Rhode and Schwarz Decade F R signal generator. Proton decouplings were performed on the Varian Associates H.A. 100 instrument equipped with a Hewlett-Packard 4204A Oscillator 10Hz-1MHz.

#### Molecular Weights and Microanalyses

Molecular weights were measured at 25°C in Analar solvents (ca. 0.02M) using a vapour pressure osometer (Model 301 A, Mechrolab) calibrated with benzil.

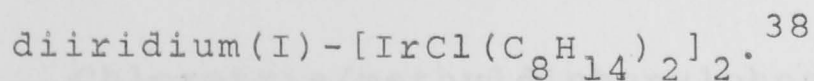
Microanalyses were carried out by the John Curtin School of Chemistry of Medical Research (Canberra) and by the Research School of Chemistry (Canberra).

Melting points (uncorrected) were measured on a Gallenkamp hotstage apparatus using samples sealed in evacuated capillaries.

#### Chemical Preparations

Unless stated otherwise all reactions were performed in an atmosphere of nitrogen.

##### A. Modified preparation of di- $\mu$ -chlorotetrakis(cyclooctene)-



A solution of chloroiridic acid (2g) in water (5ml) and iso-propanol (10ml) was refluxed for 5 minutes. Cyclooctene (3ml) was added and the solution refluxed for 1 hour. At this time water (20ml) was added and mixture refluxed for a further 15 minutes. The resulting orange oil was separated from the solution by decantation and washed with cold methanol (2x15ml). The product [IrCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub><sup>38</sup> resulted as



bright orange solid (1.6g) when diethyl ether (30ml) was added to the oil. The solid was separated by centrifuge and dried in a current of nitrogen.

Yield: 94% based on  $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ .

$\text{IrCl}_3 \cdot x\text{H}_2\text{O}$  (2g) was also used but the yield was lower (1.3g)

B. Modified preparation of di- $\mu$ -chlorobis(cycloocta-1,5-diene)diiridium(I)-[IrCl(C<sub>8</sub>H<sub>12</sub>)]<sub>2</sub><sup>39</sup>

A solution of chloroiridic acid (2g) and cycloocta-1,5-diene (3ml) in water (5ml) and ethanol (10ml) was refluxed for 3 hours. At this time water (20ml) was added and the mixture refluxed for a further 15 minutes. The resulting red oil was separated from the solution by decantation. Bright red crystals of [IrCl(C<sub>8</sub>H<sub>12</sub>)]<sub>2</sub> (1.2g) resulted when cold ethanol (15ml) was added to the oil. The crystals were filtered and washed with cold diethyl ether (2x5ml).

Yield: 92% based on  $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$ .

C. Chlorotris(triphenylphosphine)iridium(I), chlorotris-(triphenylarsine) iridium(I) and bromotris(triphenylphosphine)-iridium(I) were prepared by the literature methods.<sup>36</sup>

Chlorotris(methyldiphenylphosphine)iridium(I) was prepared from di- $\mu$ -chlorotetrakis(cyclooctene)diiridium(I) and methyldiphenylphosphine in a similar manner as was for chlorotris(triphenylphosphine)iridium(I).

D. Reaction of silanes with chlorotris(triphenylphosphine)-iridium(I)

(i) Triethoxysilane

To chlorotris(triphenylphosphine)iridium(I) (0.3g) in benzene (5ml) was added triethoxysilane (1 ml). The solution was refluxed for 15 minutes, at which time the dark red solution had turned yellow-orange. The product was precipitated with petroleum ether (b.p. 60-80°, 30ml) and recrystallized from benzene/petroleum ether (b.p. 60-80°) giving bright yellow-orange crystals, (0.22g; 82%).

(ii) Trichlorosilane

Chlorotris(triphenylphosphine)iridium(I) (0.3g) was dissolved in benzene (5ml) in a vessel attached to a vacuum transfer line. Trichlorosilane (0.6ml) was degassed thoroughly and vacuum-distilled into the reaction vessel kept at liquid nitrogen temperature. The reaction vessel was then allowed to warm up to room temperature. It was stirred at this temperature for one hour. At the end of this period, the volume of solution was slowly reduced. When this was done orange-yellow crystals (0.21g; 81%) precipitated out. These were filtered off under nitrogen, washed with a little cold benzene (2x5ml) and dried in a vacuum.

(iii) Methyldichlorosilane

By the same method described above for trichlorosilane, orange-yellow crystals (0.21g; 81%) of the methyldichlorosilane adduct were obtained.

(iv) Triphenylsilane

A mixture of chlorotris(triphenylphosphine)iridium(I) (0.3g) and triphenylsilane (0.1g) was dissolved in benzene (15ml). The dark red solution was refluxed for 45 minutes and dark orange crystals (0.23g; 77%) precipitated. The

product was filtered, washed with cold benzene (5ml) and dried in a vacuum.

(v) The adduct of triethoxysilane with bromotris(triphenylphosphine)iridium(I) was prepared in a similar manner as was for the case with chlorotris(triphenylphosphine)iridium(I).

E. Reaction of silanes with chlorotris(triphenylarsine)iridium(I)

- (i) Triethoxysilane, (ii) triphenylsilane and  
(iii) trichlorosilane

The adducts of these silanes and chlorotris(triphenylarsine)iridium(I) were prepared in a similar manner as was for their triphenylphosphine analogues.

- (iv) Methyldichlorosilane

A solution of chlorotris(triphenylarsine)iridium(I) (0.3g) in benzene (5ml) was attached to a vacuum transfer line. Methyldichlorosilane (0.6ml) was degassed thoroughly and vacuum-distilled into the reaction vessel kept at liquid nitrogen temperature. The reaction vessel was then allowed to warm up to room temperature. Bright yellow crystals of  $\text{IrHCl}(\text{SiMeCl}_2)(\text{Ph}_3\text{As})_2$  precipitated out. These were filtered off, washed with cold benzene (5ml) and dried in a vacuum. Slow addition of hexane to the filtrate gave pale yellow crystals of  $\text{IrHCl}(\text{SiMeCl}_2)(\text{Ph}_3\text{As})_3$ . These were filtered off, washed with cold pentane (2x5ml) and dried in a vacuum.



F. Reaction of silanes with chlorotris(methyldiphenylphosphine)iridium(I)

(i) Triethoxysilane

To a solution of chlorotris(methyldiphenylphosphine)iridium(I) (0.4g) in benzene (10ml) was added triethoxysilane (1ml) and the solution stirred for 5 minutes at room temperature. The solution was then evaporated to dryness at 25°C (15mm) yielding a yellow oil. Trituration of this oil with a small amount of petroleum ether (b.p. 30-40°C) yielded the product as a white solid. Recrystallization from benzene/petroleum ether (b.p. 30-40°C) gave white crystals. These were filtered off, washed with pentane (2x5ml) and dried in a vacuum.

(ii) Triphenylsilane

To a solution of chlorotris(methyldiphenylphosphine)iridium(I) (0.4g) in benzene (10ml) was added triphenylsilane (0.2g). The solution was refluxed for 2 hours, then evaporated to dryness at 25°C (15mm). The residue was recrystallized from benzene/heptane giving orange crystals of the product.

(iii) Trichlorosilane and (iv) Methylchlorosilane

The adducts of these silanes with chlorotris(methyldiphenylphosphine)iridium(I) were prepared in a similar manner as was described for their triphenylphosphine analogues.

G. Reaction of silyliridium(III) complexes with carbon monoxide

Carbon monoxide was slowly bubbled through solutions

of the silyliridium(III) complexes (ca. 0.2g) in dichloromethane (5ml) at 0°C for 5-10 minutes. Addition of hexane to these solutions precipitated the products. In cases where isomers existed no attempt was made to isolate them.

A considerable number of mononuclear complexes of transition metals in low or zero-valent states and various acetylenes have been reported over the last twenty years.<sup>40,41,42</sup> Several products have resulted from these reactions; among them were binuclear and polynuclear complexes. Such complexes are considered to be intermediates in metal catalyzed cyclooligomerizations and polymerizations of acetylenes.<sup>43,44,45</sup>

The bonding in acetylene and olefinic complexes has been a subject of much discussion.<sup>46,46,47</sup> Chatt and co-workers<sup>56,57,58</sup> have suggested that the bonding of acetylenes to transition metals (e.g. platinum) might be described in two ways, A or B:



The structure A implies that bonding is caused by donation of acetylene pi-electron density into an empty pi-orbital of the metal and back donation of electron density from a filled metal d (or sp-hybrid) orbital to an empty pi\*-orbital. The structure B implies that the pi-back

## CHAPTER 3

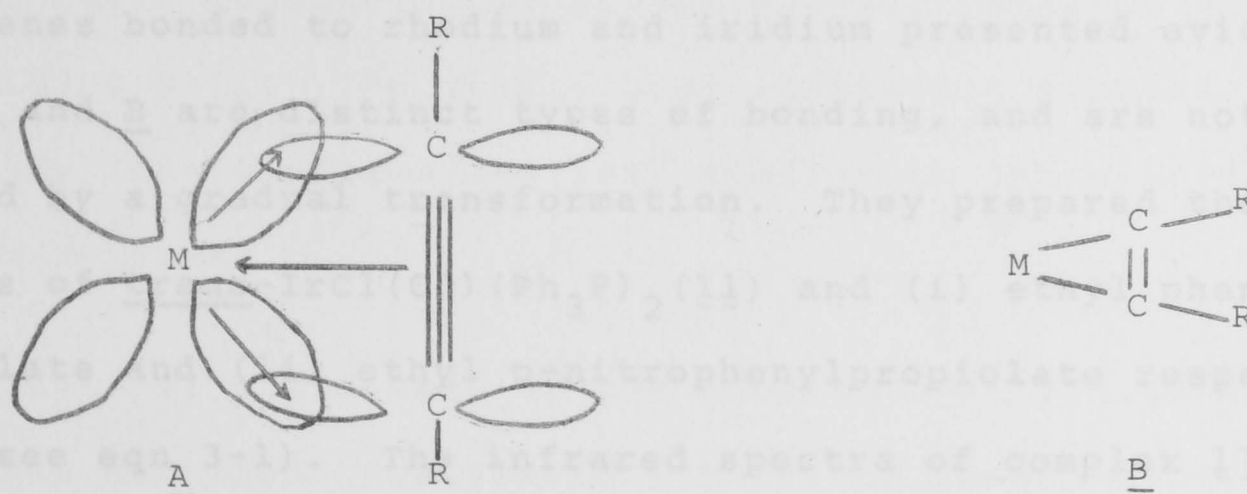
## THE ADDITION OF ACETYLENES

a. Introduction

A considerable number of mononuclear complexes of transition metals in low or zero-valent states and various acetylenes have been reported over the last twenty years.<sup>40,41,42</sup> Several products have resulted from these

reactions; among them were binuclear and polynuclear complexes. Such complexes are considered to be intermediates in metal catalyzed cyclopolymerizations and polymerizations of acetylenes.<sup>43,44,45</sup>

The bonding in acetylene and olefinic complexes has been a subject of much discussion.<sup>40,46,47</sup> Chatt and co-workers<sup>56,57,58</sup> have suggested that the bonding of acetylenes to transition metals (e.g. platinum) might be described in two ways, A or B:



The structure A implies that bonding is caused by donation of acetylene  $\pi$ -electron density into an empty p- or d-orbital of the metal and back donation of electron density from a filled metal d (or dp-hybrid) orbital to an acetylene  $\pi^*$ -orbital. The structure B implies that the electron



density in the acetylene has been reorganized to give an arrangement close to that for an olefin, and that the resulting two unpaired electrons combine with two unpaired electrons on the metal to give two " $\sigma$ " bonds between the acetylene and the metal. It is essential to note that A and B are merely different representations of the same type of bonding, with back bonding being more important in B.

The above distinction was based on the values of  $\Delta\nu(\text{C}\equiv\text{C})$  [ $\nu(\text{C}\equiv\text{C})$  for the free acetylene minus  $\nu(\text{C}\equiv\text{C})$  for the complexed acetylene] found in the acetylene complexes; for smaller value of  $\Delta\nu(\text{C}\equiv\text{C})$  [range 130-200  $\text{cm}^{-1}$ ] structure A was favoured and for larger  $\Delta\nu(\text{C}\equiv\text{C})$  [range 400-500  $\text{cm}^{-1}$ ] structure B was favoured.

Chatt<sup>56</sup> also pointed out the possibility of there existing a series of complexes in which a gradual transition occurred between bonding of types A and B. Collman and Kang<sup>31</sup>, however, on the basis of their results using different acetylenes bonded to rhodium and iridium presented evidence that A and B are distinct types of bonding, and are not related by a gradual transformation. They prepared the adducts of trans- $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  (11) and (i) ethyl phenylpropiolate and (ii) ethyl p-nitrophenylpropiolate respectively. (e.g. see eqn 3-1). The infrared spectra of complex 17 and 18 show  $\nu(\text{C}\equiv\text{C})$  for 17 at 2060  $\text{cm}^{-1}$  [smaller  $\Delta\nu(\text{C}\equiv\text{C})$ ] and for 18 at 1750  $\text{cm}^{-1}$  [larger  $\Delta\nu(\text{C}\equiv\text{C})$ ]; thus 17 possessing a type A structure and 18 a type B structure.

Recent X-ray crystal structures<sup>59,60</sup> have not fully clarified the existing ambiguities in valence states and stereo-chemical arrangement of transition metal acetylene

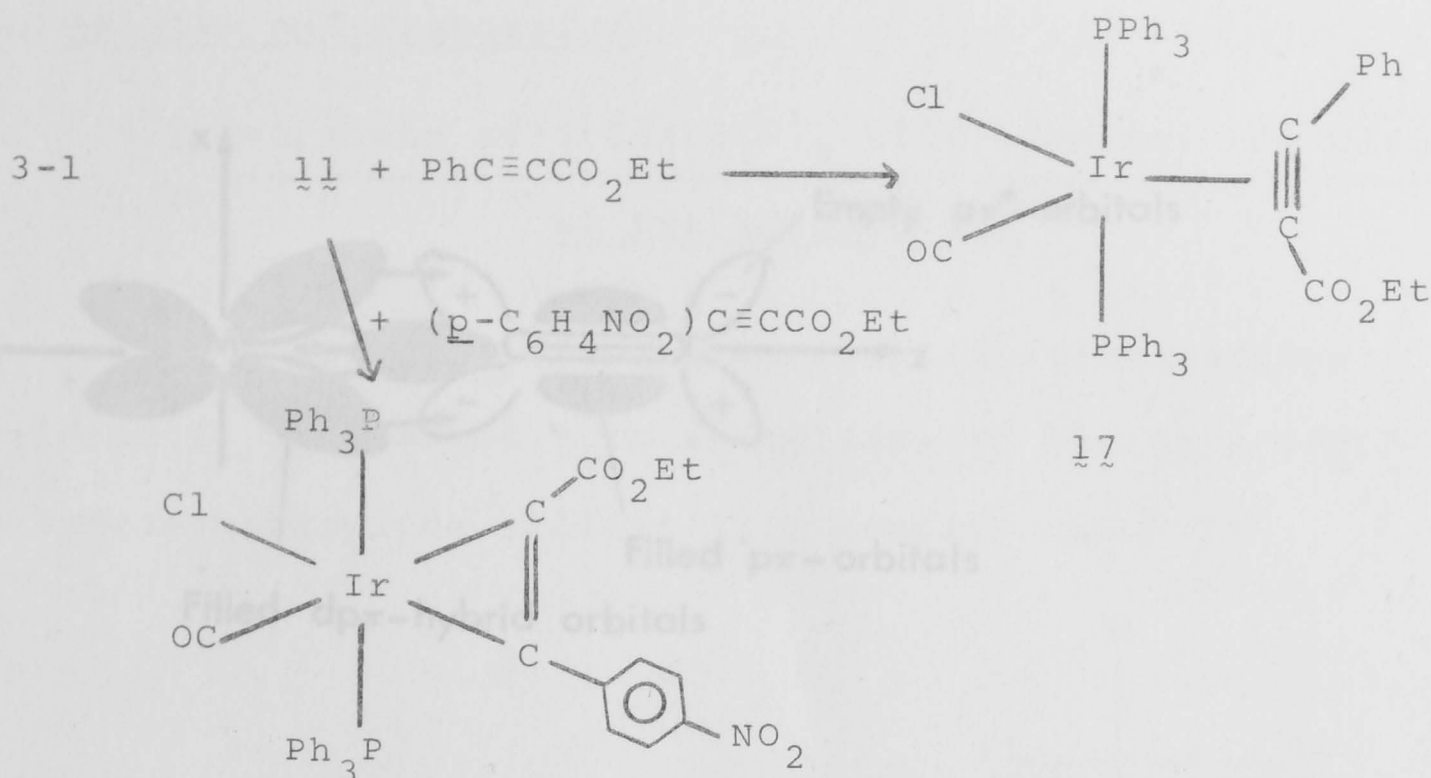
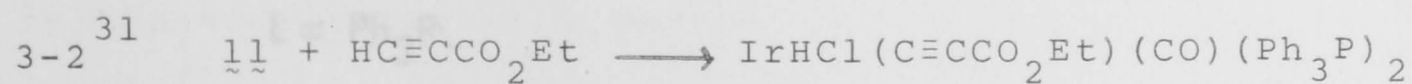


Figure 3-1. A conventional representation of the bonding in  $\text{M}-\text{C}\equiv\text{X}$  systems where  $\text{X}=\text{O}, \text{N}$  or  $\text{CR}$ .

complexes. More detailed structure determinations are required before the question of bonding can be fully answered.

Many transition metal complexes of the type  $\text{M}-\text{C}\equiv\text{CR}$  have been reported.<sup>31,51,52,61</sup> Since the acetylide ( $-\text{C}\equiv\text{CR}$ ) and cyanide ( $-\text{C}\equiv\text{N}$ ) anions and the carbon monoxide molecule ( $-\text{C}\equiv\text{O}$ ) are isoelectronic, it is thought that the bonding between these isoelectronic groups and the metal is similar (see figure 3-1). The triple bond stretching frequencies of the acetylide-complexes are very similar to those of the free acetylenes.

Table 3-1 lists some of the rhodium and iridium acetylene complexes and their acetylenic stretching frequencies. These complexes were prepared by the direct interaction of the acetylene and the iridium(I) or rhodium(I) complex, e.g.;



b. Results and Discussion

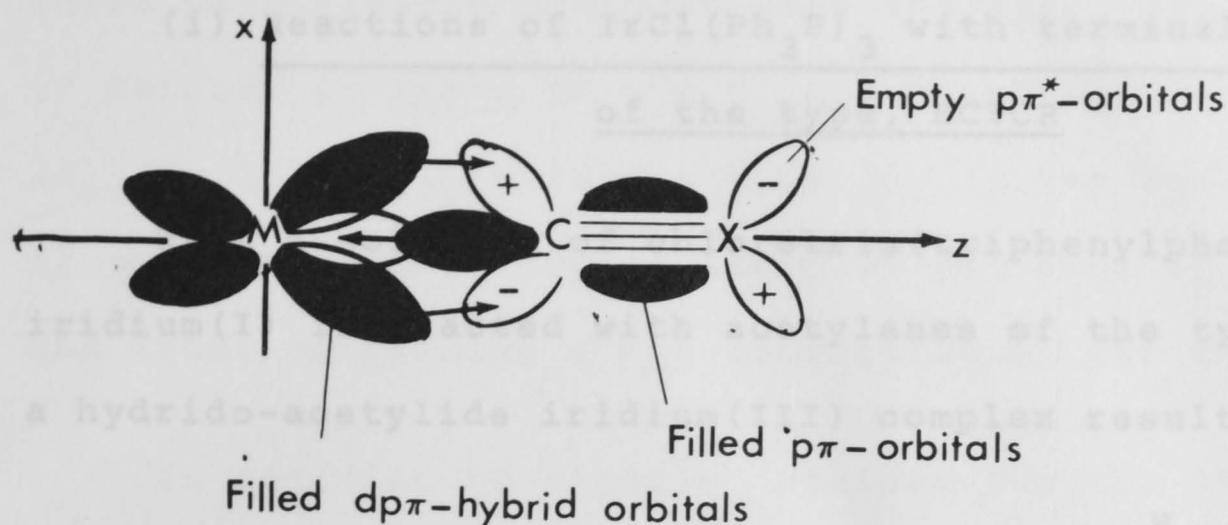


Figure 3-1. A conventional representation of the bonding in  $M-C\equiv X$  systems where  $X = O, N$  or  $CR$ .

Complexes	$\nu(C\equiv C)$ cm <sup>-1</sup>	Reference
$IrCl[MeO_2CC\equiv CCO_2Me](CO)L_2$	1770	31
$IrCl[PhC\equiv CCO_2Et](CO)L_2$	2060	31
$IrHCl[C\equiv CCO_2Et](CO)L_2$	2130	31
$RhCl[HO_2CC\equiv CCO_2H](CO)L_2$	1600	31
$RhCl[HC\equiv CCO_2H](CO)L_2$	1640	31
$IrCl[F_3CC\equiv CCF_3]L_2$	1885	50
$Ir[C\equiv CMe](CO)L_3$	2132	48

Table 3-1. Rh and Ir acetylene complexes and their  $\nu(C\equiv C)$ .

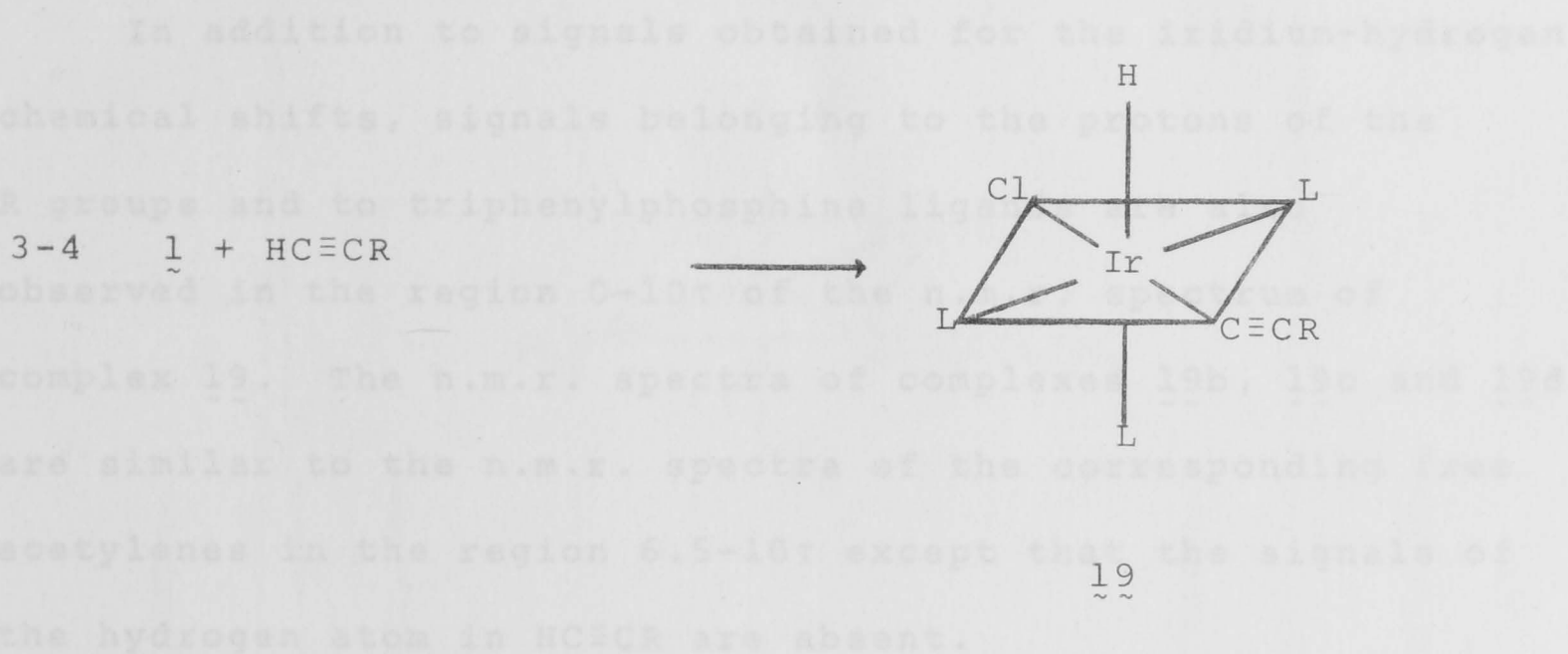
$L = Ph_3P$ .



b. Results and Discussion

(i) Reactions of  $\text{IrCl}(\text{Ph}_3\text{P})_3$  with terminal acetylenes  
of the type,  $\text{HC}\equiv\text{CR}$

When a solution of chlorotris(triphenylphosphine)-iridium(I) is reacted with acetylenes of the type  $\text{HC}\equiv\text{CR}$ , a hydrido-acetylide iridium(III) complex results:



$\text{L}=\text{Ph}_3\text{P}$ , (a)  $\text{R}=\text{CO}_2\text{CH}_3$ , (b)  $(\text{CH}_2)_2\text{CH}_3$ , (c)  $(\text{CH}_2)_3\text{CH}_3$ ,  
 (d)  $(\text{CH}_2)_2\text{OH}$ , (e) H, (f) Ph.

diphenylacetylene.

The complexes 19 all show two bands, one strong and one medium, in the infrared spectra in the region  $2000-2190\text{cm}^{-1}$  (table 3-2). The more intense band is tentatively assigned to the triple bond stretching mode of the terminally bound acetylide, and the less intense band is assigned to the iridium-hydrogen stretching mode. The reaction with acetylene of the type  $\text{DC}\equiv\text{CR}$  must be undertaken if unequivocal assignments of  $\nu(\text{Ir}-\text{H})$  and  $\nu(\text{C}\equiv\text{C})$  are to be made. The complex 19a also shows a band in its infrared spectrum at  $1675\text{cm}^{-1}$  which is characteristic of  $\nu(\text{C}=\text{O})$ .

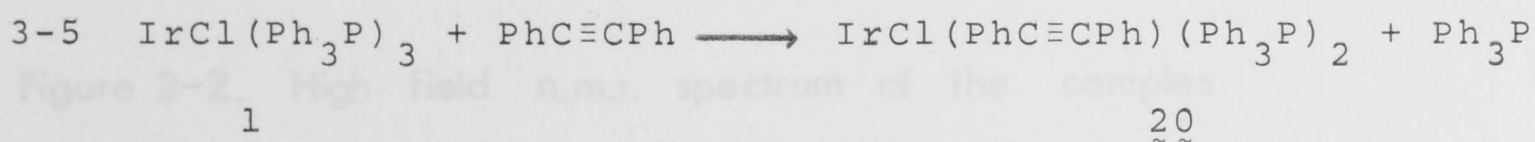
Two triplets ( $J_{\text{P}-\text{H}} = 18\text{Hz}$ ) centred at about  $21\tau$  and separated by  $154\text{Hz}$  are observed in the high field region of

the n.m.r. spectrum of complex 19 (table 3-3, figure 3-2). These data clearly indicate that the hydrogen atom attached to iridium is trans to one of the triphenylphosphine groups ( $J_{P-H} = 154\text{Hz}$ ;  $\tau_H = 21\tau$ ) and is cis to two equivalent triphenylphosphine groups (triplet pattern,  $J_{P-H} = 18\text{Hz}$ )<sup>27,28</sup> and thus, confirming a mer-configuration for the products.

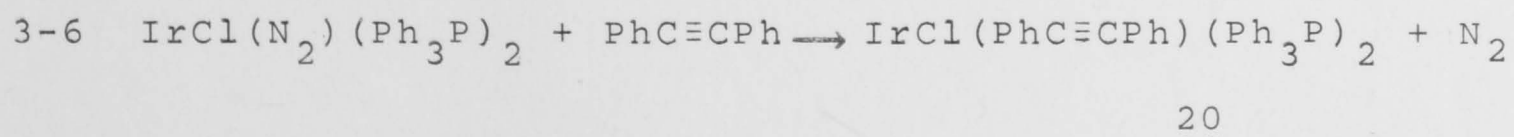
In addition to signals obtained for the iridium-hydrogen chemical shifts, signals belonging to the protons of the R groups and to triphenylphosphine ligands are also observed in the region 0-10 $\tau$  of the n.m.r. spectrum of complex 19. The n.m.r. spectra of complexes 19b, 19c and 19d are similar to the n.m.r. spectra of the corresponding free acetylenes in the region 6.5-10 $\tau$  except that the signals of the hydrogen atom in HC $\equiv$ CR are absent.

(ii) Reaction of the complex IrCl(Ph<sub>3</sub>P)<sub>3</sub> and diphenylacetylene.

When diphenylacetylene is reacted with chlorotris(triphenylphosphine)iridium(I), yellow crystals of IrCl(PhC $\equiv$ CPh)(Ph<sub>3</sub>P)<sub>2</sub> are obtained:



The product 20 is identical with that obtained from the reaction of diphenylacetylene and the complex IrCl(N<sub>2</sub>)(Ph<sub>3</sub>P)<sub>2</sub><sup>31</sup>:



and is similar to that obtained from the reaction of diphenylacetylene and the rhodium(I) complex RhCl(Ph<sub>3</sub>P)<sub>3</sub> (eqn 3-3).<sup>54</sup>

An intense band at  $1665\text{cm}^{-1}$  in the infrared spectrum of 20 is assigned to the triple bond stretching mode of the co-ordinated acetylene. The rhodium analogue has been regarded by Wilkinson and co-workers<sup>54</sup> as a square planar rhodium(I)  $\pi$ -donor ligand (structure A); whereas for the iridium complex 20, the original workers<sup>31</sup> considered the bonding in type B.

The X-ray crystal structure of  $\text{IrCl}(\text{C}\equiv\text{CCO}_2\text{CH}_3)(\text{PPh}_3)_3$  has been reported.<sup>60</sup> The structure in the crystal is described as lying between the two postulated geometries A and B, but being considerably closer to configuration A. It is therefore quite likely that the iridium complex 20 may possess a similar configuration.

(a) Reaction of the complex  $\text{IrCl}(\text{PPh}_3)_3$  and dimethyl acetylenedicarboxylate  
 The product obtained from the reaction of  $\text{IrCl}(\text{PPh}_3)_3$  and dimethyl acetylenedicarboxylate has been previously prepared by the reaction of the complex  $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$  and dimethyl acetylenedicarboxylate.<sup>55</sup>

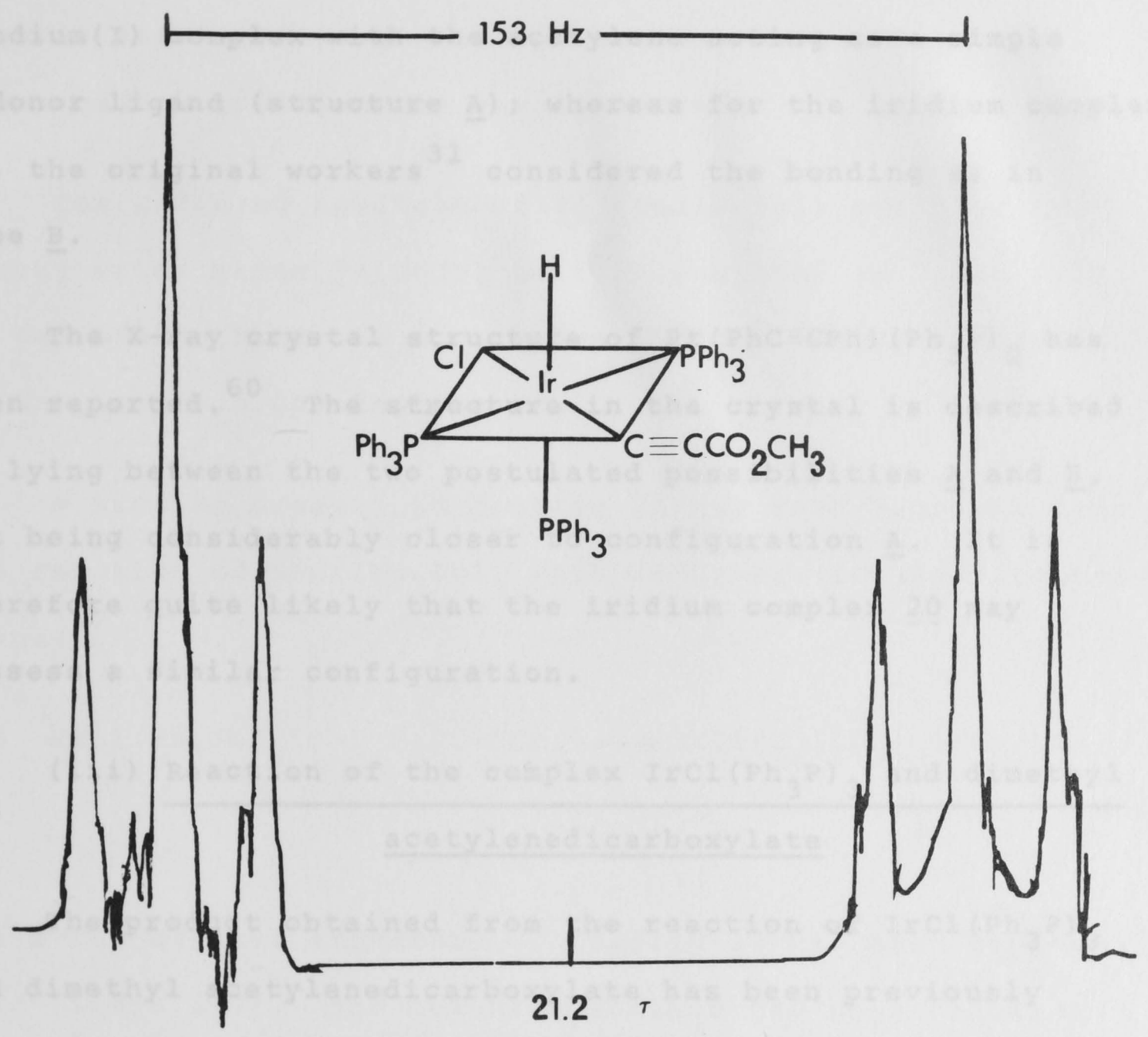
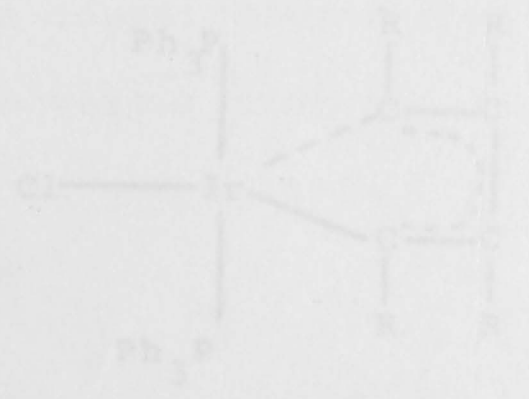
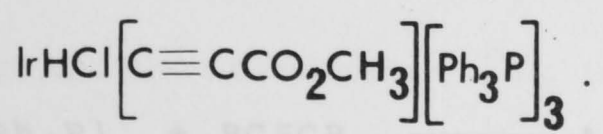


Figure 3-2. High field n.m.r. spectrum of the complex



L = N<sub>2</sub> or Ph<sub>3</sub>P; R = CO<sub>2</sub>CH<sub>3</sub>

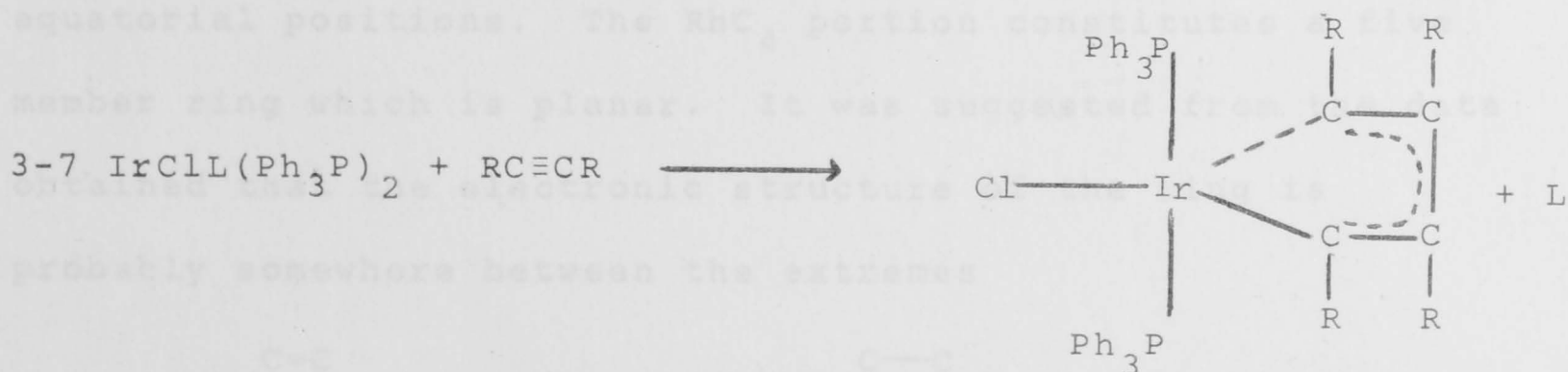


An intense band at  $1865\text{cm}^{-1}$  in the infrared spectrum of 20 is assigned to the triple bond stretching mode of the co-ordinated acetylene. The rhodium analogue has been regarded by Wilkinson and co-workers<sup>54</sup> as a square planar rhodium(I) complex with the acetylene acting as a simple  $\mu$ -donor ligand (structure A); whereas for the iridium complex 20, the original workers<sup>31</sup> considered the bonding as in type B.

The X-ray crystal structure of  $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{Ph}_3\text{P})_2$  has been reported.<sup>60</sup> The structure in the crystal is described as lying between the two postulated possibilities A and B, but being considerably closer to configuration A. It is therefore quite likely that the iridium complex 20 may possess a similar configuration.

(iii) Reaction of the complex  $\text{IrCl}(\text{Ph}_3\text{P})_3$  and dimethyl acetylenedicarboxylate

The product obtained from the reaction of  $\text{IrCl}(\text{Ph}_3\text{P})_3$  and dimethyl acetylenedicarboxylate has been previously prepared by the reaction of the complex  $\text{IrCl}(\text{N}_2)(\text{Ph}_3\text{P})_2$  and dimethyl acetylenedicarboxylate:<sup>55</sup>

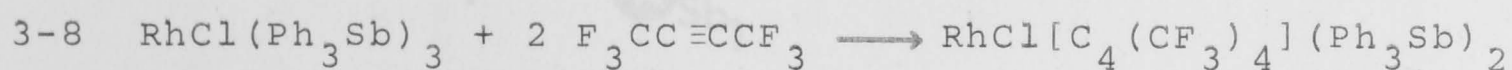


$\text{L} = \text{N}_2$  or  $\text{Ph}_3\text{P}$ ;  $\text{R} = \text{CO}_2\text{CH}_3$

The n.m.r. spectrum of complex 21 (table 3-3) gives two sharp singlets for the methyl protons of the  $\text{CO}_2\text{CH}_3$  groups. It was suggested<sup>19</sup> that this would be expected if the chlorine atom is in the trigonal plane, the different signals arising from the methyl protons on the R groups in the  $\alpha$  and  $\beta$  positions on the iridocycle.

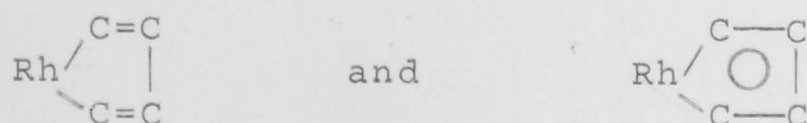
The infrared spectrum of 21 (table 3-2) exhibits two strong ester bands [ $\nu(\text{C}=\text{O})$ ] at 1715 and 1690  $\text{cm}^{-1}$ , as well as two medium bands in the region 1500 $\text{cm}^{-1}$  which are assigned to the iridocyclopentadiene ring.

A similar product to complex 21 has been prepared from the reaction of  $\text{RhCl}(\text{Ph}_3\text{Sb})_3$  with an excess of hexafluorobut-2-yne.<sup>62</sup>



22

The X-ray crystal structure of complex 22 has been reported<sup>63</sup> (see figure 3-3). The author described the co-ordination about the rhodium atom as a slightly distorted trigonal bipyramid with Sb atoms in the axial positions and a Cl atom and the 1 and 4 C atoms of the  $\text{C}_4(\text{CF}_3)_4$  moiety occupying equatorial positions. The  $\text{RhC}_4$  portion constitutes a five member ring which is planar. It was suggested from the data obtained that the electronic structure of the ring is probably somewhere between the extremes



By analogy product 21 should possess a similar structure as complex 22.

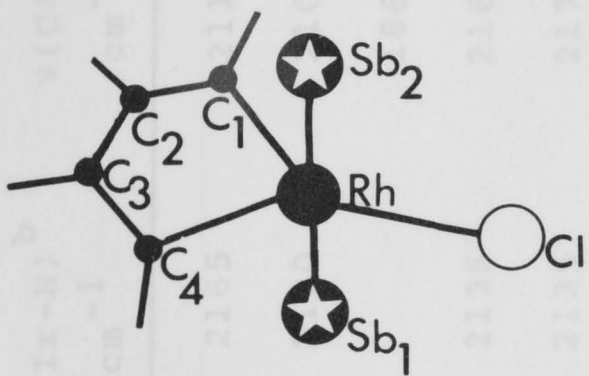


Figure 3-3. A perspective view of the  $\text{RhCl}[\text{C}_4(\text{CF}_3)_4][\text{Ph}_3\text{Sb}]_2$  molecule with phenyl and  $\text{CF}_3$  groups omitted.



Table 3-2

Infrared data for the acetylene-iridium complexes<sup>a</sup>.

Complex	$\nu(\text{Ir-H})^b$ cm <sup>-1</sup>	$\nu(\text{C}\equiv\text{C})^c$ cm <sup>-1</sup>	Other cm <sup>-1</sup>
$\text{IrHCl}(\text{C}\equiv\text{CPh})(\text{Ph}_3\text{P})_3$	2165	2115	
$\text{IrHCl}(\text{C}\equiv\text{CCO}_2\text{CH}_3)(\text{Ph}_3\text{P})_3$	2180	2100	1675... $\nu(\text{C}=\text{O})^c$
$\text{IrCl}(\text{PhC}\equiv\text{CPh})(\text{Ph}_3\text{P})_2$		1865	
$\text{IrHCl}[\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3](\text{Ph}_3\text{P})_3$	2135	2160	
$\text{IrHCl}[\text{C}\equiv\text{C}(\text{CH}_2)_2\text{CH}_3](\text{Ph}_3\text{P})_3$	2135	2170	
$\text{IrHCl}[\text{C}\equiv\text{C}(\text{CH}_2)_2\text{OH}](\text{Ph}_3\text{P})_3$	2175	2130	
$\text{IrHCl}(\text{C}\equiv\text{CH})(\text{Ph}_3\text{P})_3$	2185	1975	
$\text{IrCl}(\text{CH}_3\text{O}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3)_2(\text{Ph}_3\text{P})_2$			1550, 1500... $\nu(\text{C}=\text{C})^b$ 1690, 1715... $\nu(\text{C}=\text{O})^c$

a...all spectra were measured in the solid state as nujol mulls.

b...all bands are of medium intensities.

c...all bands are of strong intensities.

Table 3-3

<sup>1</sup>H-N.M.R. data for complexes of the type IrHCl(C≡CR)(Ph<sub>3</sub>P)<sub>3</sub><sup>a</sup>

<sup>a</sup>...all spectra measured in CDCl<sub>3</sub> with Me<sub>4</sub>Si used as internal standard.

<sup>b</sup>...represents the Ir-H coupling constant, P delay cis to H.

<sup>c</sup>...multiplet, t-triplet.

Complexes when R=	$\tau$ (Ir-H) <sup>b</sup> ( $\tau$ )	$J_{\text{trans}}^c$ Hz	$J_{\text{cis}}^c$ Hz	Other <sup>d</sup> ( $\tau$ )
CO <sub>2</sub> CH <sub>3</sub>	21.25	153.0	18.0	
Ph	21.9	155.0	18.0	
(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	21.3	154.5	18.0	≡CCH <sub>2</sub> 7.88 (m) (CH <sub>2</sub> ) <sub>2</sub> 8.82 (m) (CH <sub>3</sub> ) 9.2 (m)
(CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>	21.5	154.5	18.0	≡CCH <sub>2</sub> 7.88 (m) (CH <sub>2</sub> ) 8.74 (m) (CH <sub>3</sub> ) 9.2 (t, J <sub>H-H</sub> =7Hz)
(CH <sub>2</sub> ) <sub>2</sub> OH	19.1	156.0	18.0	CH <sub>2</sub> 7.7 (m) CH <sub>2</sub> OH 6.7 (m)
H	22.0	154.5	18.0	

Cont'd..

Table 3-3 Cont'd

Analyses of the acetylene-iridium complexes

a...all spectra measured in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  used as internal standard.

b...in all cases two triplets were obtained.

c... $J_{\text{trans}}$  represents the P-H coupling constant, P being trans to H.

$J_{\text{cis}}$  represents the P-H coupling constant, P being cis to H.

d...m=multiplet, t=triplet.

$\text{IrCl}(\text{PhC}\equiv\text{CPh})(\text{Ph}_3\text{P})_2$	c. 66.57	4.34	6.45
	f. 63.82	4.76	6.12
$\text{IrCl}(\text{PhC}\equiv\text{CPh})(\text{Ph}_3\text{P})_2$	c. 64.94	4.33	6.65
	f. 63.66	4.30	6.70
$\text{IrCl}(\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3)(\text{Ph}_3\text{P})_3$	c. 65.71	5.06	6.47
	f. 65.81	5.14	6.23
$\text{IrCl}(\text{C}\equiv\text{C}(\text{CH}_2)_2\text{CH}_3)(\text{Ph}_3\text{P})_3$	c. 65.48	4.94	6.56
	f. 63.95	5.08	6.35
$\text{IrCl}(\text{C}\equiv\text{C}(\text{CH}_2)_2\text{OMe})(\text{Ph}_3\text{P})_3$	c. 64.23	4.74	6.57
	f. 64.71	4.91	6.27
$\text{IrCl}(\text{C}\equiv\text{C}(\text{CH}_2)_3\text{SC}_6\text{H}_5)(\text{Ph}_3\text{P})_3$	c. 68.26	4.93	7.76
	f. 68.80	5.01	7.62
$\text{IrCl}(\text{C}_6\text{H}_5\text{O}_4)(\text{Ph}_3\text{P})_2$	c. 55.62	4.09	5.98
	f. 55.75	4.16	6.12



Table 3-4

Analyses of the acetylene-iridium complexes

Complex	%C	%H	%P
$\text{IrHCl}(\text{C}\equiv\text{CPh})(\text{Ph}_3\text{P})_3$	c. 66.69	4.60	8.32
	f. 66.67	4.34	8.45
$\text{IrHCl}(\text{C}\equiv\text{CCO}_2\text{CH}_3)(\text{Ph}_3\text{P})_3$	c. 63.41	4.49	8.46
	f. 63.82	4.76	8.12
$\text{IrCl}(\text{PhC}\equiv\text{CPh})(\text{Ph}_3\text{P})_2$	c. 64.54	4.33	6.65
	f. 63.66	4.30	6.70
$\text{IrHCl}[\text{C}\equiv\text{C}(\text{CH}_2)_3\text{CH}_3](\text{Ph}_3\text{P})_3$	c. 65.71	5.06	8.47
	f. 65.81	5.14	8.23
$\text{IrHCl}[\text{C}\equiv\text{C}(\text{CH}_2)_2\text{CH}_3](\text{Ph}_3\text{P})_3$	c. 65.48	4.94	8.58
	f. 65.95	5.08	8.35
$\text{IrHCl}[\text{C}\equiv\text{C}(\text{CH}_2)_2\text{OH}](\text{Ph}_3\text{P})_3$	c. 64.23	4.74	8.57
	f. 64.71	4.91	8.27
$\text{IrHCl}(\text{C}\equiv\text{CH})(\text{Ph}_3\text{P})_3 \cdot 2\text{C}_6\text{H}_6$	c. 68.26	4.93	7.76
	f. 68.88	5.01	7.62
$\text{IrCl}(\text{C}_6\text{H}_6\text{O}_4)_2(\text{Ph}_3\text{P})_2$	c. 55.62	4.09	5.98
	f. 55.75	4.16	6.12

c. Experimental

See Chapter 2, section e, for general physical measurements and preparations of the iridium(I) complex (1).

A. Interaction of acetylenes with chlorotris(triphenylphosphine)iridium(I)(i) Phenylacetylene-(HC≡CPh)

To chlorotris(triphenylphosphine)iridium(I) (0.3g) in benzene (5ml) was added phenylacetylene (1ml). The solution was stirred for 90 minutes, then evaporated to dryness at 25°C (15mm). The residue was recrystallized from chloroform/ethanol giving brown crystals (0.26g) of the adduct (79% yield) M.P. 115-20°C.

The same procedure was followed for the other acetylenes, varying only the period of stirring.

(ii) Methyl Propiolate-(HC≡CCO<sub>2</sub>CH<sub>3</sub>)

Solution stirred for 2 minutes. (0.25g; 78% yield)  
M.P. 160-62°C.

(iii) Diphenylacetylene-(PhC≡CPh)

Solution refluxed for 12 hours (0.2g; 74%)  
M.P. 215-20(d)\* °C.

(iv) 1-Hexyne-[HC≡C(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]

Solution stirred for 2 hours. (0.24g; 75%)  
M.P. 100-05(d)\* °C.

(v) 1-Pentyne [HC≡C(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>]

Solution stirred for 2 hours. (0.24g; 75%)  
M.P. 150-52 °C.

(vi) 3-Butyn-1-ol- $[\text{HC}\equiv\text{C}(\text{CH}_2)_2\text{OH}]$

Solution stirred for 45 minutes. (0.21g; 66%)

M.P. 110-15(d) \* °C.

(vii) Dimethyl Acetylenedicarboxylate- $(\text{CH}_3\text{O}_2\text{CC}\equiv\text{CCO}_2\text{CH}_3)$

Solution stirred for 12 hours. (0.22g; 71%)

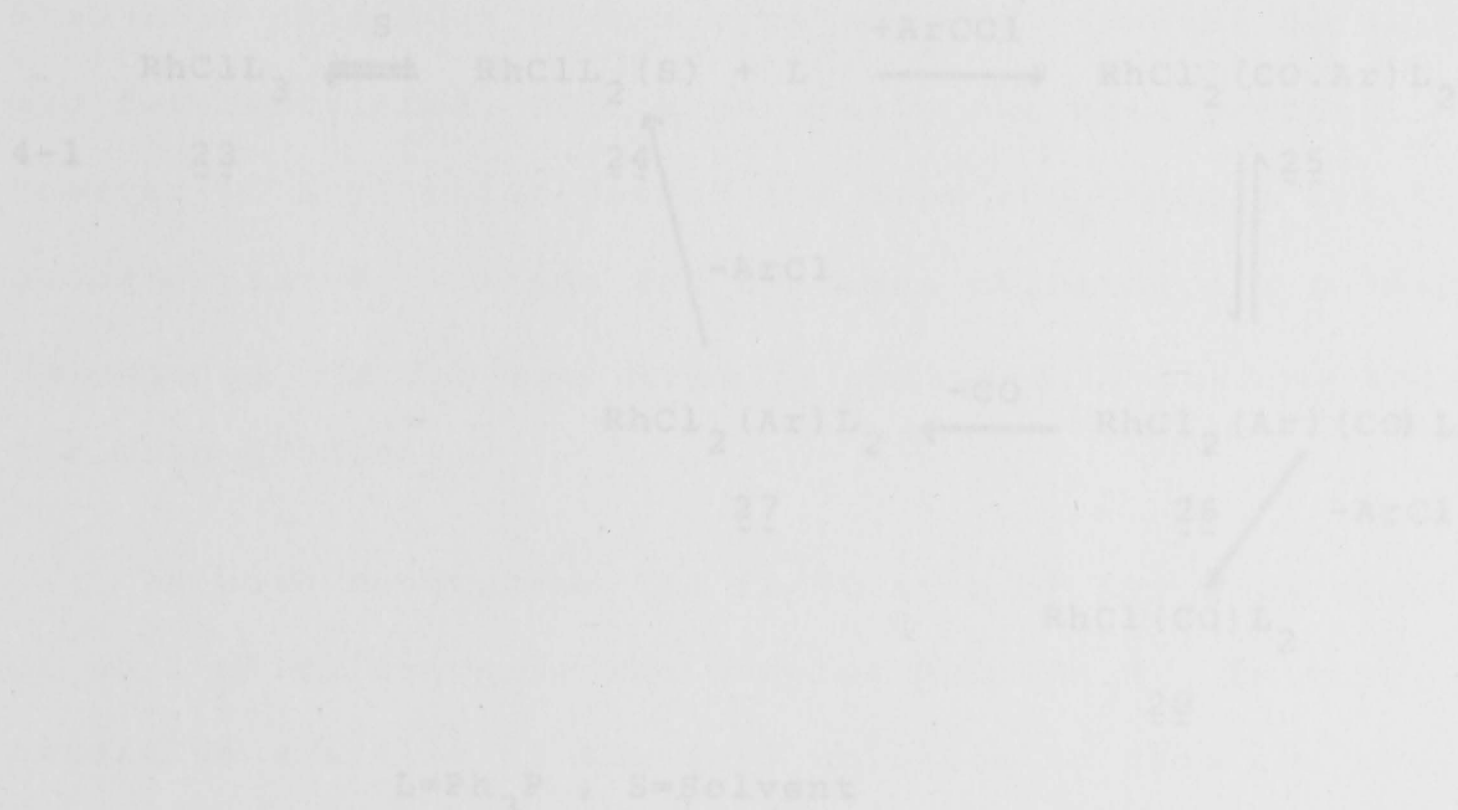
M.P. 250-51(d) \* °C.

(viii) Acetylene- $(\text{HC}\equiv\text{CH})$

The gas was bubbled through the solution for 15 minutes at room temperature. (0.22g; 71%) M.P. 150-55(d) °C.

\*...d represents decomposition point.

as the catalyst:



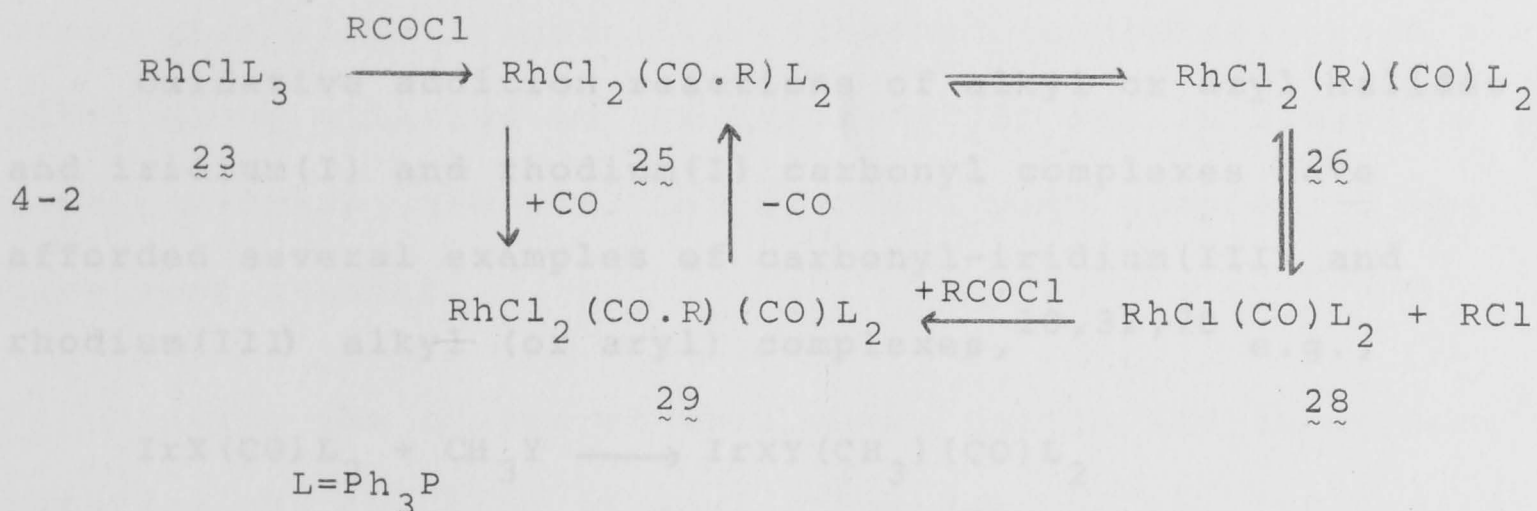
The initial step is oxidative addition of the acid chloride to the dissociated form (24) of complex 23 to form the acyl complex 25. Alkyl migration affords a supposed intermediate 26 which can eliminate carbon monoxide to form 27. Alternatively 26 can lose aryl halide to form the rhodium(II) complex 28. Intermediate 27 can also lose aryl halide to regenerate the catalyst 24. The transformation of 26 to 28





is thought to be the deactivating path and that 28 must lose carbon monoxide before catalytic activity can be regained.

On the other hand, Ohno et al<sup>65</sup> considered that the decarbonylation of acid chlorides by complex 23 is stoichiometric and that the actual catalyst is the rhodium(I) complex 28:



When acid chlorides of the type  $\text{RCH}_2\text{COCl}$  [R=aryl or alkyl] are decarbonylated, RCl is generally the main product.

However if acyl chlorides of the type  $\text{RCH}_2\text{CH}_2\text{COCl}$  are decarbonylated, olefins and hydrogen chloride are formed.

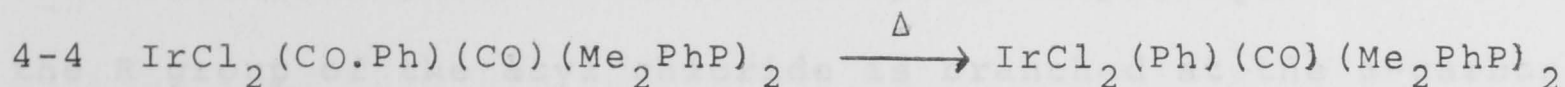
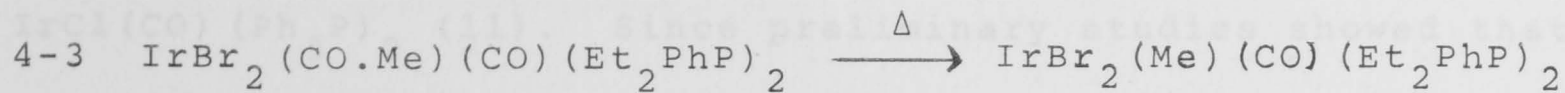
Isomers of olefins are normally obtained, 1-olefins being the main product.

In both mechanisms the first step of the decarbonylation of acyl chloride using the complex  $\text{RhCl}(\text{Ph}_3\text{P})_3$  is the oxidative addition of the acyl chloride to form the rhodium(III) complex 25. Several stable complexes of type 25 have been isolated [R=(CH<sub>2</sub>)<sub>n</sub>CH<sub>3</sub> n=4,5,14,16] and characterized.<sup>65</sup> Alkyl migration in complex 25 should then give the alkyl (or aryl) complex 26. However complex 26 has been isolated only for the methyl (R=CH<sub>3</sub>) and phenyl (R=Ph) complexes.<sup>66,67</sup>

Acyl chlorides also react with complexes of the type  $\text{IrX}(\text{CO})\text{L}_2$  [L=tertiary phosphine, X=halogen] to give

six-coordinate acyl complexes,  $\text{IrXCl}(\text{CO}\cdot\text{R})(\text{CO})\text{L}_2$ .<sup>2,32,68,69</sup>

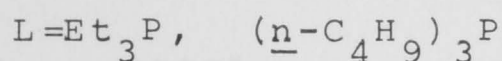
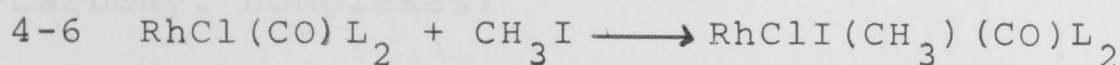
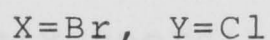
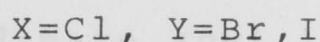
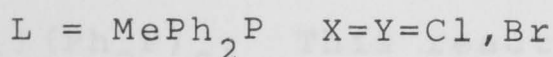
The decarbonylation of these acyl complexes to give alkyl complexes has been observed in two instances:<sup>68,69</sup>



Oxidative addition reactions of alkyl or aryl halides and iridium(I) and rhodium(I) carbonyl complexes have afforded several examples of carbonyl-iridium(III) and rhodium(III) alkyl (or aryl) complexes,<sup>10,32,70</sup> e.g.,



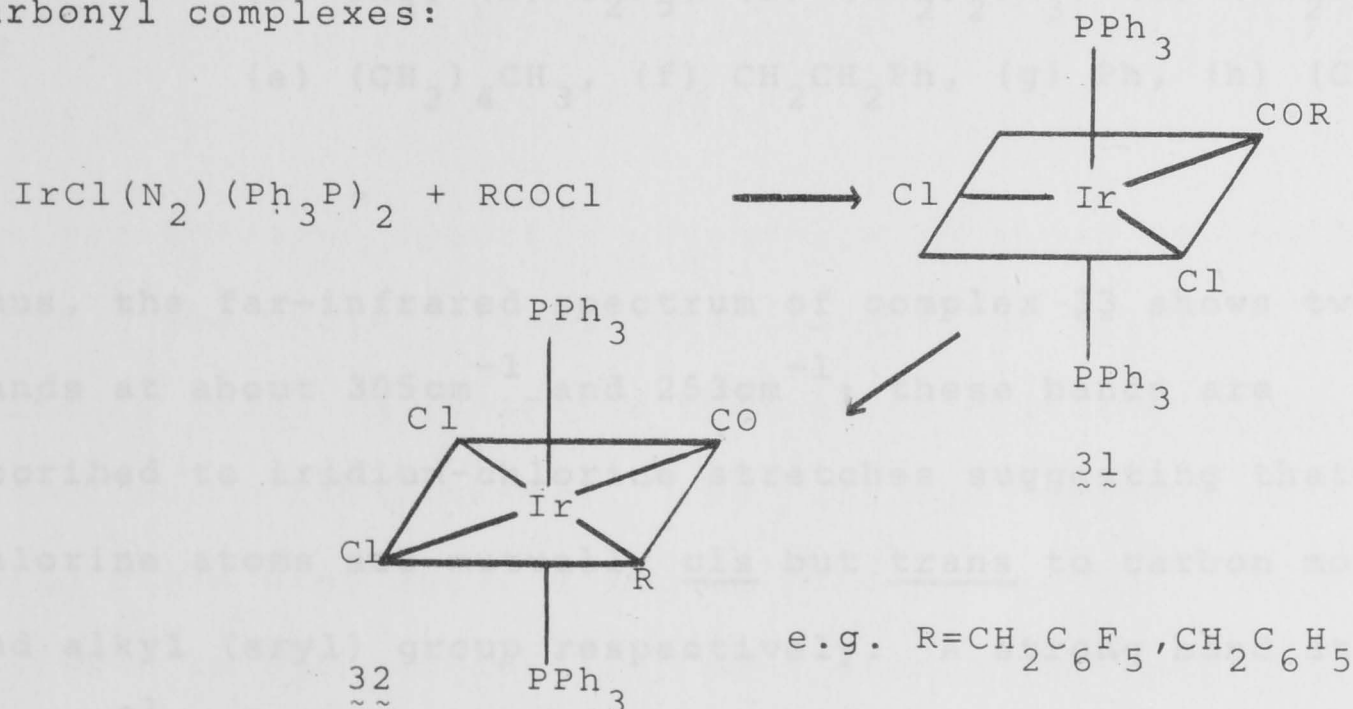
4-5



Acyl chlorides ( $\text{RCOCl}$ ) also react with the iridium(I) complex  $[\text{IrCl}(\text{CO})(\text{C}_8\text{H}_{14})_2]_2$  (30) to give bridged chloro-complexes of type  $[\text{IrCl}_2\text{R}(\text{CO})_2]_2$  (39) [ $\text{R}=(\text{a})\text{Me}, (\text{b})\text{Et}, (\text{c})\text{Pr}^i$ , or  $(\text{d})\text{Ph}$ ].<sup>38</sup> These alkyl (aryl) complexes react with an excess of tertiary phosphines to give mononuclear iridium(III) acyl complexes of type  $\text{IrCl}_2(\text{CO}\cdot\text{R})(\text{CO})\text{L}_2$  ( $\text{L}=\text{Me}_2\text{PhP}, \text{Et}_2\text{PhP}$ ). In contrast, the alkyl iridium(III) complexes undergo cleavage of the chlorine bridges when treated with pyridine (1 mole per iridium atom) without acyl formation; compounds of the type  $\text{IrCl}_2(\text{R})(\text{CO})_2\text{py}$  ( $\text{R}=\text{Me}, \text{Et}, \text{py}=\text{pyridine}$ ) are formed.

The addition reactions of the complex  $\text{IrCl}(\text{Ph}_3\text{P})_3$  (1) with acyl chlorides have been studied for the purposes of comparison with both the complexes  $\text{RhCl}(\text{Ph}_3\text{P})_3$  (23) and  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  (11). Since preliminary studies showed that reactions of acyl chlorides,  $\text{RCOCl}$ , and complex 1, where the R group of the acyl chloride is branched at the  $\alpha$ -carbon atom, give alkyl-iridium(III) carbonyl complexes, where the alkyl group attached to the iridium(III) ion is always straight-chain, the addition of  $\text{RCOCl}$  with complex 30 has also been studied.

During the course of this work, Kubota and co-workers<sup>82,83</sup> reported the reaction of acyl chlorides and the iridium(I) complex  $\text{IrCl}(\text{N}_2)(\text{Ph}_3\text{P})_2$ . This reaction proceeds through the formation of five-coordinate acyl intermediates which readily isomerize to give six-coordinate alkyl (aryl) carbonyl complexes:



Complexes of type 31 and 32 have been isolated and characterized.

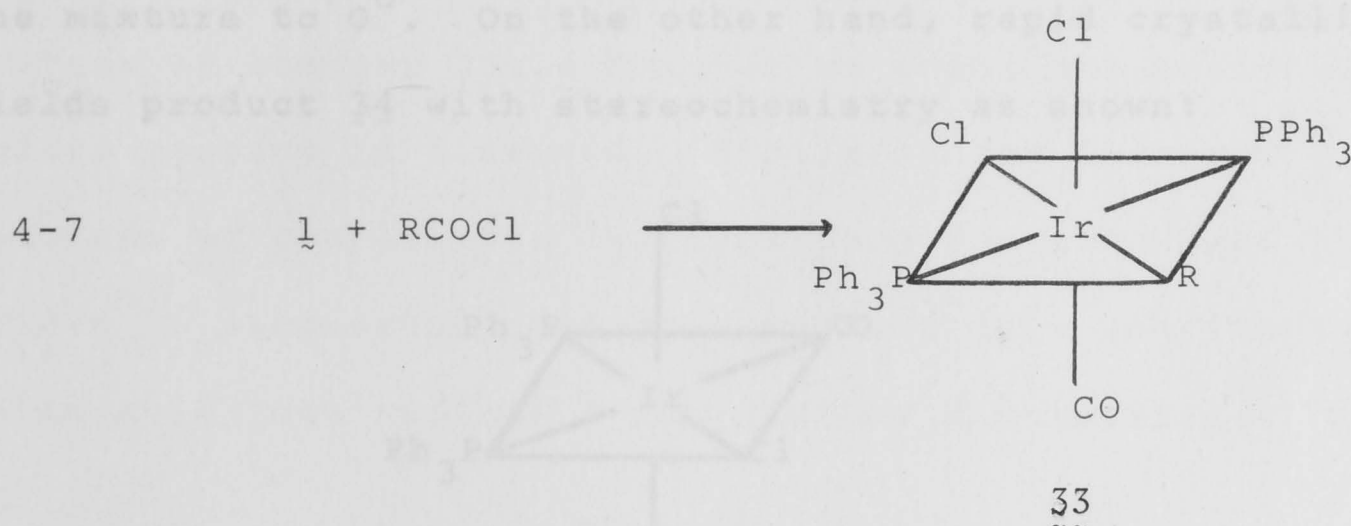
The reactions of acyl chlorides and the complexes 1 and 30 and their results are discussed in the subsequent sections.



b. Results and Discussion(1) Reaction of acyl chlorides with  $\text{IrClL}_3$ 

(1  $\text{L}=\text{Ph}_3\text{P}$ , 3  $\text{L}=\text{MePh}_2\text{P}$ ).

Acyl chlorides ( $\text{RCOCl}$ ) react with the iridium(I) complex 1 to give six-coordinate alkyl (aryl) iridium(III) complexes of type  $\text{IrCl}_2(\text{R})(\text{CO})(\text{Ph}_3\text{P})_2$  (33), the stereochemistry of which, based on far-infrared data, is generally as shown in equation 4-7:



R = (a)  $\text{CH}_3$ , (b)  $\text{C}_2\text{H}_5$ , (c)  $(\text{CH}_2)_2\text{CH}_3$ , (d)  $(\text{CH}_2)_3\text{CH}_3$ ,  
 (e)  $(\text{CH}_2)_4\text{CH}_3$ , (f)  $\text{CH}_2\text{CH}_2\text{Ph}$ , (g)  $\text{Ph}$ , (h)  $(\text{CH}_2)_6\text{CH}_3$

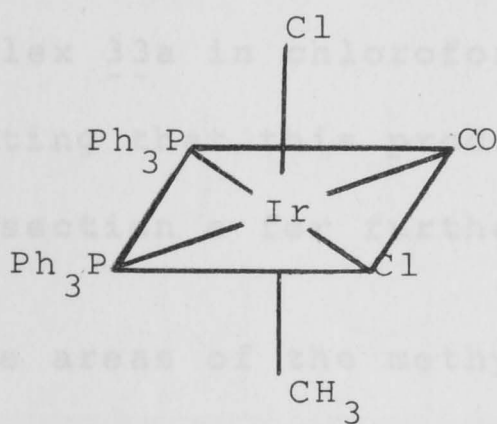
Thus, the far-infrared spectrum of complex 33 shows two bands at about  $305\text{cm}^{-1}$  and  $253\text{cm}^{-1}$ ; these bands are ascribed to iridium-chlorine stretches suggesting that the chlorine atoms are mutually cis but trans to carbon monoxide and alkyl (aryl) group respectively. A strong band at  $2030\text{cm}^{-1}$  is also observed in the infrared spectrum of complexes 33; this band is characteristic of  $\nu(\text{C}\equiv\text{O})$  when the carbonyl group is terminally bound to  $\text{Ir(III)}$  ion. These complexes are all monomeric in chloroform solution. Tables 4-1 and 4-2 list the infrared and n.m.r. data for complexes 33. The n.m.r. spectra for complexes 33c-33h



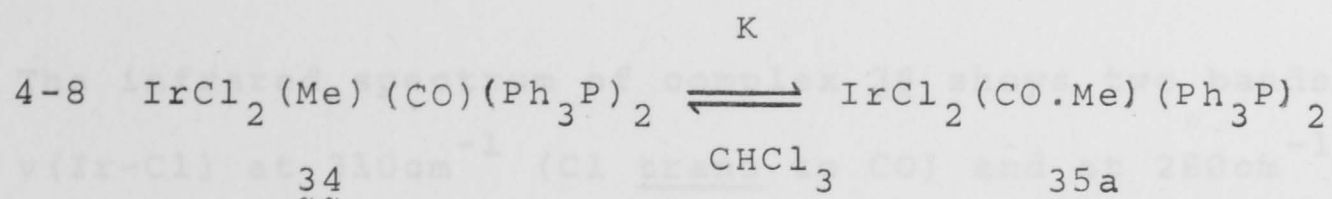
are interpreted and discussed in section C.

(i) Acetyl chloride

The reaction of acetyl chloride to the iridium(I) complex 1 gives two isomeric products which may be separated in a pure state depending on the rate of crystallization. The resonance at 9.43 $\tau$  is assigned to the methyl protons, while the singlet is assigned to the acetyl resonance. The triplet pattern presumably arises from coupling with two equivalent trans phosphorus nuclei. A similar triplet pattern is also observed at 9.43 $\tau$  for the methyl protons of complex 33a. However no resonance assignable to acetyl protons is observed. Similarly the infrared spectrum of complex 33a in chloroform shows no band at 1710 $\text{cm}^{-1}$ , suggesting that it does not isomerize to an acyl (see section C for further discussion). The relative areas of the methyl and acetyl peaks in the n.m.r. spectrum of complex 34 suggest that X (eqn 4-6) is approximately 2.0 at 34 $^{\circ}$ .



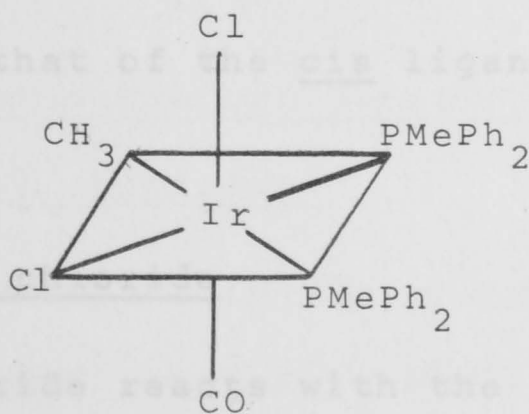
The far-infrared spectrum of complex 34 shows two bands at 290 $\text{cm}^{-1}$  and 256 $\text{cm}^{-1}$ ; these are assigned to  $\nu(\text{Ir-Cl})$ , chlorine trans to phosphine ligand and chlorine trans to methyl group respectively. The infrared spectrum in the solid state also shows a strong band at 2040 $\text{cm}^{-1}$  which is assigned to the terminal carbonyl stretching frequency. However, the infrared spectrum of complex 34 in chloroform shows a band at 1710 $\text{cm}^{-1}$  in addition to the band at 2040 $\text{cm}^{-1}$ . This band at 1710 $\text{cm}^{-1}$  indicates that the methyl complex 34 has partially isomerized to the acetyl complex,  $\text{IrCl}_2(\text{CO.Me})(\text{Ph}_3\text{P})_2$ , (35a) [ $\nu(\text{C=O}) = 1710\text{cm}^{-1}$ ].



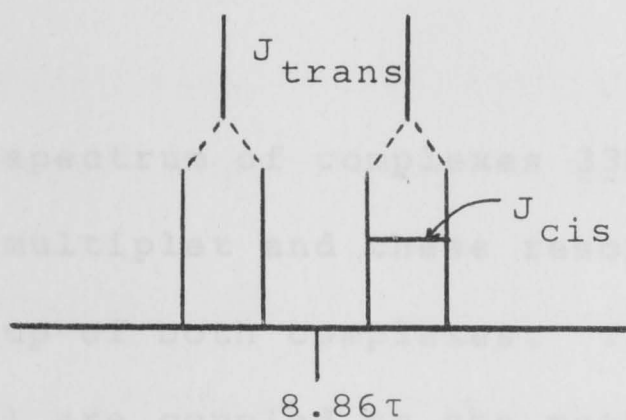
The n.m.r. spectrum of  $\underset{\sim}{34}$  in deuteriochloroform shows a triplet ( $J_{\text{P-H}}=5\text{Hz}$ ) at  $9.43\tau$  and a singlet at  $7.85\tau$ . The resonance at  $9.43\tau$  is assigned to the methyl protons, while the singlet is assigned to the acetyl resonance. The triplet pattern presumably arises from coupling with two equivalent mutually trans phosphorus nuclei. A similar triplet pattern is also observed at  $9.43\tau$  for the methyl protons of complex  $\underset{\sim}{33a}$ . However no resonance assignable to acetyl protons is observed. Similarly the infrared spectrum of complex  $\underset{\sim}{33a}$  in chloroform shows no band at  $1710\text{cm}^{-1}$ , suggesting that this product does not isomerize to an acyl (see section e for further discussion).

The relative areas of the methyl and acetyl peaks in the n.m.r. spectrum of complex  $\underset{\sim}{34}$  suggest that K (eqn 4-8) is approximately 2.0 at  $34^\circ$ .

Acetyl chloride also reacts with the complex  $\text{IrCl}(\text{MePh}_2\text{P})_3$  (3) but only one product ( $\underset{\sim}{36}$ ) of stereochemistry as shown can be isolated:



The infrared spectrum of complex **36** shows two bands due to  $\nu(\text{Ir-Cl})$  at  $310\text{cm}^{-1}$  (Cl trans to CO) and at  $280\text{cm}^{-1}$  (Cl trans to  $\text{MePh}_2\text{P}$ ) and one strong band (solid and solution) at  $2020\text{cm}^{-1}$  which is assigned to  $\nu(\text{C}\equiv\text{O})$ . The n.m.r. spectrum of **36** in deuteriochloroform confirms its stereochemistry as shown above; the methyl protons of the phosphine ligands give rise to two doublets ( $J_{\text{P-H}} = 10.5\text{Hz}$ ), one at  $7.85\tau$  and the other at  $8.24\tau$ . These data are characteristic of methyl diphenyl phosphine ligands in a mutually cis configuration for Ir(III) complexes. In the n.m.r. spectrum, four lines or two overlapping doublets at  $8.86\tau$  are observed for the methyl group attached to the iridium atom:

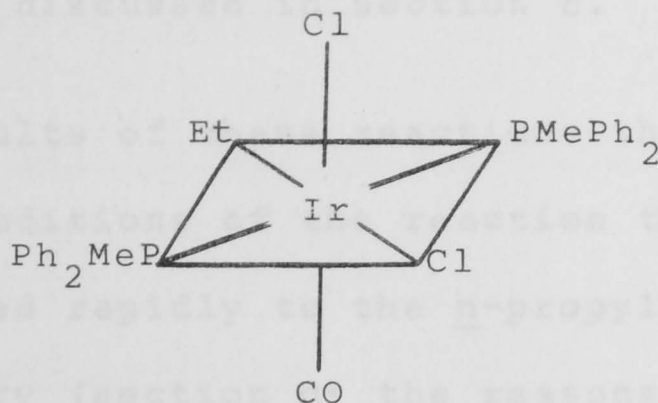


This pattern would be expected for complex **36** of stereochemistry shown above since the phosphine ligands are inequivalent, the coupling constant of the trans phosphine being greater than that of the cis ligand ( $J_{\text{trans}} = 7\text{Hz}$ ,  $J_{\text{cis}} = 4\text{Hz}$ ).

(ii) Propionyl chloride

Propionyl chloride reacts with the iridium(I) complex **1** to give complex **33b** (eqn 4-7), and with iridium(I) complex **3** to give a product of formula  $\text{IrCl}_2(\text{Et})(\text{CO})(\text{MePh}_2\text{P})_2$  (**37**) and stereochemistry similar to complex **33b**:





37

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Thus, the far-infrared spectrum of 37 shows bands at  $307\text{cm}^{-1}$  (Cl trans to CO) and at  $251\text{cm}^{-1}$  (Cl trans to Et). The phosphine ligands are shown to be mutually trans since a triplet ( $J_{\text{P-H}}=5\text{Hz}$ ) at  $7.59\tau$  is observed in the n.m.r. spectrum for the methyl protons attached to the phosphorus nuclei.

The n.m.r. spectrum of complexes 33b and 37 also shows a triplet and a multiplet and these resonances are assigned to the ethyl group of both complexes. The methyl protons (triplet pattern) are coupled to the methylene protons ( $J_{\text{H-H}}=8\text{Hz}$ ) and no apparent phosphorus coupling is observed to these protons. However the multiplet pattern (methylene protons) arises because there is likely to be phosphorus coupling from both  $^{31}\text{P}$  nuclei together with the hydrogen coupling from the methyl protons.

(iii) Butanoyl chloride and 2-methyl propanoyl chloride  
(isobutyryl chloride)

Complex 33c is obtained in 80% yield from the reaction of butanoyl chloride and complex 1, and in 55% yield from the reaction of 2-methyl propanoyl chloride and complex 1. The infrared and n.m.r. data for the products from the different reactions are identical. The n.m.r. signals are



assigned and discussed in section c.

The results of these reactions therefore suggest that under the conditions of the reaction the isopropyl complex has isomerized rapidly to the n-propyl isomer, complex 33c. In the summary (section d) the reasons and proposed mechanism for this isomerization are discussed.

(iv) Pentanoyl chloride and 2-methyl butanoyl chloride

The reaction of 2-methylbutanoyl chloride and complex 1 gives complex 33d (eqn 4-7) in 41% yield and the hydrido-iridium(III) complex  $\text{IrHCl}_2(\text{Ph}_3\text{P})_3^{36}$  (38; 42%), as shown by n.m.r. and infrared spectroscopy.

Complex 33d may also be prepared in 64% yield by the reaction of pentanoyl chloride and complex 1.

(v) Hexanoyl chloride and 2-ethyl butanoyl chloride

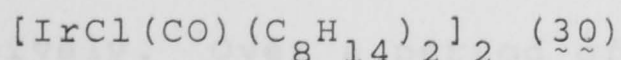
The reactions of these isomeric acyl chlorides and complex 1 give complex 33e (eqn 4-7) in both instances as shown by infrared and n.m.r. spectroscopy; 79% yield is obtained when hexanoyl chloride is reacted but only 30% yield is obtained with 2-ethyl butanoyl chloride.

(vi) 3-phenyl propionyl chloride and 2-phenyl propionyl chloride

The complex 33f is obtained in 80% yield from the reaction of 3-phenyl propionyl chloride and complex 1. However when 2-phenyl propionyl chloride reacts with complex 1 three products result, among them complex 33f (40% yield). The other two products isolated are complex 11 (32%) and complex 38 (24%); these complexes are identified

by their infrared spectra.

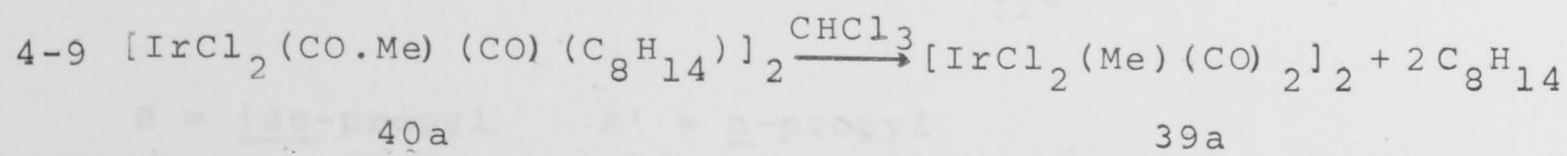
(2) Reactions of acyl chlorides with complex



(i) Acetyl chloride

Shaw and Singleton showed that the addition of acetyl chloride to a solution of complex 30 in boiling benzene gives the compound  $[\text{IrCl}_2(\text{Me})(\text{CO})_2]_2$  (39a) as handsome white prisms.<sup>38</sup> The infrared spectrum of complex 39a shows no band characteristic of an acetyl group but there are two very strong absorptions due to carbonyl stretching frequencies at 2137 and 2083 $\text{cm}^{-1}$ .

However when the experiment is repeated in cold benzene and the reaction quenched almost immediately (ca. 5 minutes) after the addition of acetyl chloride, an acyl-iridium complex of formula  $[\text{IrCl}_2(\text{CO}\cdot\text{Me})(\text{CO})(\text{C}_8\text{H}_{14})]_2$  (40a) results. The infrared spectrum of complex 40a in the solid state shows a band at 1720 $\text{cm}^{-1}$ , which is assigned to the acetyl stretching frequency  $[\nu(\text{C}=\text{O})]$ , and another strong band at 2080 $\text{cm}^{-1}$  assigned to the terminal carbonyl stretching frequency (table 4-3). The infrared spectrum in chloroform solution shows the appearance of a second band at 2130 $\text{cm}^{-1}$  and the slow disappearance of the band at 1720 $\text{cm}^{-1}$ ; this suggests that the acetyl complex is isomerizing to the alkyl complex in chloroform solution:



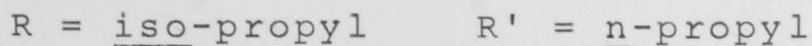
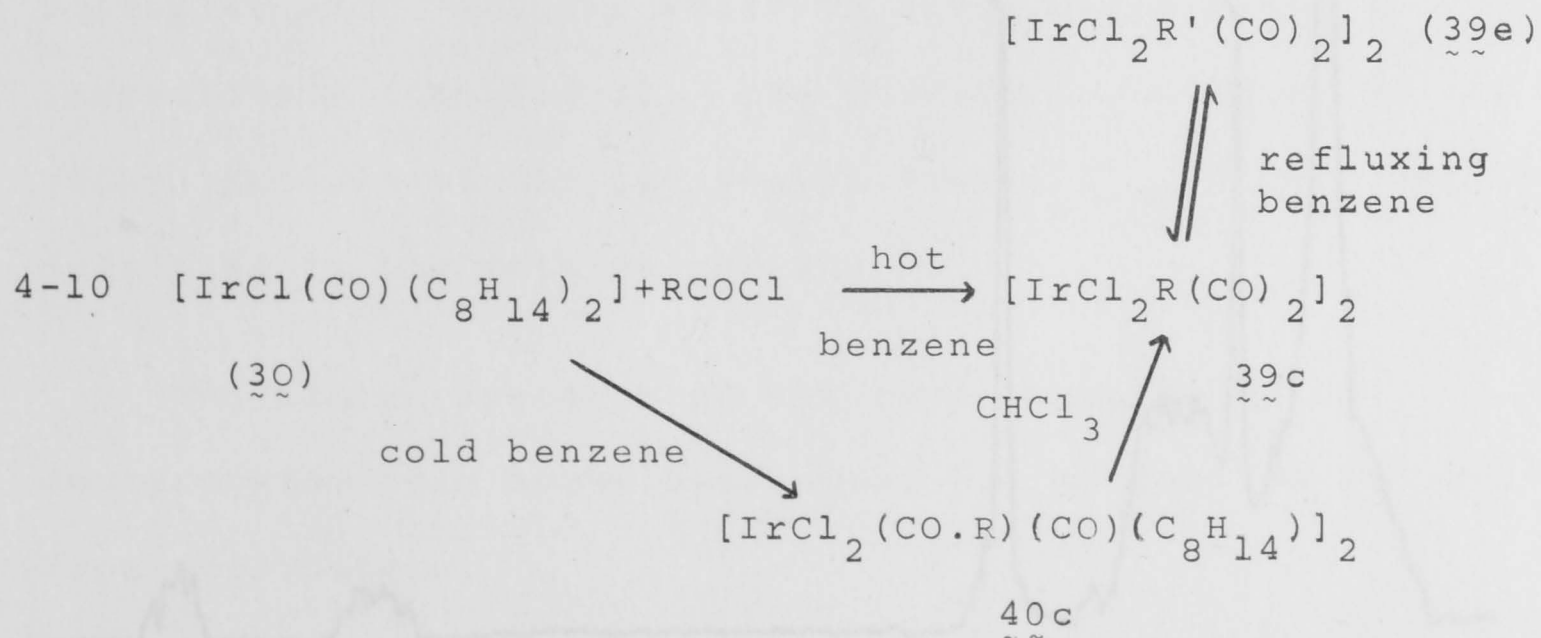
A similar phenomenon is observed when the n.m.r. spectrum of complex 40a is measured in deuteriochloroform. Besides

signals due to free and coordinated cyclooctene, two sharp singlets are observed at 7.37 $\tau$  and 8.18 $\tau$ . These resonances are assigned to the acetyl protons and to the methyl protons respectively. Over a period of 20 minutes the singlet at 8.18 $\tau$  increases in intensity at the expense of the one at 7.37 $\tau$  (see figure 4-1).

The olefinic protons of the free and coordinated cyclooctene resonate at 4.4 $\tau$  and at 5.15 $\tau$  respectively. In a similar fashion the resonance at 5.15 $\tau$  decreases in intensity while the one at 4.4 $\tau$  increases. The n.m.r. spectrum also shows the complex multiplets due to the methylene protons of free and coordinated cyclooctene at 7.8 $\tau$  and 8.5 $\tau$ .

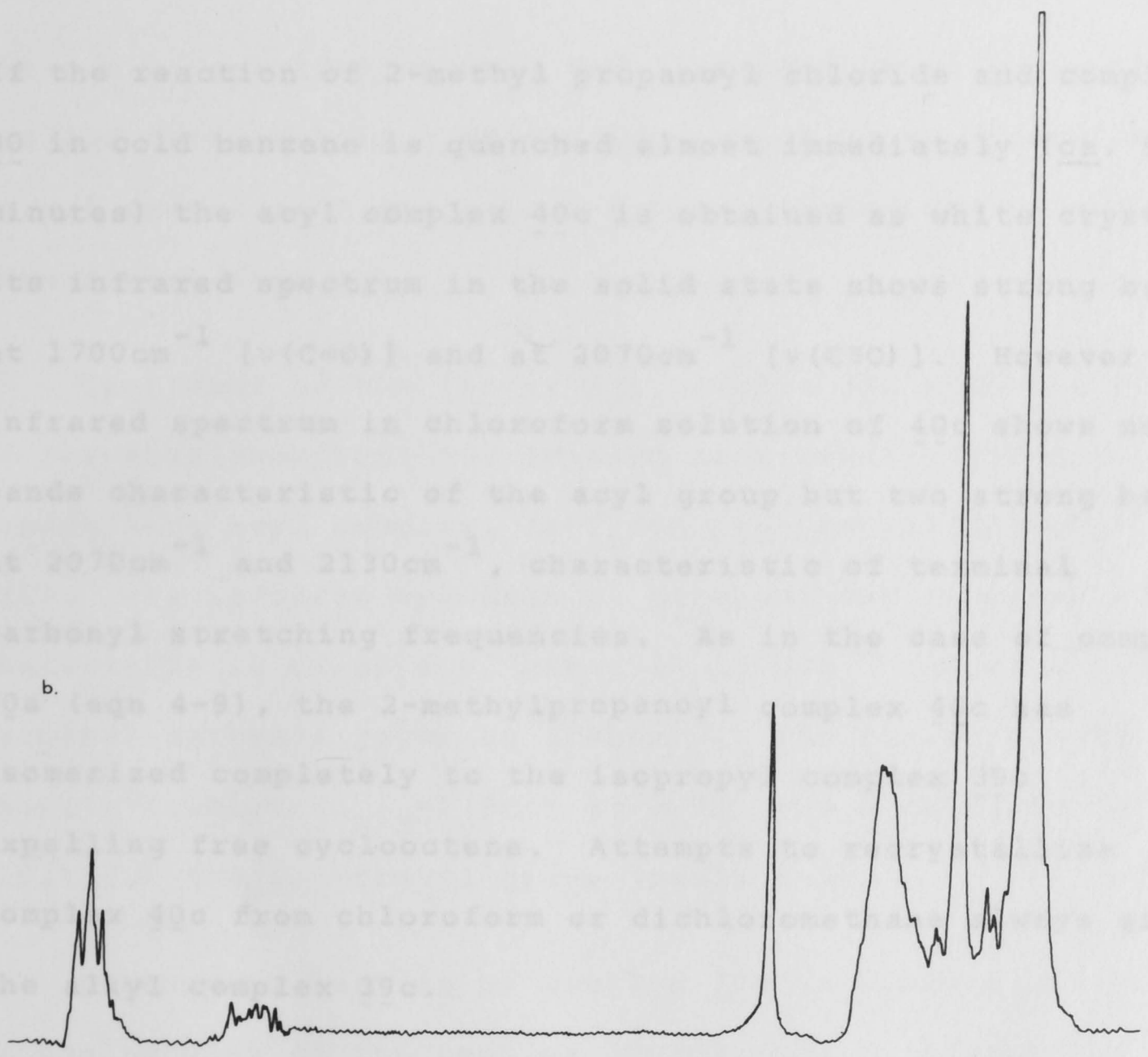
(ii) 2-methyl propanoyl chloride (isobutyryl chloride)

2-methyl propanoyl chloride reacts with complex 30 to give different products depending on the conditions of the reaction:





If the reaction of 2-methyl propanoyl chloride and complex 30 in cold benzene is quenched almost immediately (ca. 5 minutes) the acyl complex 40c is obtained as white crystals. Its infrared spectrum in the solid state shows two bands at  $1700\text{cm}^{-1}$  ( $\nu(\text{C=O})$ ) and at  $2070\text{cm}^{-1}$  ( $\nu(\text{C}\equiv\text{O})$ ). However the infrared spectrum in chloroform solution of 40c shows no bands characteristic of the acyl group but two strong bands at  $2070\text{cm}^{-1}$  and  $2130\text{cm}^{-1}$ , characteristic of terminal carbonyl stretching frequencies. As in the case of complex 40a (eqs 4-9), the 2-methylpropanoyl complex 40c is isomerized completely to the isopropyl complex 40b by expelling free cyclooctene. Attempts to recrystallize complex 40c from chloroform or dichloromethane give the acyl complex 39c.



Complex 39c can also be prepared from the reaction of 2-methyl propanoyl chloride and complex 30 in hot benzene. The n.m.r. spectrum of complex 39c in deuteriochloroform is very simple, consisting of a doublet at 7.22 $\tau$  and a multiplet at 6.72 $\tau$ , the relative areas being 1 and 1 respectively (table 4-5). The doublet is assigned to the methyl protons of the iso-propyl group, and the multiplet to the methine proton.

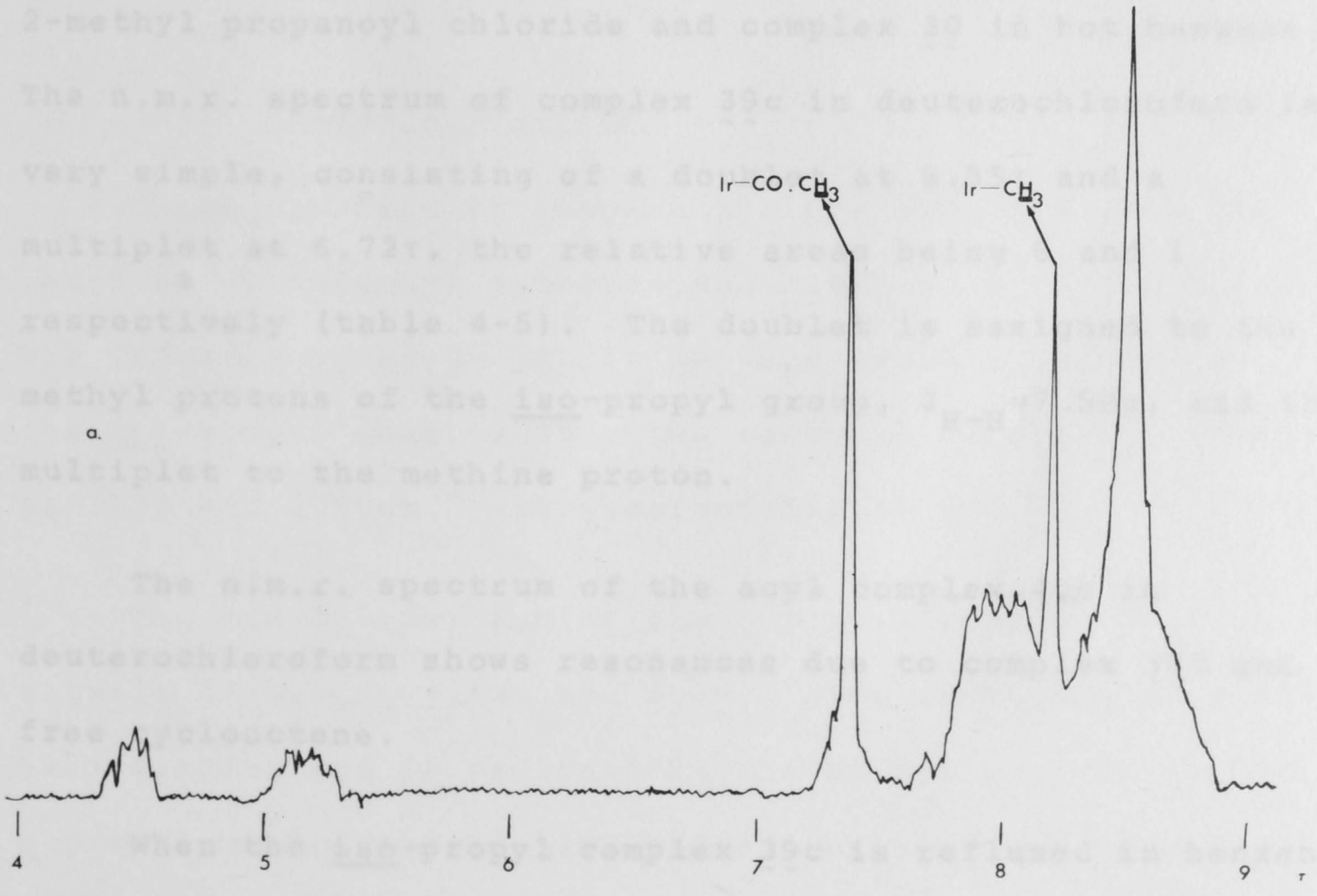


Figure 4-1. a. The n.m.r. spectrum of the complex  $[\text{IrCl}_2[\text{CO.Me}][\text{CO}][\text{C}_8\text{H}_{14}]]_2$  measured in  $\text{CDCl}_3$ .  
 b. The spectrum after 20 minutes.



If the reaction of 2-methyl propanoyl chloride and complex 30 in cold benzene is quenched almost immediately (ca. 5 minutes) the acyl complex 40c is obtained as white crystals. Its infrared spectrum in the solid state shows strong bands at  $1700\text{cm}^{-1}$  [ $\nu(\text{C}=\text{O})$ ] and at  $2070\text{cm}^{-1}$  [ $\nu(\text{C}\equiv\text{O})$ ]. However the infrared spectrum in chloroform solution of 40c shows no bands characteristic of the acyl group but two strong bands at  $2070\text{cm}^{-1}$  and  $2130\text{cm}^{-1}$ , characteristic of terminal carbonyl stretching frequencies. As in the case of complex 40a (eqn 4-9), the 2-methylpropanoyl complex 40c has isomerized completely to the isopropyl complex 39c expelling free cyclooctene. Attempts to recrystallize complex 40c from chloroform or dichloromethane always give the alkyl complex 39c.

Complex 39c can also be prepared from the reaction of 2-methyl propanoyl chloride and complex 30 in hot benzene. The n.m.r. spectrum of complex 39c in deuteriochloroform is very simple, consisting of a doublet at  $8.55\tau$  and a multiplet at  $6.72\tau$ , the relative areas being 6 and 1 respectively (table 4-5). The doublet is assigned to the methyl protons of the iso-propyl group,  $J_{\text{H-H}}=7.5\text{Hz}$ , and the multiplet to the methine proton.

The n.m.r. spectrum of the acyl complex 40c in deuteriochloroform shows resonances due to complex 39c and free cyclooctene.

When the iso-propyl complex 39c is refluxed in benzene for 90 minutes an equilibrium mixture of the iso-propyl (50%) and the n-propyl (50%) complexes (39c and 39e) is obtained.

The n.m.r. spectrum of this equilibrium mixture shows the signals characteristic of the iso-propyl group (described above) and also of the n-propyl group (described below) (see figure 4-2).

Treatment of the iso-propyl complex 39c with two moles of triphenylphosphine per iridium atom readily gives the mononuclear acyl complex,  $\text{IrCl}_2(\text{CO}\cdot\text{iso-propyl})(\text{CO})(\text{Ph}_3\text{P})_2$  (41). The infrared spectrum of 41 shows the expected bands characteristic of an acyl group at  $1670\text{cm}^{-1}$  and of a terminal carbonyl group at  $2045\text{cm}^{-1}$ . The n.m.r. spectrum shows a doublet ( $J_{\text{H-H}}=7.5\text{Hz}$ ) at  $9.90\tau$  and a multiplet at  $7.01\tau$  for the iso-propyl group (table 4-4).

Continuous heating of complex 39c in benzene gives bronze needles of the complex  $[\text{IrHCl}_2(\text{CO})_2]_2$  identified by its infrared spectrum.<sup>13</sup>

(iii) Butanoyl chloride

White crystals of complex 39e are obtained from the reaction of butanoyl chloride and complex 30 in hot benzene. The infrared spectrum of 39e is very similar to that of the iso-propyl complex 39c; two carbonyl stretching frequencies at  $2135$  and  $2085\text{cm}^{-1}$  are observed (table 4-3).

The n.m.r. spectrum of the n-propyl complex 39e shows signals at  $9.01\tau$ ,  $8.32\tau$  and  $7.34\tau$ . The resonance at  $9.01\tau$  is a triplet and is assigned to the methyl protons of the n-propyl group; the triplet pattern arises from coupling ( $J_{\text{H-H}}=8\text{Hz}$ ) with the protons on the  $\beta$ -carbon atom. The  $\beta$ -methylene protons resonate at  $8.32\tau$  as a sextet; they are coupled to the  $\alpha$ -methylene protons and the methyl protons

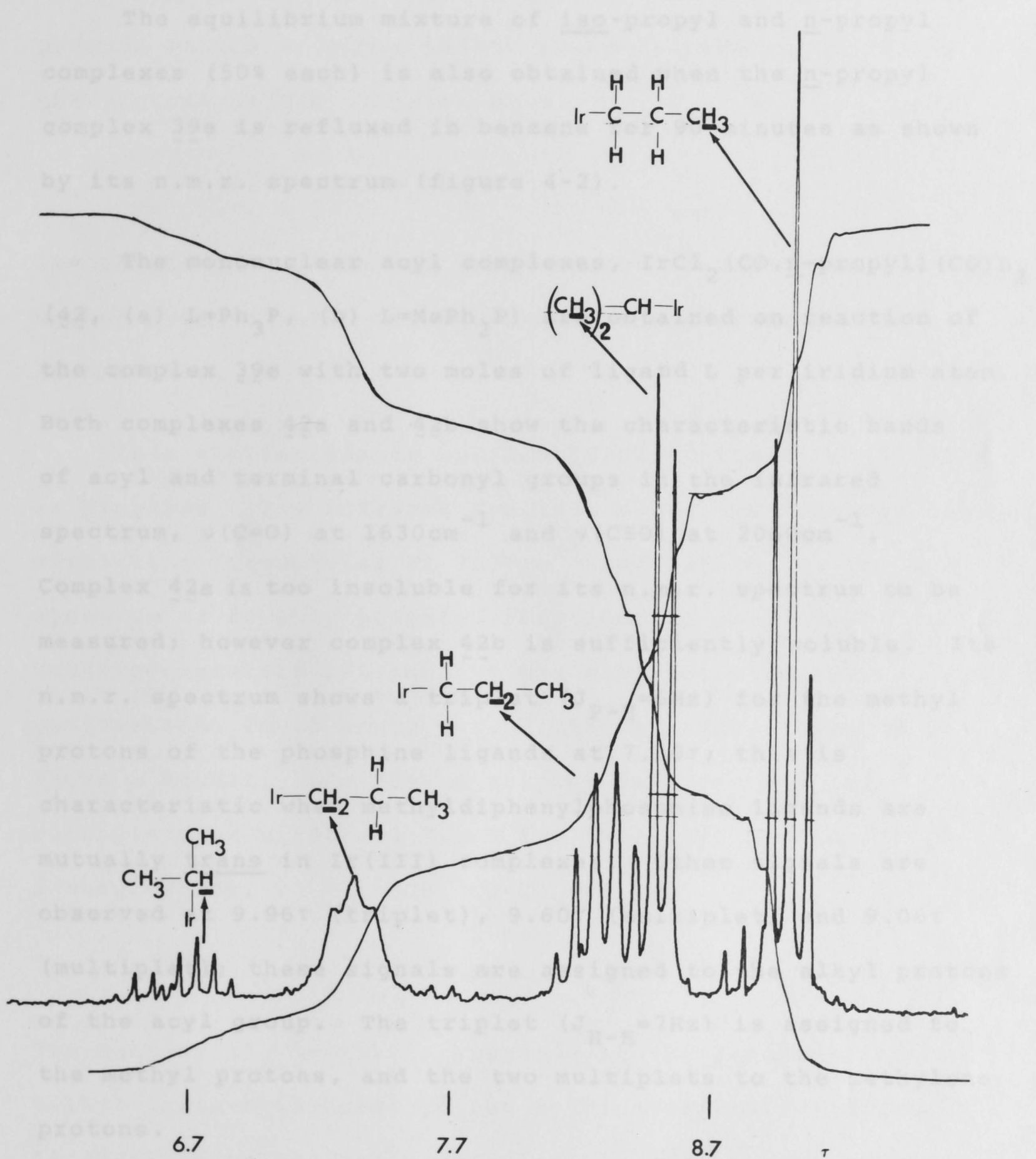
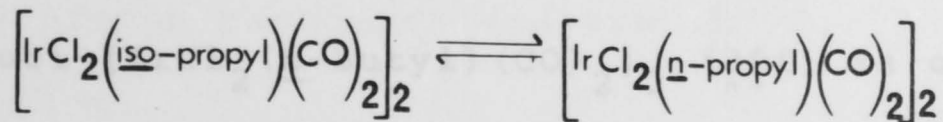


Figure 4-2. The n.m.r. spectrum of the equilibrium mixture





( $J_{\text{H-H}}=8\text{Hz}$ ). The methylene protons on the  $\alpha$ -carbon atom appear as a multiplet at  $7.34\tau$ .

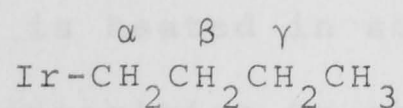
The equilibrium mixture of iso-propyl and n-propyl complexes (50% each) is also obtained when the n-propyl complex  $39e$  is refluxed in benzene for 90 minutes as shown by its n.m.r. spectrum (figure 4-2).

The mononuclear acyl complexes,  $\text{IrCl}_2(\text{CO}\cdot\text{n-propyl})(\text{CO})\text{L}_2$  ( $42$ , (a)  $\text{L}=\text{Ph}_3\text{P}$ , (b)  $\text{L}=\text{MePh}_2\text{P}$ ) are obtained on reaction of the complex  $39e$  with two moles of ligand  $\text{L}$  per iridium atom. Both complexes  $42a$  and  $42b$  show the characteristic bands of acyl and terminal carbonyl groups in the infrared spectrum,  $\nu(\text{C}=\text{O})$  at  $1630\text{cm}^{-1}$  and  $\nu(\text{C}\equiv\text{O})$  at  $2060\text{cm}^{-1}$ . Complex  $42a$  is too insoluble for its n.m.r. spectrum to be measured; however complex  $42b$  is sufficiently soluble. Its n.m.r. spectrum shows a triplet ( $J_{\text{P-H}}=6\text{Hz}$ ) for the methyl protons of the phosphine ligands at  $7.50\tau$ ; this is characteristic when methyldiphenylphosphine ligands are mutually trans in Ir(III) complexes. Other signals are observed at  $9.96\tau$  (triplet),  $9.60\tau$  (multiplet) and  $9.06\tau$  (multiplet); these signals are assigned to the alkyl protons of the acyl group. The triplet ( $J_{\text{H-H}}=7\text{Hz}$ ) is assigned to the methyl protons, and the two multiplets to the methylene protons.

(iv) Pentanoyl chloride and 2-methyl butanoyl chloride

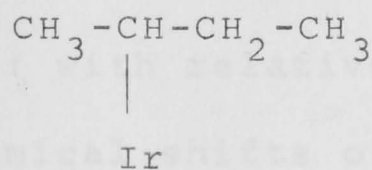
The product  $[\text{IrCl}_2(\text{n-butyl})(\text{CO})_2]_2$  ( $39f$ ) is obtained from the reaction of pentanoyl chloride and complex  $30$  in hot benzene. The infrared spectrum gives the expected terminal carbonyl stretches at  $2140$  and  $2085\text{cm}^{-1}$ . The n.m.r.

spectrum in deuteriochloroform shows signals at 9.09 $\tau$ , 8.54 $\tau$  and 7.31 $\tau$  with relative areas of 3, 4 and 2 respectively. The multiplet at 8.54 $\tau$  is assigned to the resonances of the protons on the  $\beta$ - and  $\gamma$ -carbon atoms and that at 7.31 $\tau$  to the protons on the  $\alpha$ -carbon atom:



The triplet ( $J_{\text{H-H}}=8\text{Hz}$ ) at 9.09 $\tau$  is the resonance due to the methyl protons which are coupled to the protons on the  $\gamma$ -carbon atom.

In a similar manner complex  $[\text{IrCl}_2(2\text{-butyl})\text{CO}]_2$  (39g) is prepared. The infrared spectrum shows two terminal carbonyl stretching frequencies at 2135 $\text{cm}^{-1}$  and 2085 $\text{cm}^{-1}$ . The n.m.r. spectrum of freshly prepared solutions of complex 39g in deuteriochloroform obtained at the earliest time when measurements could begin (ca. 5 minutes after preparation) shows a doublet at 8.55 $\tau$ , a triplet at 9.04 $\tau$  and two multiplets at 6.80 $\tau$  and 7.90 $\tau$  for the alkyl protons of the 2-butyl group:



The doublet ( $J_{\text{H-H}}=8\text{Hz}$ ) is assigned to the resonance of the methyl protons adjacent to the methine proton. The triplet is assigned to the other methyl protons which are coupled to the methylene protons. The multiplet at 6.80 $\tau$  is due to the methine proton resonance and that at 7.90 $\tau$  to the methylene protons.

However if the spectrum is measured at various times over a period of three hours, signals belonging to the

n-butyl complex 39f appear and continue to grow in intensity while those of complex 39g decrease until they disappear almost completely. The equilibrium apparently favours the formation of the straight-chain alkyl in this system (39f and 39g). This is also confirmed by the fact that when complex 39f is heated in solution no 2-butyl complex results; instead decomposition to the complex  $[\text{IrHCl}_2(\text{CO})_2]_2$  is observed. Similarly this iridium-hydrido complex is formed when complex 39g is gently heated in benzene.

(v) 3-phenyl propionyl chloride and 2-phenyl propionyl chloride

These two isomeric acyl chlorides on reaction with complex 30 give the complexes  $[\text{IrCl}_2\text{R}(\text{CO})_2]_2$  (39h R= $\alpha$ -phenethyl, 39i R= $\beta$ -phenethyl) as beautiful off-white crystals. Their infrared spectrum shows the two carbonyl stretching frequencies at 2135 and 2085  $\text{cm}^{-1}$ . The n.m.r. spectrum of complex 39h is very simple; signals at 5.50 $\tau$  (quartet;  $\text{CH}_3$ ), 8.30 $\tau$  (doublet; CH) and 2.6 $\tau$  (multiplet; Ph) are observed. While the n.m.r. spectrum of complex 39i gives two multiplets at 2.8 $\tau$  and 7.15 $\tau$  with relative areas being 5 and 4 respectively. The chemical shifts of the two sets of methylene protons are apparently coincident and they resonate as a multiplet at 7.15 $\tau$ .

All attempts to produce an equilibrium mixture by heating either complex in solution result in decomposition.

(vi) Hexanoyl chloride

The interaction of hexanoyl chloride and complex 30 gives white crystals of  $[\text{IrCl}_2(\text{n-pentyl})(\text{CO})_2]_2$  (39j). Its infrared spectrum is similar to those of the other alkyl



complexes; it shows two strong terminal carbonyl stretching frequencies at  $2130\text{cm}^{-1}$  and  $2085\text{cm}^{-1}$ . The n.m.r. spectrum of 39j shows three multiplets at  $8.46\tau$ ,  $8.31\tau$  and  $7.32\tau$  and a triplet at  $9.01\tau$  which is assigned to the methyl protons (table 4-5).

c. Assignments of n.m.r. signals of complexes 33c-33h

(eqn 4-7)

Table 4-2 lists the n.m.r. data for the alkyl-iridium complexes 33 and figure 4-3 shows a schematic representation of the chemical shifts of the alkyl protons of these complexes. From models of the complexes it is apparent that carbon atoms  $C_3$  and  $C_4$  of the alkyl groups are above and below the plane of the phenyl rings of the triphenylphosphine ligands (see figure 4-5). Thus, the protons attached to these carbon atoms will be abnormally shielded because of the ring current effect generated by the phenyl rings.<sup>79</sup> This shielding effect causes a shift to higher  $\tau$ -value.

The n.m.r. spectrum of the n-propyl complex 33c shows a triplet at  $9.88\tau$  (area 3) and a multiplet at  $8.90\tau$  (area 4). The triplet ( $J_{\text{H-H}}=7.5\text{Hz}$ ) is assigned to the methyl protons of the n-propyl group and the multiplet to the methylene protons. The methyl protons are attached to carbon atom  $C_3$  and presumably this is the reason for its high chemical shift value.

The n.m.r. spectrum of the n-butyl complex 33d in deuterobenzene shows three multiplets at  $9.50\tau$  (5),  $8.70\tau$  (2) and  $8.40\tau$  (2). The resonance at  $9.50\tau$  is probably due to the methyl protons (on  $C_4$ ) and the methylene protons on

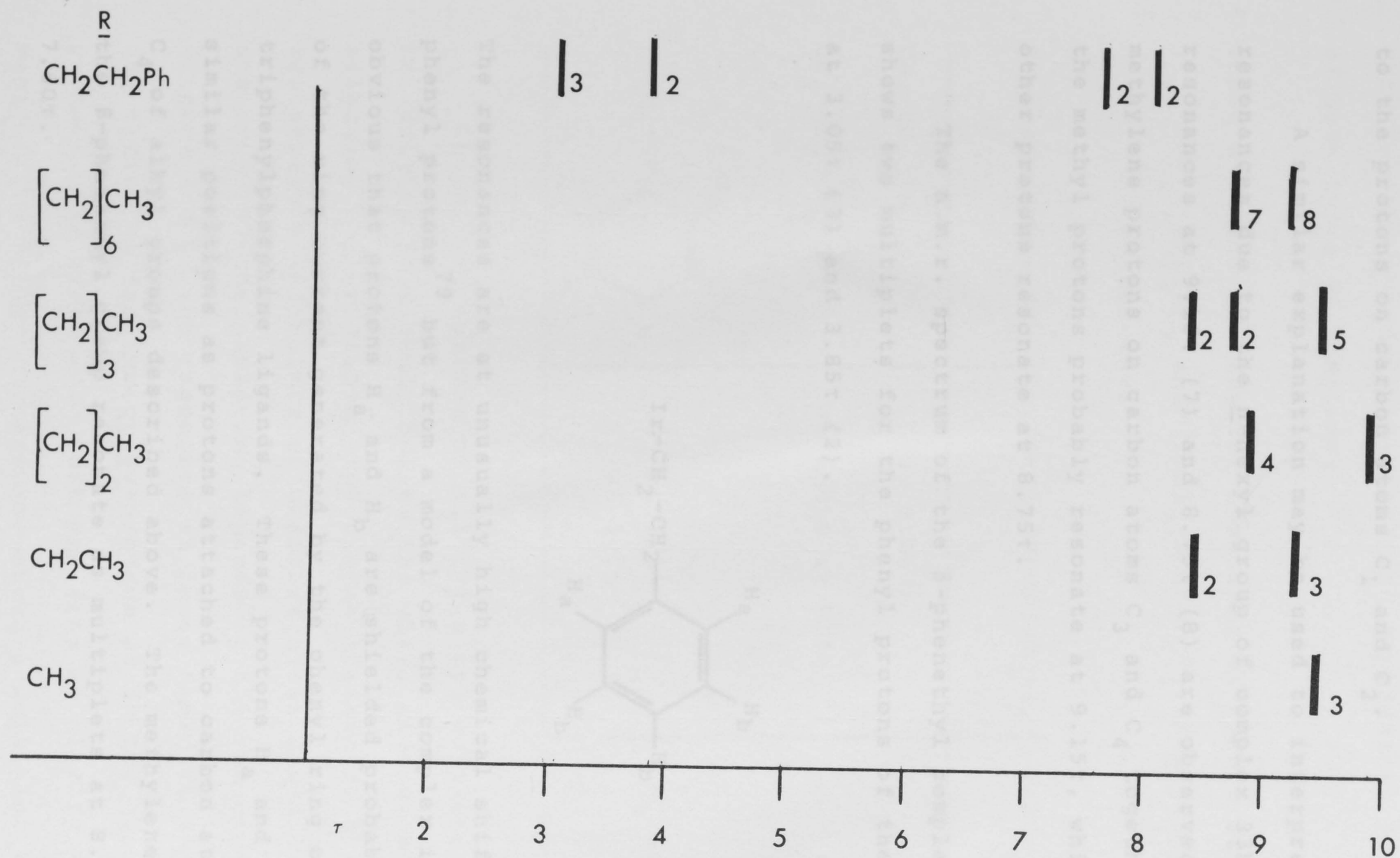
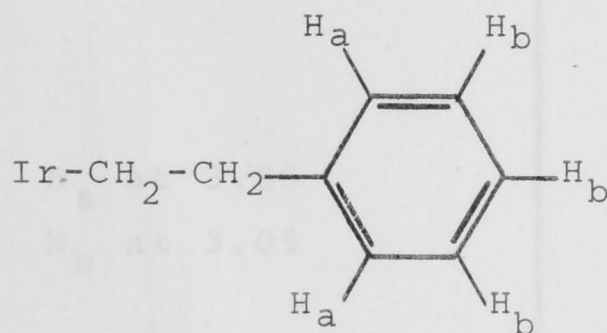


Figure 4-3. Schematic representation of alkyl [R] resonances of complexes  $\text{IrCl}_2[\text{R}](\text{CO})(\text{Ph}_3\text{P})_2$  with relative intensities adjacent to the resonances.

carbon atom  $C_3$ ; both sets of protons are probably in the ring current path. The other two multiplets are assigned to the protons on carbon atoms  $C_1$  and  $C_2$ .

A similar explanation may be used to interpret the resonances due to the *n*-hexyl group of complex 33h; two resonances at  $9.15\tau$  (7) and  $8.75\tau$  (8) are observed. The methylene protons on carbon atoms  $C_3$  and  $C_4$  together with the methyl protons probably resonate at  $9.15\tau$ , while the other protons resonate at  $8.75\tau$ .

The n.m.r. spectrum of the  $\beta$ -phenethyl complex 33f shows two multiplets for the phenyl protons of the alkyl group at  $3.05\tau$  (3) and  $3.85\tau$  (2).



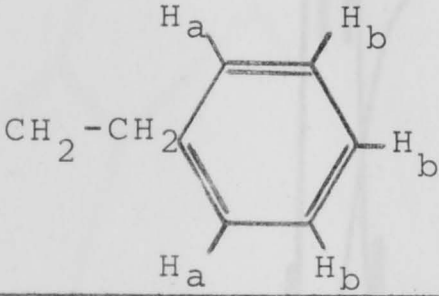
The resonances are at unusually high chemical shifts for phenyl protons<sup>79</sup> but from a model of the complex it is obvious that protons  $H_a$  and  $H_b$  are shielded probably because of the ring current generated by the phenyl ring of the triphenylphosphine ligands. These protons  $H_a$  and  $H_b$  are in similar positions as protons attached to carbon atoms  $C_3$  and  $C_4$  of alkyl groups described above. The methylene protons of the  $\beta$ -phenethyl group resonate as multiplets at  $8.10\tau$  and  $7.60\tau$ .

The n.m.r. data for the complexes of type  $[\text{IrCl}_2\text{R}(\text{CO})_2]_2$  (R=alkyl) lend support to the idea that ring currents are



responsible for the observed abnormally high chemical shifts for the R groups of complex 33. Table 4-7 shows the n.m.r. data for the n-propyl, n-butyl and  $\beta$ -phenethyl complexes of both types of complexes.

Table 4-7 N.m.r. data for complexes of type  $\text{IrCl}_2(\text{R})(\text{CO})(\text{Ph}_3\text{P})_2$  and  $[\text{IrCl}_2(\text{R})(\text{CO})_2]_2$ ; R=n-propyl, n-butyl,  $\beta$ -phenethyl

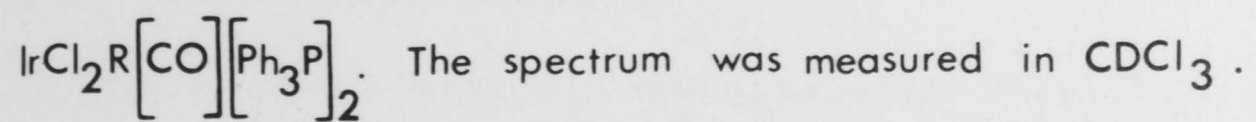
Complexes when R=	For $\text{IrCl}_2(\text{R})(\text{CO})(\text{Ph}_3\text{P})_2$ $\tau$	$[\text{IrCl}_2(\text{R})(\text{CO})_2]_2$ $\tau$
$\text{CH}_2-\text{CH}_2-\overset{\text{A}}{\text{CH}_3}$	A at 9.88	A at 9.01
$\text{CH}_2-\overset{\text{B}}{\text{CH}_2}-\overset{\text{A}}{\text{CH}_2}-\text{CH}_3$	A and B at 9.50	A at 9.09 B at 8.54
	$\text{H}_a$ at 3.85 $\text{H}_b$ at 3.05	$\text{H}_a$ and $\text{H}_b$ at 2.8

The n.m.r. spectra of all the alkyl complexes 33 show in addition to signals due to the alkyl groups, signals belonging to the triphenylphosphine ligands of these complexes. Two separate multiplets of relative areas 2 and 3 are observed for the phosphine ligands of all the complexes (figure 4-4). The resonance at lower field ( $2.05\tau$ ) could be due either to the two ortho-protons or to the two meta-protons. No additional work was done to clarify the assignment. Free triphenylphosphine shows a multiplet at  $2.6-2.7\tau$  in its n.m.r. spectrum measured in deuteriochloroform; this chemical shift is similar to that of the multiplet of area 3



Figure 4-5. Model showing relative positions of R and Ph groups.

Figure 4-4. The triphenylphosphine resonances of complexes



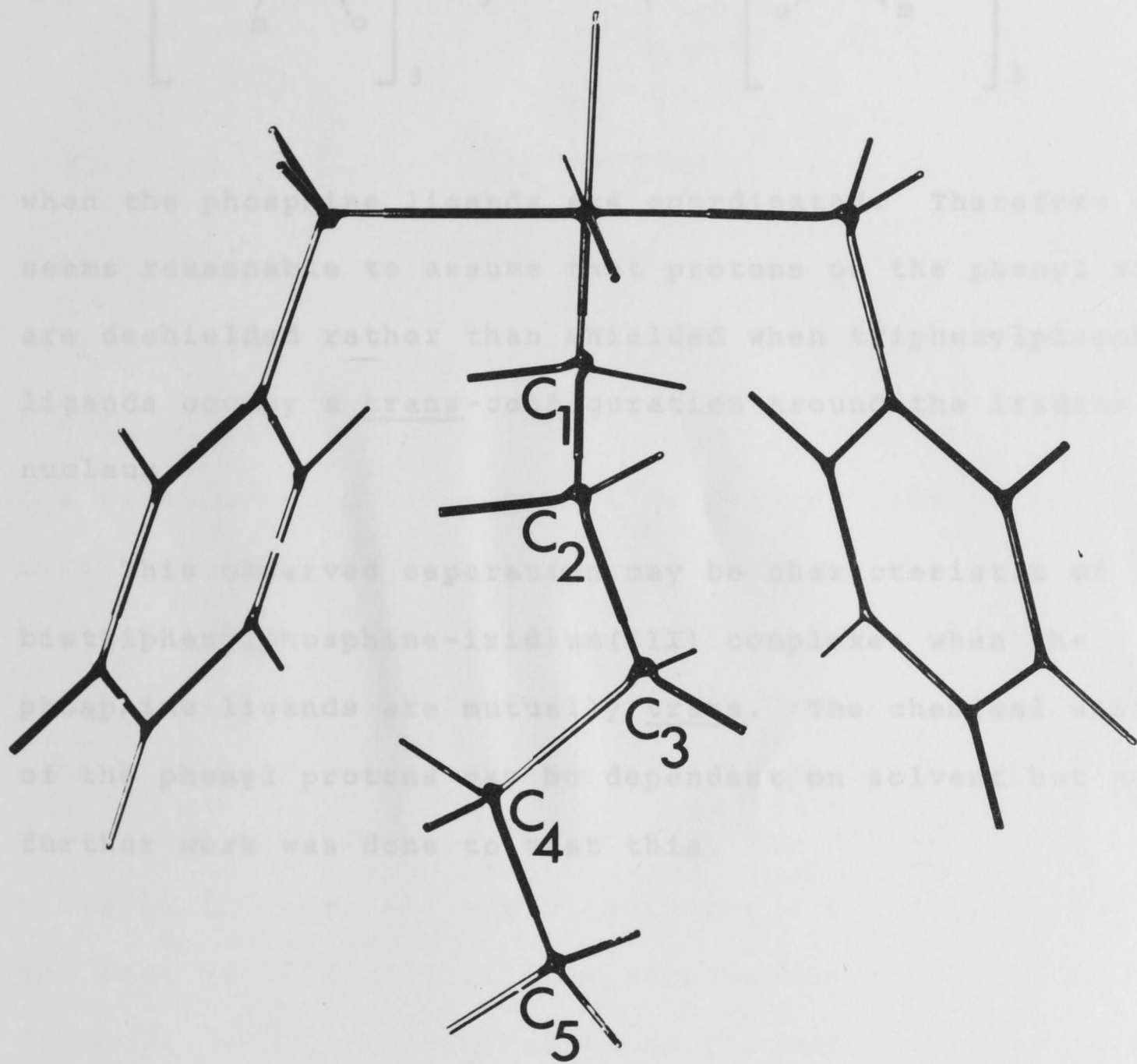
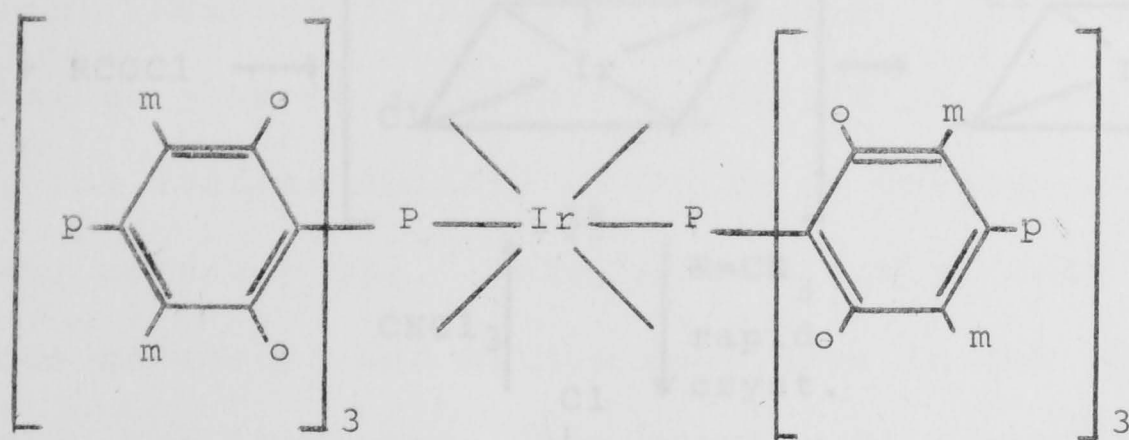


Figure 4-5. Model showing relative positions of R and Ph groups.



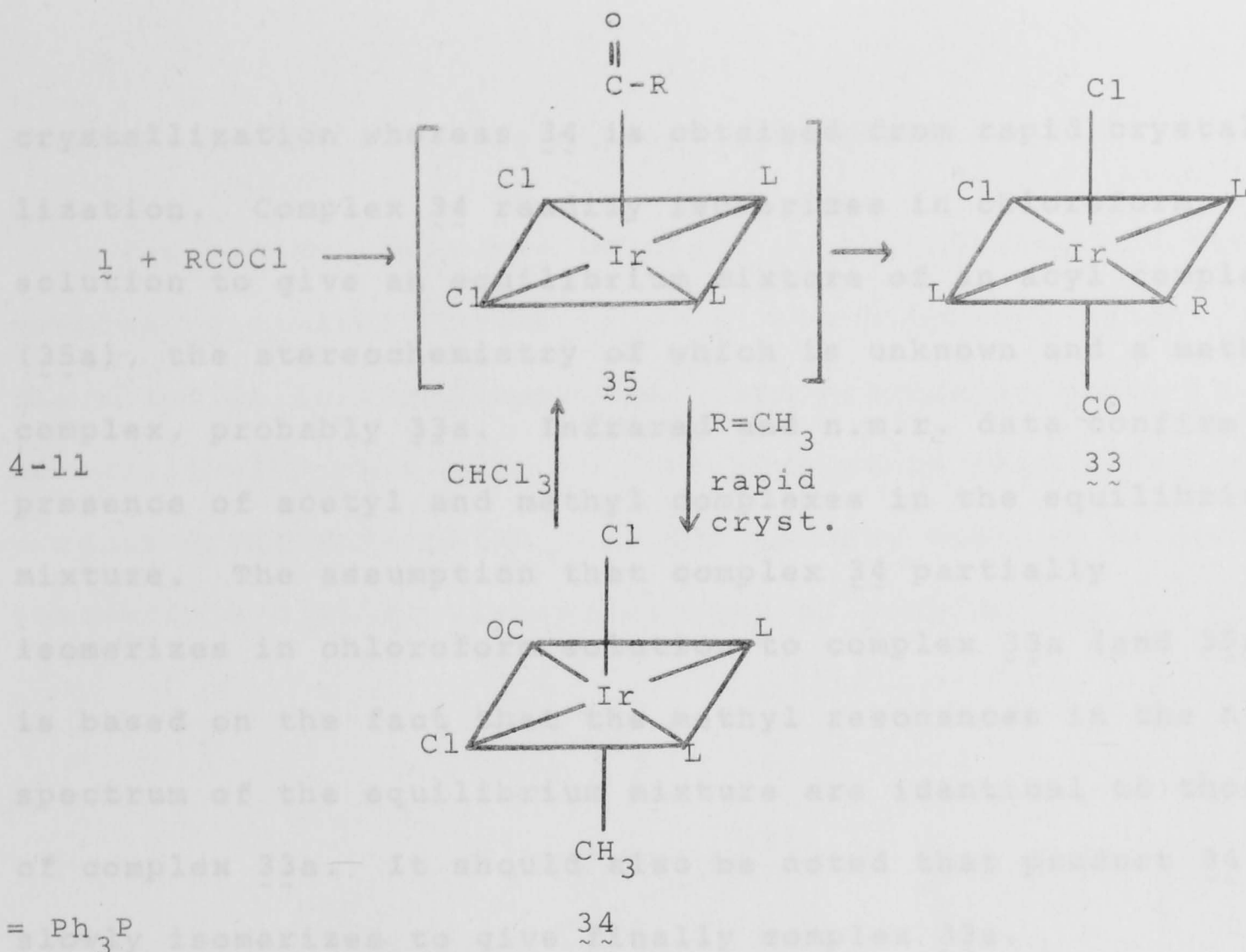


when the phosphine ligands are coordinated. Therefore it seems reasonable to assume that protons on the phenyl rings are deshielded rather than shielded when triphenylphosphine ligands occupy a trans-configuration around the iridium nucleus.

This observed separation may be characteristic of bistrisphenylphosphine-iridium(III) complexes when the phosphine ligands are mutually trans. The chemical shifts of the phenyl protons may be dependent on solvent but no further work was done to test this.

#### d. Summary of results and discussion

Acyl chlorides react with chlorotris(triphenylphosphine)-iridium(I) (1) to form stable alkylcarbonyl-iridium(III) complexes (33) (see equation 4-11).



The first step of the addition is probably the nucleophilic attack of **1** on the acyl chloride, cleaving the C-Cl bond and expelling one mole of triphenylphosphine to give a five-coordinate intermediate **35**. This is followed by spontaneous migration of R and rearrangement to form complex **33**. Intermediate **35** has not been isolated in any of the reactions but there is infrared and n.m.r. evidence for its existence in the case of  $\text{R}=\text{CH}_3$  (**35a**). The spontaneous migration of R, **35** to **33**, should be contrasted to the more difficult migration of R with loss of carbon monoxide in the decarbonylation of complexes  $\text{IrCl}_2(\text{CO}\cdot\text{R})(\text{CO})\text{L}_2$  ( $\text{L}=\text{tertiary phosphine}$ ). This difference may be due to the fact that intermediate **35** is coordinatively unsaturated  $[\text{Ir}(\text{III})]$  whereas the complexes  $\text{IrCl}_2(\text{CO}\cdot\text{R})(\text{CO})\text{L}_2$  are all coordinatively saturated  $d^6$  octahedral complexes.

The oxidative addition of acetyl chloride to complex **1** yields two products **33a** and **34**; **33a** is the product of slow

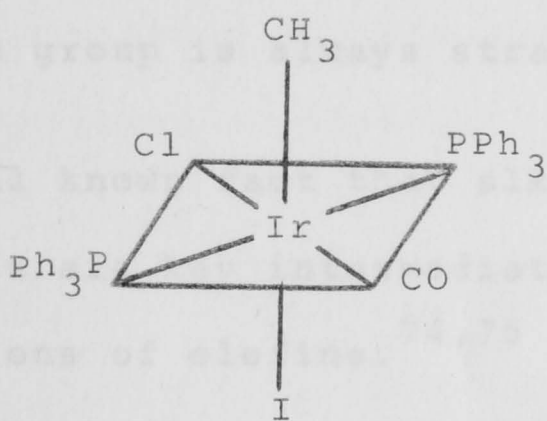
crystallization whereas  $\underline{34}$  is obtained from rapid crystallization. Complex  $\underline{34}$  readily isomerizes in chloroform solution to give an equilibrium mixture of an acyl complex ( $\underline{35a}$ ), the stereochemistry of which is unknown and a methyl complex, probably  $\underline{33a}$ . Infrared and n.m.r. data confirm the presence of acetyl and methyl complexes in the equilibrium mixture. The assumption that complex  $\underline{34}$  partially isomerizes in chloroform solution to complex  $\underline{33a}$  (and  $\underline{35a}$ ) is based on the fact that the methyl resonances in the n.m.r. spectrum of the equilibrium mixture are identical to those of complex  $\underline{33a}$ . It should also be noted that product  $\underline{34}$  slowly isomerizes to give finally complex  $\underline{33a}$ .

A similar alkyl-acyl isomerization was also observed by Wilkinson et al for the addition of acetyl chloride to complex  $\text{RhCl}(\text{Ph}_3\text{P})_3$ <sup>66</sup> ( $\underline{23}$ ) and for the reaction of trans- $\text{RhX}(\text{CO})\text{L}_2$  [ $\text{X}=\text{Cl}, \text{I}, \text{L}=\text{Ph}_3\text{P}, \text{Ph}_3\text{As}, \text{Et}_3\text{P}$ ] with iodomethane.<sup>71</sup> The latter reaction yields ultimately the acyl-rhodium(III) products  $\text{RhXI}(\text{CO.Me})\text{L}_2$ , but it was shown that these products are obtained only by isomerization of an intermediate in which the alkyl group is directly bonded to the metal. In contrast the reaction of acetyl chloride and complex  $\underline{23}$  gives the acyl-rhodium(III) complex as the first product which in turn isomerizes in solution to the alkyl-rhodium(III) complex, yielding finally an equilibrium mixture of both rhodium(III) complexes. It was pointed out<sup>71</sup> that the position of the equilibrium depends on the strength of the metal-carbon bond in both species and hence on the migrational ability of the alkyl group. Studies on the manganese systems, e.g.  $\text{Mn}(\text{CO.Me})(\text{CO})_5$  suggest that the alkyl group migration is the most likely mechanism for the



carbonyl insertion or decarbonylation reactions.<sup>72,73</sup>

The product from the reaction of iodomethane and the complex trans-IrCl(CO)(Ph<sub>3</sub>P)<sub>2</sub> (11) shows no acyl bands in the solution infrared spectrum<sup>70</sup> and presumably there is no equilibrium involving an acyl complex in this case. The product IrClI(Me)(CO)(Ph<sub>3</sub>P)<sub>2</sub> (43) is very similar to and possesses a similar stereochemistry as complex 33a.



43

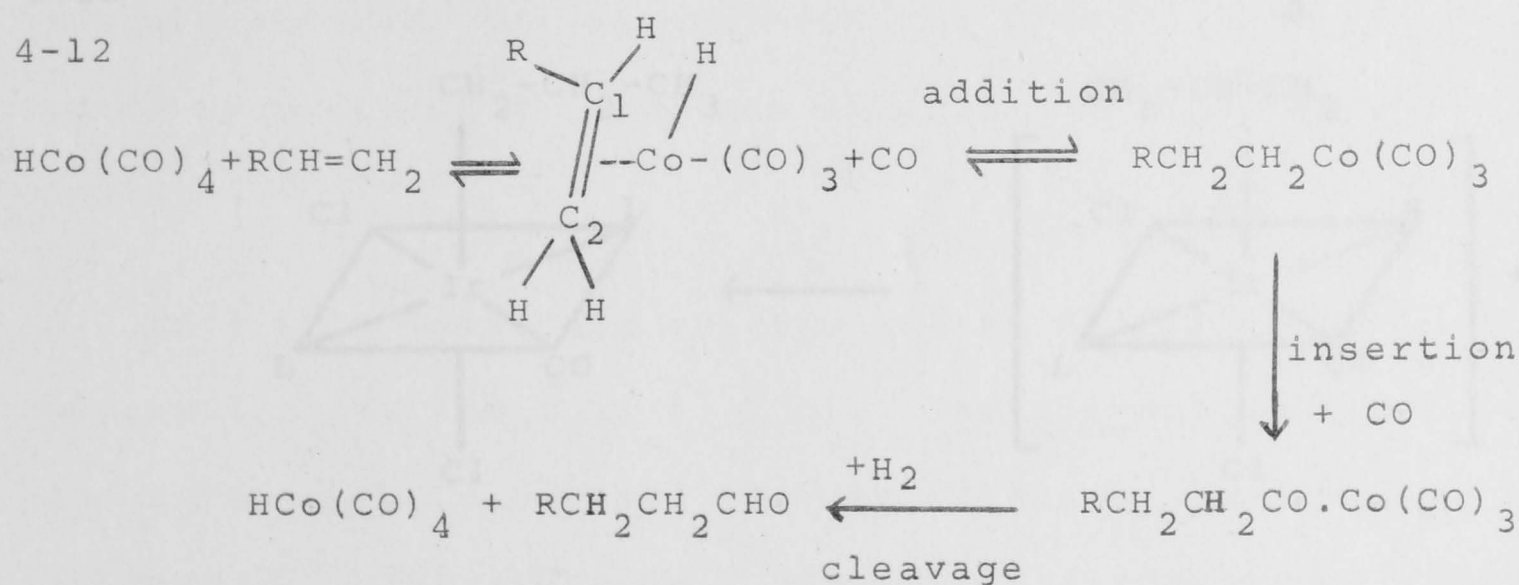
In view of this fact and the fact that acetyl chloride reacts with complex IrCl(MePh<sub>2</sub>P)<sub>3</sub> (3) to give a stable product (36) with the phosphine ligands mutually cis (see below), it would be reasonable to suggest that steric hindrance caused by the bulky triphenylphosphine ligands in a cis-configuration is the main reason why complex 34 readily isomerizes to 35 and 33a, and finally to complex 33a, the more stable isomer.

Acetyl chloride reacts with complex 3 to give complex 36 of stereochemistry as shown on page 49. Collman et al.<sup>32</sup> have prepared an isomer of 36 with a trans-configuration of phosphines and mutually cis chlorine atoms. Both isomers are extremely stable in solution and they show no evidence of isomerizing to acyl complexes. It is surprising though not to observe any alkyl-acyl equilibrium in solution for

product 36 in view of its close similarity to complex 34.

An interesting feature of the oxidative addition of acyl chlorides (RCOCl) to complex 1 arises when R is branched at the  $\alpha$ -carbon atom. Four isomeric acyl chlorides react with complex 1, butanoyl chloride and 2-methyl propanoyl chloride, 2-methyl butanoyl- and pentanoyl chloride, 2-ethyl butanoyl- and hexanoyl chloride and 2-phenyl propionyl- and 3-phenyl propionyl chloride, and in all cases products (33) where the R group is always straight-chain are isolated.

It is a well known fact that alkyl derivatives of transition metals are key intermediates in many homogeneous catalytic reactions of olefins.<sup>74,75</sup> Many of the catalysts used for these reactions normally possess a metal-hydrogen bond or are able to form such a bond in situ during the reaction. The mechanism proposed for the carbonylation of olefins to aldehydes (hydroformylation reaction) catalyzed by the complex  $\text{HCo}(\text{CO})_4$  is:<sup>76,77,78</sup>



The first two steps of this mechanism produce the metal-alkyl intermediate by addition of the hydrogen atom on the cobalt atom to the coordinated olefin. Insertion of carbon monoxide gives the acyl complex which in turn reacts with



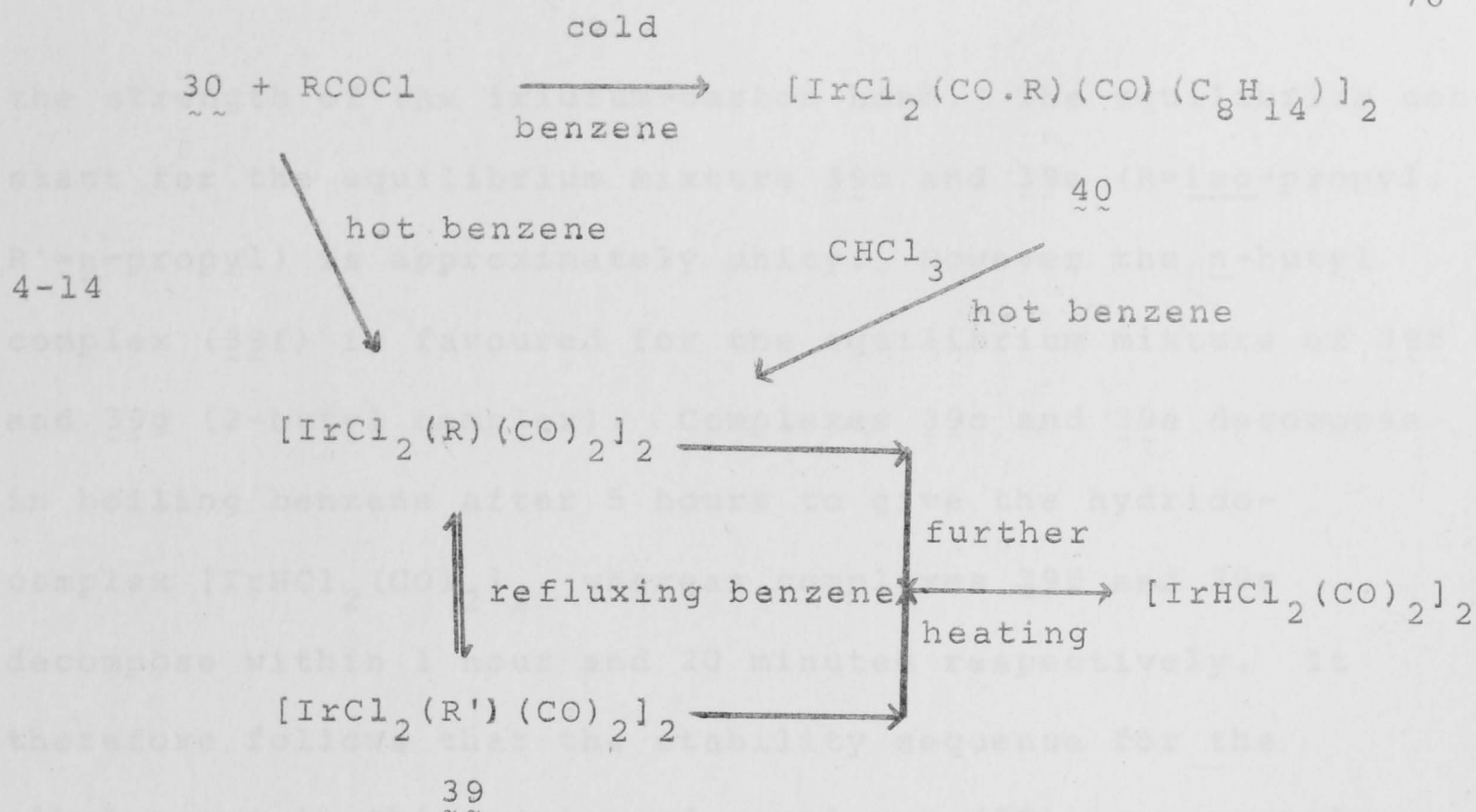


The three main points of this proposed mechanism are that (1) isomerization of the branched-alkyl group occurs after the formation of the acyl  $\underline{35b}$  since the complex  $\text{IrCl}_2\text{-}[\text{CO.}\underline{\text{iso.}}\text{propyl}](\text{CO})(\text{Ph}_3\text{P})_2$  is extremely stable, (2) the instability of intermediate  $\underline{33i}$  is probably due mainly to steric hindrance caused by the bulky triphenylphosphine group and (3) the addition of the hydrogen atom attached to the iridium nucleus (in  $\underline{44}$ ) always adds in an anti-Markownikoff sense to the coordinated olefin to give product  $\underline{33}$ .

It is also possible for the intermediate  $\underline{44}$  to expell hydrogen chloride and free olefin with formation of complex  $\underline{11}$ . This is observed in the reaction of 2-phenyl propionyl chloride with complex  $\underline{1}$ ; the complexes  $\underline{33f}$  and  $\text{IrHCl}_2\text{-}(\text{Ph}_3\text{P})_3$  ( $\underline{38}$ ) are also formed. It is not clear why the other branched-acyl chlorides do not also give complex  $\underline{11}$  but the complex  $\underline{38}$  as side products when they react with complex  $\underline{1}$ . The ready hydrolysis of the acyl chlorides to generate hydrogen chloride may account for the product  $\underline{38}$  which is formed by addition of hydrogen chloride to the starting complex  $\underline{1}$ .<sup>36</sup>

Acyl chlorides also readily add to the iridium(I) complex  $[\text{IrCl}(\text{CO})(\text{C}_8\text{H}_{14})_2]_2$  ( $\underline{30}$ ). These reactions have been studied and discussed in some detail by Shaw and Singleton.<sup>38</sup> Therefore only additional observations will be discussed.

Based on the results obtained in the present work, the reaction scheme for the addition of acyl chlorides to complex  $\underline{30}$  is:



R = straight-chain alkyl, R' = branched-chain alkyl

R = branched-chain alkyl, R' = straight-chain alkyl

The initial step is the oxidative addition of the acyl chloride to complex 30 to give complex 40; 1 mole of cyclooctene is expelled during this step. This is only achieved using cold benzene as solvent. When the reaction is performed in hot benzene the alkyl complex 39 is formed instantly. The acyl complex 40 readily isomerizes in chloroform solution with loss of cyclooctene to give the alkyl complex 39 which in refluxing benzene produces an equilibrium mixture of branched-chain and straight-chain alkyl complexes. Continuous heating of complex 39 leads to the formation of complex  $[\text{IrHCl}_2(\text{CO})_2]_2$  presumably with expulsion of olefin. This is also observed when the complex  $\text{IrCl}_2(\text{Et})(\text{CO})_2\text{py}$  is heated; ethylene and pyridine are detected and the complex  $[\text{IrHCl}_2(\text{CO})_2]_2$  is formed.<sup>38</sup>

The position of the equilibrium in the equilibrium mixture in complex 39 depends on the alkyl group and thus on

the strength of the iridium-carbon bond. The equilibrium constant for the equilibrium mixture  $\underline{39c}$  and  $\underline{39e}$  (R=iso-propyl, R'=n-propyl) is approximately unity. However the n-butyl complex ( $\underline{39f}$ ) is favoured for the equilibrium mixture of  $\underline{39f}$  and  $\underline{39g}$  (2-butyl complex). Complexes  $\underline{39c}$  and  $\underline{39e}$  decompose in boiling benzene after 5 hours to give the hydrido-complex  $[\text{IrHCl}_2(\text{CO})_2]_2$ , whereas complexes  $\underline{39f}$  and  $\underline{39g}$  decompose within 1 hour and 20 minutes respectively. It therefore follows that the stability sequence for the alkyl group in this series of complexes ( $\underline{39}$ ) is n-propyl=iso-propyl>n-butyl>2-butyl.

A similar mechanism as outlined in equation 4-13 for the isomerization of branched - chain alkyl to straight-chain alkyl in complexes  $\underline{33}$  may be applied in this case. The formation of the hydrido-complex  $[\text{IrHCl}_2(\text{CO})_2]_2$  and the possible expulsion of free olefin when complexes  $\underline{39}$  are decomposed lend support to the formation of an intermediate such as  $\underline{44}$  (eqn. 4-13). The stability of the branched-alkyl complexes  $\underline{39}$  compared with the unstable intermediate such as  $\underline{33i}$  (eqn. 4-13) clearly shows the possible role played by the sterically hindered triphenylphosphine ligands in complexes of type  $\underline{33i}$ .

#### e. Experimental

##### Materials

Acetyl chloride, propionyl chloride, butanoyl chloride, octanoyl chloride, benzoyl chloride, 2-methyl propanoyl chloride, 2-ethyl butanoyl chloride and 2-methyl butanoyl chloride were obtained commercially. Pentanoyl chloride



Table 4-1

Infrared data for alkyl-iridium complexes prepared from  $\text{IrClL}_3^a$ 

Complex	$\nu(\text{C}\equiv\text{O}) \text{ cm}^{-1}$		$\nu(\text{Ir}-\text{Cl})^b$
	Nujol Mull	In $\text{CH}_2\text{Cl}_2$	$\text{cm}^{-1}$
$\text{IrCl}_2(\text{Me})(\text{CO})(\text{Ph}_3\text{P})_2$	2040	2040, 1710 <sup>c</sup>	290, 256
$\text{IrCl}_2(\text{Me})(\text{CO})(\text{Ph}_3\text{P})_2$	2050, 2030	2040	300, 253
$\text{IrCl}_2(\text{Et})(\text{CO})(\text{Ph}_3\text{P})_2$	2045, 2025	2035	307, 252
$\text{IrCl}_2(\text{n-propyl})(\text{CO})(\text{Ph}_2\text{P})_2$	2040, 2025	2030	305, 254
$\text{IrCl}_2(\text{n-butyl})(\text{CO})(\text{Ph}_3\text{P})_2$	2040, 2030	2035	306, 254
$\text{IrCl}_2(\text{n-pentyl})(\text{CO})(\text{Ph}_3\text{P})_2$	2040, 2030	2035	302, 252
$\text{IrCl}_2(\text{n-heptyl})(\text{CO})(\text{Ph}_3\text{P})_2$	2030, 2020	2025	305, 253
$\text{IrCl}_2(\text{Ph})(\text{CO})(\text{Ph}_3\text{P})_2$	2045		315, 268
$\text{IrCl}_2(\text{CH}_2\text{CH}_2\text{Ph})(\text{CO})(\text{Ph}_3\text{P})_2$	2025		312, 250
$\text{IrCl}_2(\text{Me})(\text{CO})(\text{MePh}_2\text{P})_2$	2020	2020	310, 280
$\text{IrCl}_2(\text{Et})(\text{CO})(\text{MePh}_2\text{P})_2$	2040, 2025	2030	307, 251

a...  $\text{L}=\text{Ph}_3\text{P}, \text{MePh}_2\text{P}$       b... All bands are of strong intensities      c... Due to  $\nu(\text{C}=\text{O})$

Table 4-2

<sup>1</sup>H-n.m.r. data for alkyl-iridium complexes prepared from IrClL<sub>3</sub><sup>a,b</sup>

Complex	$\tau$ -values <sup>c,d</sup>
IrCl <sub>2</sub> (Me)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	9.43(t) ; 7.85(s) Jp = 5Hz
IrCl <sub>2</sub> (Me)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	9.43(3;t) Jp = 5Hz
IrCl <sub>2</sub> (Et)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	9.22(3;t) ; 8.46(2;m) Jh = 8Hz
IrCl <sub>2</sub> ( <u>n</u> -propyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	9.88(3;t) ; 8.90(4;m) Jh = 7.5Hz
IrCl <sub>2</sub> ( <u>n</u> -butyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub> <sup>e</sup>	9.50(5;m) ; 8.70(2;m) ; 8.40(2;m)
IrCl <sub>2</sub> ( <u>n</u> -pentyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	8.3-9.7(11;m)
IrCl <sub>2</sub> ( <u>n</u> -heptyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub> <sup>e</sup>	9.15(7;m) ; 8.75(8;m)
IrCl <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> Ph)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	3.85(2;m) ; 3.05(3;m) ; 8.10(2;m) ; 7.60(2;m)
IrCl <sub>2</sub> (Me)(CO)(MePh <sub>2</sub> P) <sub>2</sub>	7.85(3;d) ; 8.24(3;d) Jp = 10.5Hz 8.86(3;4 lines)
IrCl <sub>2</sub> (Et)(CO)(MePh <sub>2</sub> P) <sub>2</sub>	7.59(3;t) Jp = 5Hz 9.25(3;t) ; 8.77(2;m) Jh = 8Hz

cont'd...

Table 4-2 Cont'd...

a... L =  $\text{Ph}_3\text{P}$  ,  $\text{MePh}_2\text{P}$

b... all spectra were measured in  $\text{CDCl}_3$  unless stated otherwise.

c... the relative intensities are given in parentheses together with the patterns where t = triplet, d = doublet, m = multiplet, s = singlet.

d...  $J_p$  represents the apparent phosphorus-hydrogen coupling constant and  $J_h$  the apparent hydrogen-hydrogen coupling constant.

e... spectrum measured in  $\text{C}_6\text{D}_6$ .



Table 4-3

Infrared data for alkyl- and acyl-iridium complexes prepared

from  $[\text{IrCl}(\text{CO})(\text{C}_8\text{H}_{14})_2]_2^{\text{a}}$ 

Complex	$\nu(\text{C}\equiv\text{O})$ $\text{cm}^{-1}$	$\nu(\text{C}=\text{O})$ $\text{cm}^{-1}$
$[\text{IrCl}_2(\text{CO}\cdot\text{Me})(\text{CO})(\text{C}_8\text{H}_{14})]_2^{\text{b}}$	2080	1720
$[\text{IrCl}_2(\underline{\text{n}}\text{-propyl})(\text{CO})_2]_2$	2135, 2085	
$[\text{IrCl}_2(\text{CO}\cdot\underline{\text{n}}\text{-propyl})(\text{CO})(\text{Ph}_3\text{P})_2]$	2060	1630
$[\text{IrCl}_2(\underline{\text{iso}}\text{-propyl})(\text{CO})_2]_2$	2130, 2080	
$\text{IrCl}_2(\text{CO}\cdot\underline{\text{iso}}\text{-propyl})(\text{CO})(\text{Ph}_3\text{P})_2$	2045	1670
$[\text{IrCl}_2(\underline{\text{n}}\text{-butyl})(\text{CO})_2]_2$	2140, 2085	
$[\text{IrCl}_2(\text{CO}\cdot\underline{\text{iso}}\text{-propyl})(\text{CO})(\text{C}_8\text{H}_{14})]_2^{\text{b}}$	2070	1700
$[\text{IrCl}_2(2\text{-butyl})(\text{CO})_2]_2$	2135, 2085	
$[\text{IrCl}_2(\underline{\text{n}}\text{-pentyl})(\text{CO})_2]_2$	2130, 2085	
$\text{IrCl}_2(\text{CO}\cdot\underline{\text{n}}\text{-pentyl})(\text{CO})(\text{Ph}_3\text{P})_2$	2070	1625
$[\text{IrCl}_2(\text{CH}_2\text{CH}_2\text{Ph})(\text{CO})_2]_2$	2135, 2085	
$[\text{IrCl}_2(\text{PhCHMe})(\text{CO})_2]_2$	2135, 2085	
$\text{IrCl}_2(\text{CO}\cdot\underline{\text{n}}\text{-propyl})(\text{CO})(\text{MePh}_2\text{P})_2$	2060	1630

a... all spectra were measured in the solid state as nujol mull.

b... in  $\text{CHCl}_3$  solution  $\nu(\text{C}=\text{O})$  disappears and another  $\nu(\text{C}\equiv\text{O})$  appears at  $2130\text{cm}^{-1}$ .

Table 4-4

 $^1\text{H}$ -n.m.r. data for the acyl-iridium complexes.<sup>a</sup>

<u>Complex</u>	<u><math>\tau</math>-values<sup>b,c</sup></u>
$\text{IrCl}_2(\text{CO}\cdot\text{n-propyl})(\text{CO})(\text{MePh}_2\text{P})_2$	9.96(3;t), 9.60(2;m), 9.06(2;m) Jh = 7Hz 7.50(3;t) Jp = 6Hz
$\text{IrCl}_2(\text{CO}\cdot\text{iso-propyl})(\text{CO})(\text{Ph}_3\text{P})_2$	9.90(6;d), 7.01(1;m) Jh = 7.5Hz
$[\text{IrCl}_2(\text{CO}\cdot\text{Me})(\text{CO})(\text{C}_8\text{H}_{14})]_2^e$	7.37(s), 8.18(s)

a... all spectra were measured in  $\text{CDCl}_3$

b... Jh represents the apparent hydrogen-hydrogen coupling constant and Jp, the apparent phosphorus-hydrogen coupling constant.

c... the relative intensities and spectral patterns are given in parentheses; t = triplet, m = multiplet, s = singlet, d = doublet.

e... the singlet at  $7.37\tau$  decreases in intensity while the singlet at  $8.18\tau$  increases. Signals for free and coordinated  $\text{C}_8\text{H}_{14}$  are also observed.

Table 4-5

 $^1\text{H-n.m.r. data for the complexes of the type } [\text{IrCl}_2(\text{R})(\text{CO})_2]_2^{\text{a}}$ 

Complex when R=	$\tau$ -values <sup>b</sup>				J (H-H) Hz
	A	B	C	D	
A B C CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -	9.01 (t)	8.32 (s)	7.34 (m)		8.0
A B A CH <sub>3</sub> -CH-CH <sub>3</sub>	8.55 (d)	6.72 (m)			7.5
A B B C CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -	9.09 (t)	8.54 (m)	7.31 (m)		8.0
A B C D CH <sub>3</sub> -CH-CH <sub>2</sub> -CH <sub>3</sub>	8.55 (d)	6.80 (m)	7.90 (m)	9.04 (t)	8.0
A B B C D CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -	9.01 (t)	8.64 (m)	8.31 (m)	7.32 (m)	7.5
A B B C <sub>6</sub> H <sub>5</sub> -CH <sub>2</sub> -CH <sub>2</sub> -	2.7-2.9 (m)	7.15 (m)			
A B C C <sub>6</sub> H <sub>5</sub> -CH-CH <sub>3</sub>	2.5-2.9 (m)	5.50 (q)	8.30 (d)		7.5

a... all spectra were measured in CHCl<sub>3</sub>

b... t = triplet, m = multiplet, d = doublet, q = quartet, s = sextet.



Table 4-6

Analyses of the alkyl- and acyl-iridium complexes<sup>a</sup>

Complex	%C	%H	%Cl	Mol. Wt.
IrCl <sub>2</sub> (Me)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 54.94	3.97	8.55	
	f. 55.22	4.14	8.71	
IrCl <sub>2</sub> (Et)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 55.46	4.18	8.41	844
	f. 55.95	4.21	8.27	848
IrCl <sub>2</sub> ( <u>n</u> -propyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 55.94	4.34	8.16	858
	f. 56.25	4.48	8.31	864
IrCl <sub>2</sub> ( <u>n</u> -butyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 56.44	4.47	8.13	872
	f. 56.72	4.61	8.26	893
IrCl <sub>2</sub> ( <u>n</u> -pentyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 56.90	4.62	7.99	886
	f. 57.21	4.75	8.13	873
IrCl <sub>2</sub> ( <u>n</u> -heptyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 57.76	4.96	7.75	914
	f. 58.57	4.73	7.71	940
IrCl <sub>2</sub> (Ph)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 57.82	3.96	7.96	
	f. 56.84	4.29	8.06	
IrCl <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> Ph)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 58.68	4.27	7.71	920
	f. 58.86	4.41	7.91	916
IrCl <sub>2</sub> (Me)(CO)(MePh <sub>2</sub> P) <sub>2</sub>	c. 47.58	4.14	10.03	
	f. 47.80	4.37	9.83	
IrCl <sub>2</sub> (Et)(CO)(Ph <sub>2</sub> P) <sub>2</sub>	c. 48.32	4.34	9.85	
	f. 48.43	4.30	9.76	

cont'd..

Table 4-6 cont'd

Complex	%C	%H	%Cl	Mol.Wt.
[IrCl <sub>2</sub> (CH <sub>2</sub> CH <sub>2</sub> Ph)(CO) <sub>2</sub> ] <sub>2</sub>	c. 28.30	2.14	16.73	
	f. 27.85	2.24	16.50	
[IrCl <sub>2</sub> (n-butyl)(CO) <sub>2</sub> ] <sub>2</sub>	c. 19.15	2.41	18.87	
	f. 19.41	2.58	18.65	
[IrCl <sub>2</sub> (PhCHMe)(CO) <sub>2</sub> ] <sub>2</sub>	c. 28.30	2.14	16.73	
	f. 28.41	2.26	16.57	
[IrCl <sub>2</sub> (n-propyl)(CO) <sub>2</sub> ] <sub>2</sub>	c. 16.58	1.95	19.57	
	f. 16.71	1.82	19.43	
IrCl <sub>2</sub> (CO.n-propyl)(CO)(MePh <sub>2</sub> P) <sub>2</sub>	c. 48.81	4.36	9.29	
	f. 49.11	4.41	9.07	
IrCl <sub>2</sub> (CO.n-propyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 55.52	4.20	7.91	
	f. 55.78	4.31	7.72	
IrCl <sub>2</sub> (CO.iso-propyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 55.52	4.20	7.91	
	f. 55.69	4.48	7.76	
IrCl <sub>2</sub> (CO.n-pentyl)(CO)(Ph <sub>3</sub> P) <sub>2</sub>	c. 56.44	4.52	7.75	
	f. 57.02	4.71	7.62	

a... c = calculated, f = found.

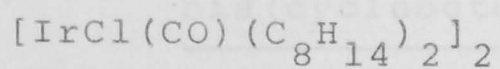
hexanoyl chloride and 3-phenyl propionyl chloride were prepared by reaction of oxalyl chloride and the corresponding carboxylic acid.<sup>94</sup> 2-phenyl propionyl chloride was prepared from the aldehyde<sup>95</sup> which was converted to the acid<sup>96</sup> and finally to the chloride by reaction with oxalyl chloride.

See Chapter 2 section e for general physical measurements and preparations of the iridium(I) complexes 1 and 3.

A. Improved preparation of di- $\mu$ -chlorododicarbonyltetrakis-(cyclooctene)diiridium(I)-[IrCl(CO)(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub><sup>38</sup>

A solution of chloroiridic acid (2g) in water (5 ml) and n-propanol (10 ml) was refluxed for 5 minutes. Cyclooctene (3 ml) was added and the solution refluxed for a further 1 hour. At this time water (20 ml) was added and the solution refluxed for a further 10 minutes. The resulting lemon-yellow oil was separated from the solution by decantation and washed with cold methanol (2 x 15 ml). Lemon-yellow prisms of the product (1.14 g) resulted when diethyl ether was added to the oil. The product was separated by centrifuge and dried in a current of nitrogen. (Yield : 62% based on H<sub>2</sub>IrCl<sub>6</sub>.6H<sub>2</sub>O).

B. Interaction of acyl chlorides (RCOCl) with di- $\mu$ -chlorododicarbonyltetrakis(cyclooctene)diiridium(I)



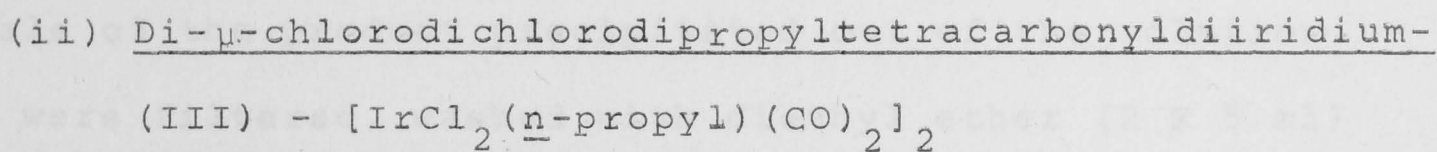
Preparations

(i) Di- $\mu$ -chlorodichlorodiacetyldicarbonylbis(cyclooctene)diiridium(III)-[IrCl<sub>2</sub>(CO.Me)(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub>

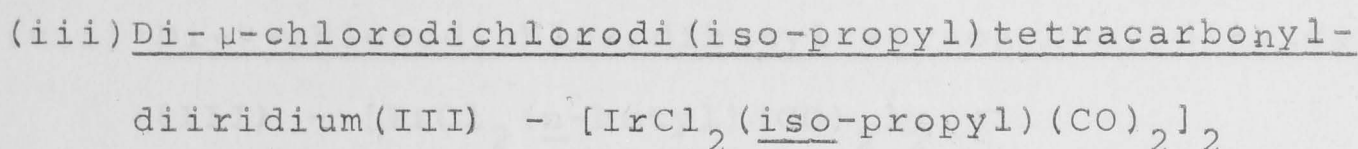
To a suspension of di- $\mu$ -chlorododicarbonyltetrakis-



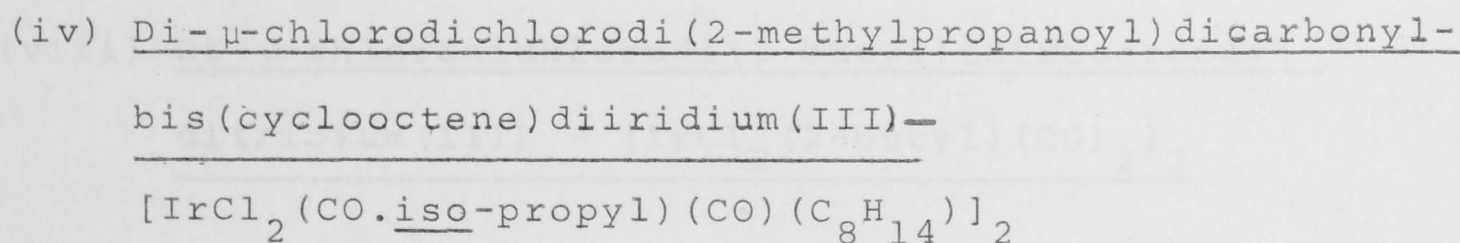
(cyclooctene)diiridium(I) (0.3g) in benzene (10 ml) was added acetyl chloride (0.5 ml). The mixture was then stirred until most of the solid dissolved (ca. 6 minutes). The solution was then filtered and light petroleum ether (b.p. 100-120°) added. When most of the benzene was removed at 25°C (15 mm), off-white prisms of the product resulted. These were filtered and washed with n-pentane (2 x 10 ml).



To a solution of di- $\mu$ -chlorodicarbonyltetrakis(cyclooctene)diiridium(I) (0.3g) in boiling benzene (10 ml) was added butanoyl chloride (0.5 ml). The hot solution was filtered, light petroleum ether (b.p. 100-120°) was added and most of the benzene removed at 25°C (15 mm). This precipitated the required product as off-white crystals.

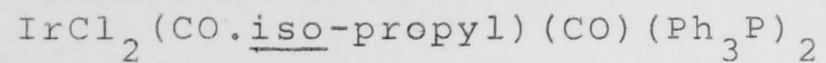


This was similarly prepared from 2-methyl propanoyl chloride (0.5 ml) and di- $\mu$ -chlorodicarbonyltetrakis(cyclooctene)diiridium(I) (0.3g) in boiling benzene and isolated like the n-propyl complex above (ii).



This was prepared in a similar manner to the acetyl complex described above (i).

(v) Dichloro(2-methylpropanoyl)carbonylbis(triphenylphosphine)iridium(III) -



Triphenylphosphine (0.4g) was added to a solution of di- $\mu$ -chlorodichlorodi(iso-propyl)tetracarbonyldiiridium(III) (0.2g) in dichloromethane (5 ml). Upon addition of diethyl ether and cooling the mixture to 0°C, white crystals of the product precipitated out of the solution. These were filtered, washed with diethyl ether (2 x 5 ml) and dried in a stream of nitrogen.

(vi) Dichlorobutanoylcarbonylbis(triphenylphosphine)iridium(III) -  
 $\underline{\text{IrCl}_2(\text{CO}.\underline{\text{n}}\text{-propyl})(\text{CO})(\text{Ph}_3\text{P})_2}$

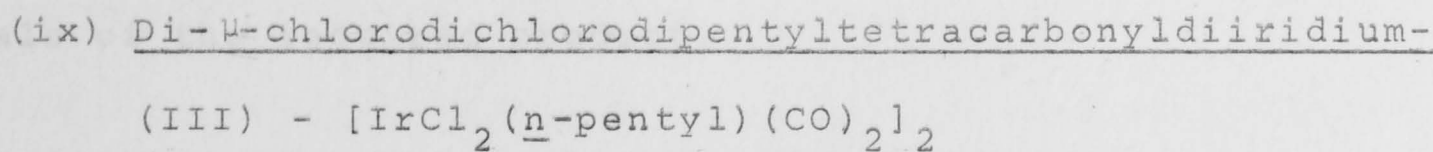
This was prepared in a similar manner to the 2-methylpropanoyl complex described above (v).

(vii) Di- $\mu$ -chlorodichlorodibutyltetracarbonyldiiridium(III) -  
 $\underline{[\text{IrCl}_2(\underline{\text{n}}\text{-butyl})(\text{CO})_2]_2}$

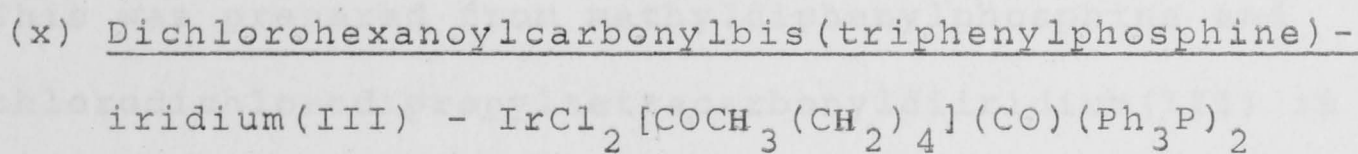
This was similarly prepared from pentanoyl chloride (0.5 ml) and di- $\mu$ -chlorodicarbonyltetrakis(cyclooctene)diiridium(I) (0.3g) in boiling benzene (5 ml) and isolated like the n-propyl complex above (ii).

(viii) Di- $\mu$ -chlorodichlorodi(2-butyl)tetracarbonyldiiridium(III) -  
 $\underline{[\text{IrCl}_2(2\text{-butyl})(\text{CO})_2]_2}$

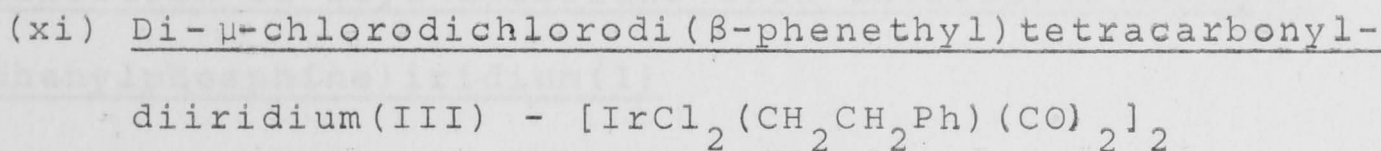
This was prepared in a similar manner to the n-propyl complex described above (ii).



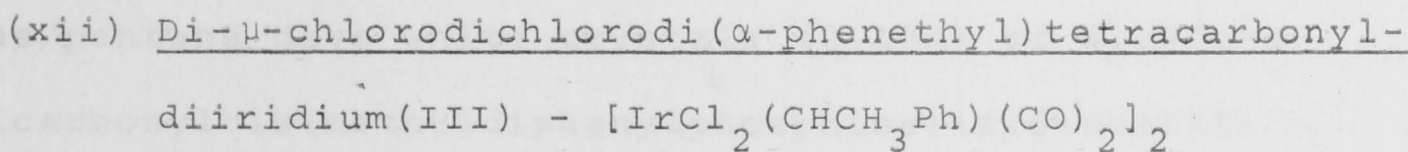
This was prepared in a similar manner to the n-propyl complex described above (ii).



This was prepared in a similar manner to the 2-methylpropanoyl complex described above (v).



This was similarly prepared from 3-phenyl propionyl chloride (0.5 ml) and di- $\mu$ -chlorodicarbonyltetrakis(cyclooctene)diiridium(I) (0.3g) in boiling benzene (5 ml) and isolated like the n-propyl complex above (ii). Recrystallization from dichloromethane/light petroleum ether (b.p. 40-60°) gave beautiful off-white crystals.

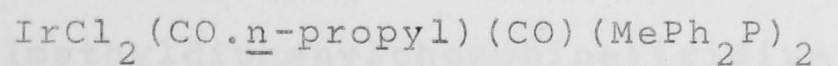


To a suspension of di- $\mu$ -chlorodicarbonyltetrakis(cyclooctene)diiridium(I) (0.3g) in benzene (10 ml) was added 2-phenyl propionyl chloride (0.5 ml) and the mixture stirred for 3 hours. After which time the solution was filtered. The filtrate was then evaporated at 25°C (15 mm) giving a pale yellow-oil. Light yellow solid resulted when pentane was added to the oil. Recrystallization of the solid from dichloromethane/petroleum ether (b.p. 40-60°) gave white



crystals of the required product.

(xiii) Dichlorobutanoylcarbonylbis(methyldiphenylphosphine)iridium(III)—



This was prepared from methyldiphenylphosphine and di- $\mu$ -chlorodichlorodipropyltetracarbonyldiiridium(III) in dichloromethane and isolated like the 2-methylpropanoyl complex described above (v).

C. Interaction of acyl chlorides with chlorotris(methyldiphenylphosphine)iridium(I)

(i) Acetyl chloride- $\text{CH}_3\text{COCl}$

To a solution of chlorotris(methyldiphenylphosphine)iridium(I) (0.3g) in benzene (5 ml) was added acetyl chloride (0.5 ml). The dark red solution went colourless almost immediately. The solution was then stirred for 10 minutes. White solid precipitated upon addition of pentane (30 ml.). Recrystallization of the solid from dichloromethane/pentane gave white crystals (0.19g) of dichloromethylcarbonylbis(methyldiphenylphosphine)iridium(III) -  $\text{IrCl}_2(\text{Me})(\text{CO})(\text{MePh}_2\text{P})_2$ . These were filtered, washed with pentane (2 x 10 ml) and dried in a stream of nitrogen. (Yield : 73%).

(ii) Propionyl chloride- $\text{CH}_3\text{CH}_2\text{COCl}$

To a solution of chlorotris(methyldiphenylphosphine)iridium(I) (0.3g) in benzene (5 ml) was added propionyl chloride (0.5 ml) and the mixture stirred at 60°C for 4 hours.

Pentane was then added slowly to the cooled solution precipitating the product as white crystals. Recrystallization of the product from dichloromethane/petroleum ether (b.p. 40-60°) gave white crystals (0.18g) of dichloroethylcarbonylbis(methyldiphenylphosphine)iridium(III)—  
 $\text{IrCl}_2(\text{Et})(\text{CO})(\text{MePh}_2\text{P})_2$ . These were filtered, washed with pentane (2 x 10 ml) and dried in a stream of nitrogen. (Yield = 70%).

D. Interaction of acyl chlorides with chlorotris(triphenylphosphine)iridium(I)

Preparations

(i) Dichloromethylcarbonylbis(triphenylphosphine)iridium(III) -  $\text{IrCl}_2(\text{Me})(\text{CO})(\text{Ph}_3\text{P})_2$

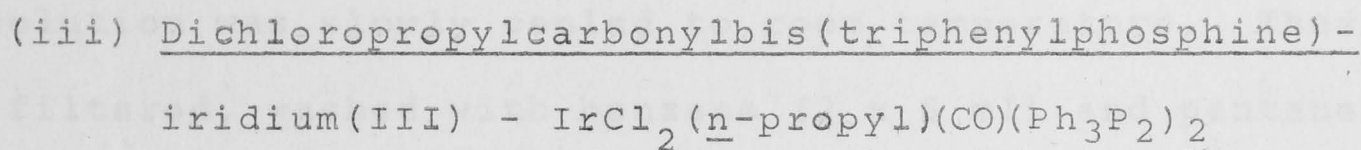
To a solution of chlorotris(triphenylphosphine)iridium(I) (0.45g) in benzene (5 ml) was added acetyl chloride (0.5 ml) and the mixture refluxed for 15 minutes. Diethyl ether (15 ml) was added to the solution which was then cooled to 0°C. White crystals (0.28g) of dichloromethylcarbonylbis(triphenylphosphine)iridium(III) resulted. These were filtered, washed with diethyl ether and dried in a stream of nitrogen. (Yield = 76%).

(ii) Dichloroethylcarbonylbis(triphenylphosphine)iridium(III) -  $\text{IrCl}_2(\text{Et})(\text{CO})(\text{Ph}_3\text{P})_2$

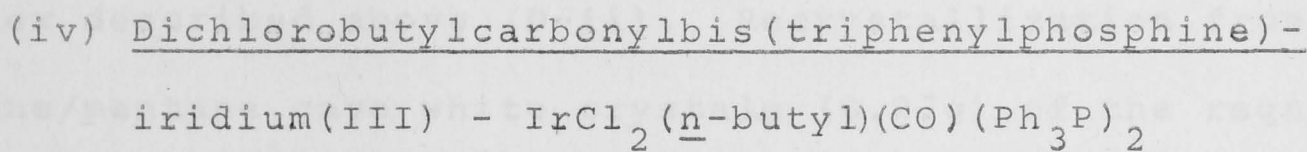
To a solution of chlorotris(triphenylphosphine)iridium(I) (0.45g) in benzene (5 ml) was added propionyl chloride (0.5 ml) and the mixture refluxed for 45 minutes. Hexane (10 ml) was added to the solution which was then cooled to



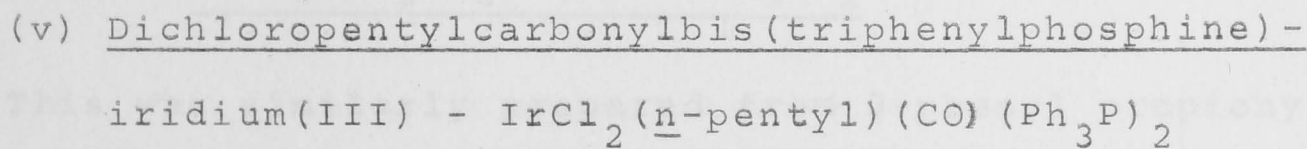
-10°C. This precipitated the product as white crystals. Recrystallization of the product from dichloromethane/diethyl ether gave white crystals (0.29g) of dichloroethylcarbonylbis(triphenylphosphine)iridium(III). These were filtered, washed with diethyl ether (2 x 10 ml) and dried in a stream of nitrogen. (Yield = 77.5%).



This was prepared in a similar manner to the ethyl complex described above (D-ii). Recrystallization from dichloromethane/hexane gave white crystals (0.31g) of the required product. (Yield = 81%).

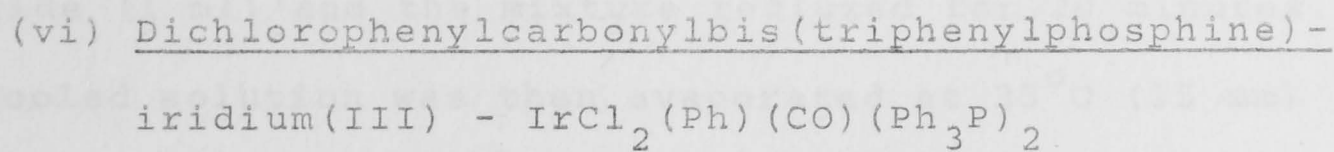


White crystals of the required product were obtained in a similar manner described for the ethyl complex above (D-ii). (0.25g; 64% yield).

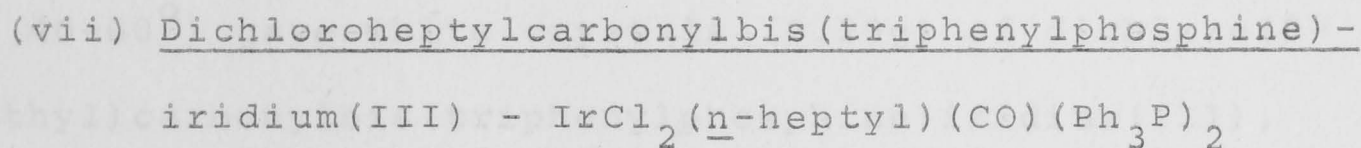


This was similarly prepared from hexanoyl chloride (0.5 ml) and chlorotris(triphenylphosphine)iridium(I) (0.45g) in refluxing benzene for 30 minutes and isolated like the ethyl complex (D-ii). It formed white crystals (0.31g) of the required product. (Yield = 79%).

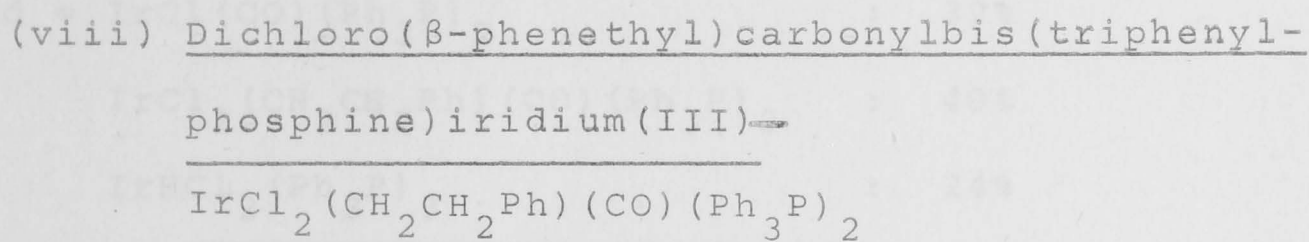




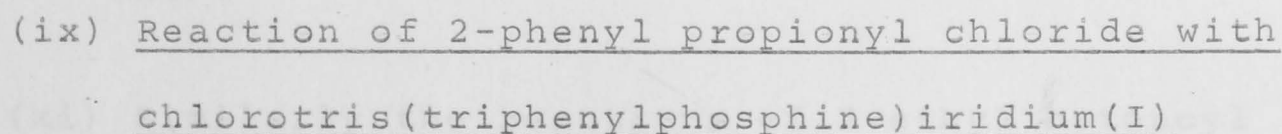
To a solution of chlorotris(triphenylphosphine)iridium-(I) (0.45g) in benzene (5 ml) was added benzoyl chloride (0.5 ml) and the mixture refluxed for 50 minutes. White crystals (0.32g) of the required product were obtained when the solution was slowly cooled to room temperature. These were filtered, washed with benzene (2 x 5 ml) and pentane (2 x 10 ml) and dried in a stream of nitrogen. (yield = 81%).



This was prepared in a similar manner to the ethyl complex described above (D-ii). Recrystallization from benzene/pentane gave white crystals (0.27g) of the required product. (Yield = 67.5%).



This was similarly prepared from 3-phenyl propionyl chloride (0.5 ml) and chlorotris(triphenylphosphine)iridium-(I) (0.45g) in refluxing benzene (5 ml) for 15 minutes. The product was isolated like the ethyl complex (D-ii) giving white crystals (0.3g) of the required product. (Yield = 79%).



To a solution of chlorotris(triphenylphosphine)iridium-(I) (0.8g) in benzene (10 ml) was added 2-phenyl propionyl

chloride (1 ml) and the mixture refluxed for 20 minutes. The cooled solution was then evaporated at 25°C (15 mm) giving a yellow oil. Diethyl ether when added to this oil precipitated a yellow solid (0.2g) which was filtered and washed with diethyl ether. The solid when recrystallized from chloroform/diethyl ether gave lemon-yellow crystals (0.16g) of chlorocarbonylbis(triphenylphosphine)iridium(I).

The diethyl ether filtrate was then evaporated at 25°C (15 mm) giving a light yellow oil. This oil was redissolved in dichloromethane. Slow addition of light petroleum ether (b.p. 40-60°C) gave white crystals (0.29g) of dichloro( $\beta$ -phenethyl)carbonylbis(triphenylphosphine)iridium(III),  $\text{IrCl}_2(\text{CH}_2\text{CH}_2\text{Ph})(\text{CO})(\text{Ph}_3\text{P})_2$ . These were filtered, washed with pentane (2 x 10 ml) and dried in a stream of nitrogen. The remaining filtrate give white crystals (0.2g) of dichlorohydridotris(triphenylphosphine)iridium(III),  $\text{IrHCl}_2(\text{Ph}_3\text{P})_3$  when dichloromethane was slowly evaporated off.

(Yield = $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$	:	32%
$\text{IrCl}_2(\text{CH}_2\text{CH}_2\text{Ph})(\text{CO})(\text{Ph}_3\text{P})_2$	:	40%
$\text{IrHCl}_2(\text{Ph}_3\text{P})_3$	:	24%

(x) When 2-methylpropanoyl chloride (0.5 ml) was reacted with chlorotris(triphenylphosphine)iridium(I) (0.45g) in a similar manner described for the propionyl chloride reaction (D-ii), white crystals (0.2g) of dichloropropyl-carbonylbis(triphenylphosphine)iridium(III) were obtained. (Yield = 55%).

(xi) Similarly the reactions of 2-ethyl butanoyl chloride (0.5 ml) and 2-methyl butanoyl chloride (0.5ml) with

chlorotris(triphenylphosphine)iridium(I) (0.45g) gave dichloropentylcarbonylbis(triphenylphosphine)iridium(III) and dichlorobutylcarbonylbis(triphenylphosphine)iridium(III) as products respectively.

White crystals of dichlorohydridotris(triphenylphosphine)iridium(III) were also obtained from the reactions.

Yield = With 2-ethyl butanoyl chloride 0.12g  
product, 30.5%

With 2-methyl butanoyl chloride 0.16g  
product, 41%



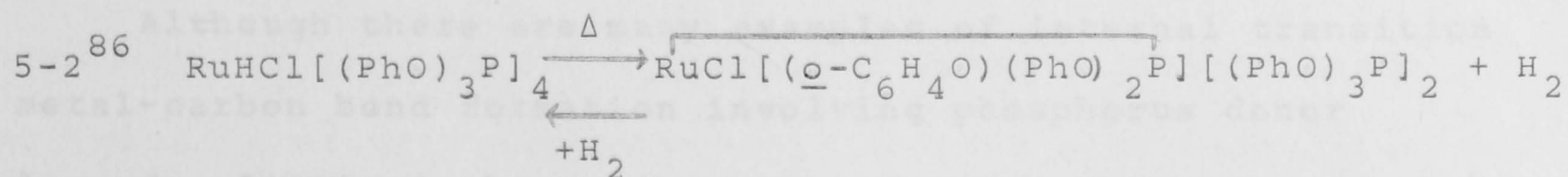
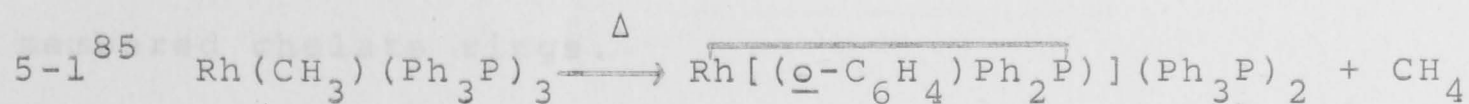
## CHAPTER 5

HYDROGEN ABSTRACTION REACTIONSa. Introduction

Interactions between metal ions and carbon-hydrogen bonds of coordinated ligands are well established phenomena, especially in complexes containing ligands such as aryl phosphines and phosphites.<sup>84</sup> In these reactions, an aryl C-H bond in the phosphine or phosphite ligands of the transition metal complex reacts with the central metal atom to form a metal-carbon bond.

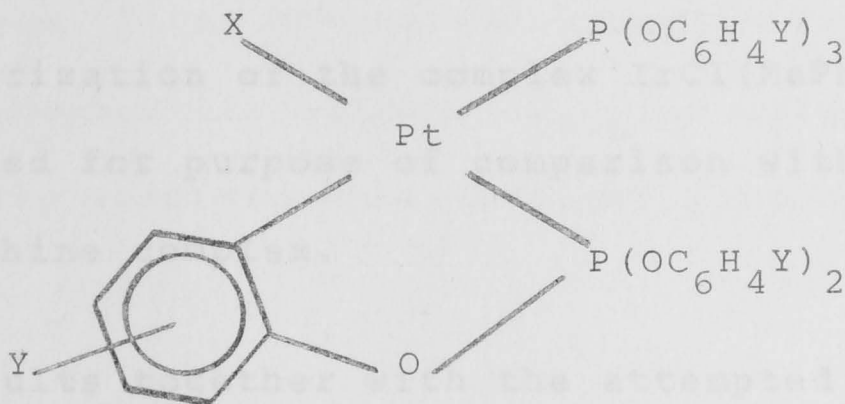
Bennett and Milner<sup>36</sup> have shown that the complexes  $\text{IrCl}(\text{Ph}_3\text{M})_3$  (M=P, As or Sb) isomerize on heating in benzene to give iridium(III)-hydride complexes,  $\text{IrHCl}[(\text{o-C}_6\text{H}_4)\text{Ph}_2\text{M}](\text{Ph}_3\text{M})_2$ . Although the overall reaction is simply an isomerization, it was suggested<sup>84</sup> that these reactions may also be termed as oxidative addition reactions. The four-coordinate  $d^8$  iridium(I) complexes  $\text{IrCl}(\text{Ph}_3\text{M})_3$  (M=P, As or Sb) are converted to six-coordinate,  $d^6$  iridium(III) complexes by addition of an ortho C-H bond of a phenyl ring to the metal.

More commonly the initial and final oxidation states of the metal are the same since substitution is accompanied by elimination, e.g.:



In the latter example, involvement of the ortho-position was proved by deuteration studies.<sup>86</sup>

The conversion of o-tolylphosphine complexes of platinum(II), trans-PtCl<sub>2</sub>[Ph(o-C<sub>6</sub>H<sub>4</sub>Me)<sub>2</sub>P]<sub>2</sub> into metal-carbon bonded complexes by intramolecular attack at the o-methyl group in preference to the aromatic CH group of the coordinated o-tolylphosphine has recently been reported.<sup>89</sup> Robinson et al<sup>90</sup> have recently shown that the metal-ortho-carbon bonded complexes,



X = Cl, Br, I; Y = H, o-Me, m-Me, p-Me

may be prepared by heating the corresponding platinum complexes cis-PtX<sub>2</sub>[(OPh-Y)<sub>3</sub>P]<sub>2</sub> in decalin.

The difference in behaviour between the ortho-tolylphosphine and phosphite complexes in these reactions was rationalized<sup>90</sup> in terms of the steric requirements of the resultant chelate ring. Both reactions give rise to products with sterically favoured five-membered chelate rings in preference to the less sterically favourable four- and six-membered chelate rings.

Although there are many examples of internal transition, metal-carbon bond formation involving phosphorus donor ligands, little is known about the factors which promote such

metal-carbon bond formation. Bulky substituents on tertiary phosphines and the formation of sterically favoured five-membered chelate ring have been shown to promote internal metal-carbon bond formation.<sup>89,90</sup>

A series of complexes containing both tertiary phosphines and triphenylphosphite has been prepared; the behaviour of these complexes towards internal metal-carbon bond formation is of interest because either four- or five-membered chelate rings can be formed depending on whether hydrogen is abstracted from the phosphite or the phosphines.

The isomerization of the complex  $\text{IrCl}(\text{MePh}_2\text{P})_3$  (3) has been studied for purpose of comparison with the analogous triphenylphosphine complex.

These results together with the attempted preparations of the complex  $\text{IrCl}[(\text{PhO})_3\text{P}]_3$  are discussed in the subsequent section.

#### b. Results and Discussion

A general method for preparing planar iridium(I) complexes of the type  $\text{IrClL}_3$  (L = tertiary phosphine or arsine) is to displace cyclooctene from the complex  $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$  with an excess of the ligand L.<sup>36</sup> Attempts to prepare the triphenylphosphite complex  $\text{IrCl}[(\text{PhO})_3\text{P}]_3$  by this method give a colourless crystalline solid in almost quantitative yield, which is formulated as  $\text{IrHCl}[(\text{O}-\text{C}_6\text{H}_4\text{O})(\text{PhO})_2\text{P}][(\text{PhO})_3\text{P}]_2$  (45a) on the basis of analytical and spectroscopic data. The same complex is obtained by treating complex 1 with three equivalents of triphenylphosphite, and has also been reported briefly and independently of this work as a product of the



reaction of triphenylphosphite with the cycloocta-1,5-diene complexes  $[\text{IrHCl}_2(1,5\text{-C}_8\text{H}_{12})]_2$  and  $[\text{IrCl}(1,5\text{-C}_8\text{H}_{12})]_2$  or with  $\text{IrCl}(\text{CO})(\text{PhO})_3\text{P}]_2$ .<sup>87</sup>

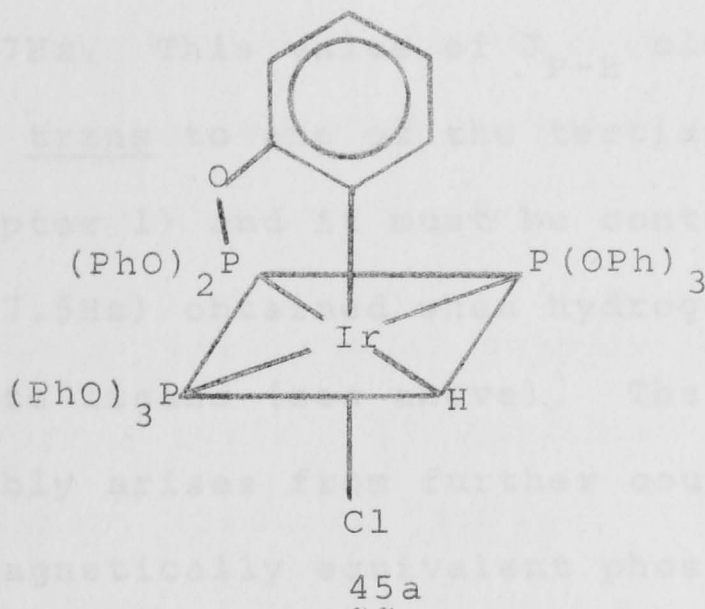
Complex 45a is monomeric in chloroform, and its infrared spectrum shows a band at  $2080\text{cm}^{-1}$  assignable to  $\nu(\text{Ir-H})$ . In addition to complex aromatic absorption in the region  $2.6\text{-}3.4\tau$ , proton n.m.r. spectrum shows a widely spaced pair of 1:2:1 triplets centred at  $19.75\tau$ . The infrared frequency, the chemical shift and the large splitting ( $J_{\text{P-H}} = 277.5\text{Hz}$ ) are all characteristic of hydrogen trans to a phosphorus donor in an octahedral hydrido-iridium(III) complex (see Chapter 1); although  $J_{\text{P-H}}$  is larger than the values generally observed when tertiary phosphines are present.

The 1:2:1 triplet pattern presumably arises from further coupling with two equivalent, strongly coupled, mutually trans phosphorus atoms ( $J_{\text{P-H}} = 18\text{Hz}$ ), which are both cis to the hydrogen atom.

The infrared spectrum of complex 45a also shows strong bands at  $1105$ ,  $1038$  and  $800\text{ cm}^{-1}$  which are absent from the spectra of triphenylphosphite and the rhodium(I) complex,  $\text{RhCl}[(\text{PhO})_3\text{P}]_3$ . Absorptions at  $1100$  and  $800\text{ cm}^{-1}$  have been observed in the infrared spectrum of the chelate  $\sigma$ -phenyl complex  $\text{RuHCl}[(\text{o-C}_6\text{H}_4\text{O})(\text{PhO})_2\text{P}][(\text{PhO})_3\text{P}]_3$  (eqn 5-2) which is formed by the reversible loss of hydrogen from the complex  $\text{RuHCl}[(\text{PhO})_3\text{P}]_4$ .<sup>86</sup>

It is therefore reasonable to assume that complex 45a on the basis of its infrared and n.m.r. data possesses

the following stereochemistry:



An earlier report<sup>87</sup> showed that when complex 45a is heated in decalin, hydrogen is expelled and a second metal-carbon  $\sigma$ -bond is formed. The X-ray crystal structure of this product has been performed<sup>88</sup> and it confirms the presence of meta-ortho-carbon bonds originating from the interaction of the metal with ortho-carbon atoms of two different phosphite ligands.

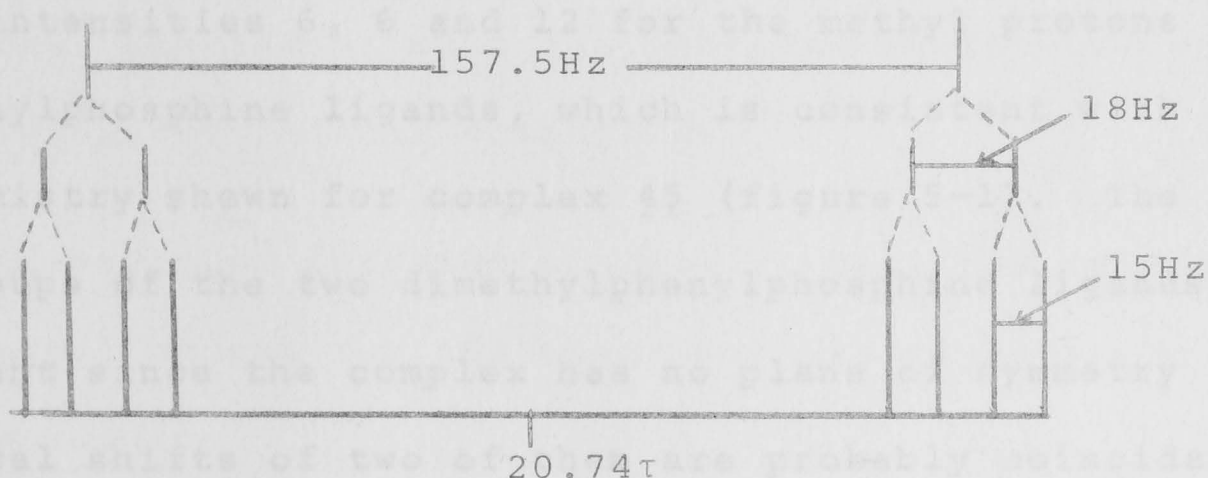
When the complex  $[\text{IrCl}(1,5\text{-C}_8\text{H}_{12})]_2$  is reacted with triphenylphosphite in equimolar proportions for one hour and the resulting solution reacted with 2.5 equivalents of a number of ligands L, white crystals of complex  $\text{IrHCl}[(\text{o-C}_6\text{H}_4\text{O})(\text{PhO})_2\text{P}]_2$  (45) [L = (b)  $\text{Ph}_3\text{P}$ , (c)  $\text{MePh}_2\text{P}$ , (d)  $\text{Me}_2\text{PhP}$ , (e)  $\text{Ph}_3\text{As}$ ] are obtained.

The infrared spectrum of complex 45 shows a band in the region  $2050\text{-}2120\text{cm}^{-1}$  (table 5-1) which is assigned to the iridium-hydrogen stretching mode. In addition to this band, sharp bands are observed in the region of  $1030\text{-}1050\text{cm}^{-1}$  and at  $800\text{cm}^{-1}$  for complex 45 in the infrared spectrum. These bands are typical of the metal-ortho-carbon group  $(\text{PhO})_2\text{-}(\text{o-C}_6\text{H}_4\text{O})\text{P}$  derived from the triphenylphosphite ligand.



The high field n.m.r. spectrum of complexes 45b and 45d shows two 1:2:1 triplets at about  $21\tau$  and separated by approximately 157Hz. This value of  $J_{P-H}$  clearly indicates that hydrogen is trans to one of the tertiary phosphine ligands (see Chapter 1) and it must be contrasted with the larger value (277.5Hz) obtained when hydrogen is trans to a triphenylphosphite ligand (see above). The 1:2:1 triplet pattern presumably arises from further coupling ( $J_{P-H} = 18\text{Hz}$ ) with two magnetically equivalent phosphorus atoms which are both cis to the hydrogen atom.

However, for complex 45c the high field n.m.r. spectrum shows two widely spaced pairs of doublets centred at  $20.74\tau$ :



The large  $J_{P-H}$  (157.5Hz) suggests that the hydrogen atom is trans to one of the methyldiphenylphosphine ligands. The two pairs of doublets arise from further coupling with two inequivalent phosphorus atoms ( $J_{P-H} = 15\text{Hz}$  and  $18\text{Hz}$ ) which are both cis to the hydrogen atom. On the basis of the high field n.m.r. spectrum of complex 45c it is reasonable to assume that the group V donor atoms of the complex possess a fac-configuration (see figure 5-1).

The high field n.m.r. spectrum of complex 45e is very simple; a single doublet ( $J_{P-H} = 18\text{Hz}$ ) centred at  $23.3\tau$  is



observed. The small splitting suggests that the hydrogen atom is definitely not trans to the phosphorus nucleus but cis to it. By comparison with its analogues, complex 45e should possess a stereochemistry in which the hydrogen atom is trans to a triphenylarsine ligand.

The 0-10 $\tau$  n.m.r. spectrum of complex 45c confirms the fac-stereochemistry (figure 5-1) suggested on the basis of its high field n.m.r. spectrum (above). Two doublets are observed for the methyl protons attached to the phosphorus nuclei. This is in accord with a cis-configuration for the phosphine ligands. The low field n.m.r. spectrum of dimethylphenylphosphine complex 45d shows three doublets of relative intensities 6, 6 and 12 for the methyl protons of the dimethylphosphine ligands, which is consistent with the stereochemistry shown for complex 45 (figure 5-1). The four methyl groups of the two dimethylphenylphosphine ligands are inequivalent since the complex has no plane of symmetry but the chemical shifts of two of them are probably coincident. On the basis of the high field n.m.r. spectrum of complex 45d, one of the phosphine ligands is assumed to be trans to hydrogen atom. The other phosphine ligand is unlikely to be trans to the phosphite ligand, since such a configuration would give a more complex spectrum for the methyl protons; this arrangement would result in a possible ABX<sub>3</sub>X<sub>3</sub>' spin system with J<sub>A-B</sub> probably very large. Therefore it is reasonable to suggest that complex 45d and 45c possess similar stereochemistries (figure 5-1).

When the hydride-complexes 45b, 45c and 45d are heated in toluene/heptane white crystalline products (46) are obtained,

the analyses of which are very similar to those of complexes 45b, 45c and 45d. The infrared spectra of complexes 46 show no band due to  $\nu(\text{Ir-H})$  in the region  $2000-2200\text{cm}^{-1}$  but are otherwise similar to those of complex 45 (b,c,d) in the region  $2000-600\text{cm}^{-1}$ .

The low field n.m.r. spectrum of the methyldiphenylphosphine complex 46c shows a doublet (relative intensity 6) for the methyl protons of the methyldiphenylphosphine ligands, and for complex 46d the methyl protons of the dimethylphenylphosphine ligands give rise to two doublets. These data suggest that the two phosphine ligands in complexes 46c and 46d are in equivalent positions around the iridium atom, consistent with the proposed stereochemistry as shown in figure 5-1 for complex 46.

On the basis of infrared and n.m.r. data the following stereochemical course for the reactions discussed above may be proposed:

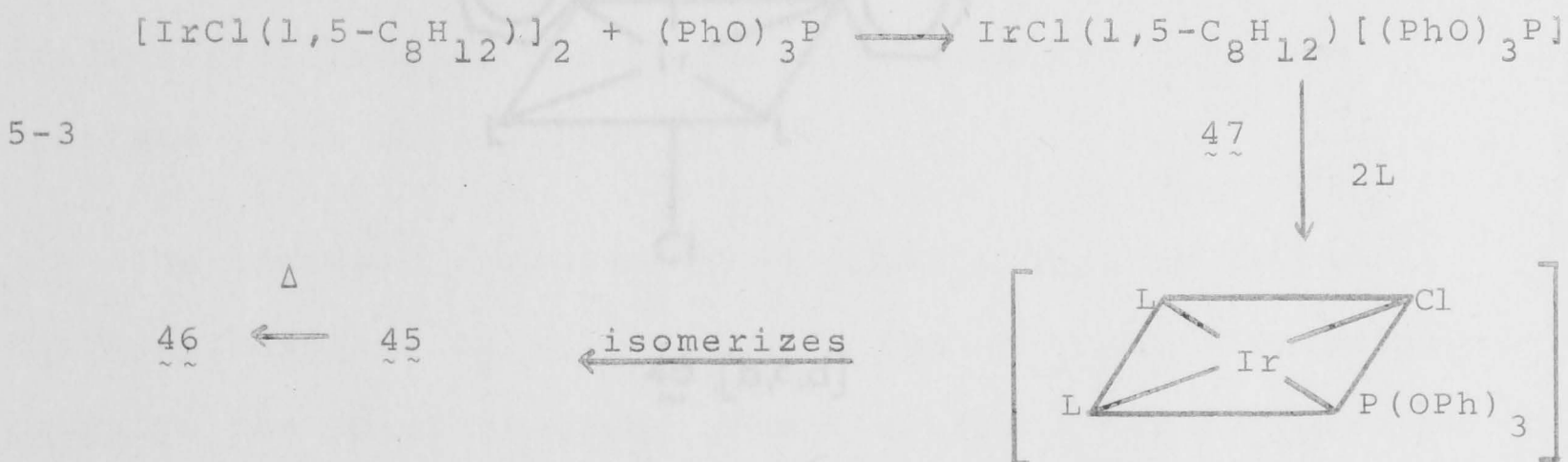


Figure 5-1. Proposed stereochemistries for complexes 45 and 46.



The product 45 results from the cleavage of the chlorine-iridium bridge in the complex  $[\text{IrCl}(\text{L})_2(\text{H})]_2$  by the phosphite ligand. Similar complexes of type  $\text{MCl}(\text{L})_2(\text{H})$  ( $\text{M} = \text{Ir, Rh}$ )

L = a. tertiary phosphite have been reported.

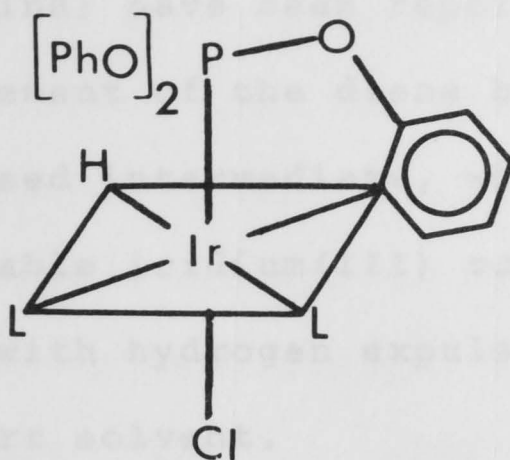
step in the displacement of the chlorine atom by the phosphite

yield 48 as a supposed intermediate which readily loses a chloride

to form the more stable complex 45. Complex 45 is probably

is formed probably with hydrogen expulsion when complex 45

is heated in an inert solvent.



L = b.  $\text{Ph}_3\text{P}$

c.  $\text{MePh}_2\text{P}$

d.  $\text{Me}_2\text{PhP}$

e.  $\text{Ph}_3\text{As}$

45

Attempts to recover 45 by adding 45 to a solution of benzene at one atmosphere to complex 45 failed. Apparently under these conditions the reaction 45 to 46 is irreversible.

c. Isomerization of the iridium(III) complex,  $[\text{IrCl}(\text{L})_2(\text{H})]_2$

On heating complex 3 (see chapter 2, section 4) in

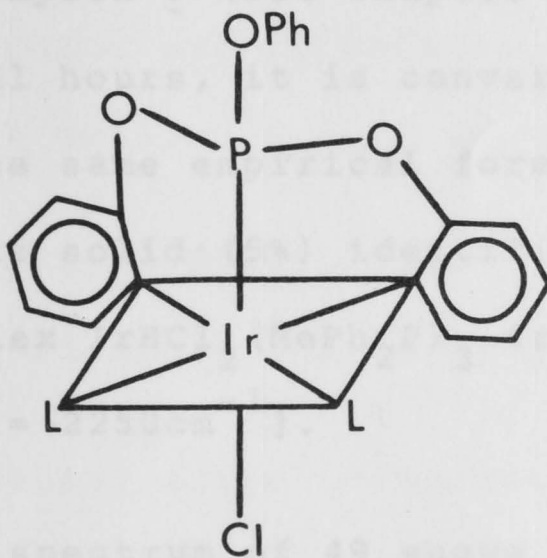
benzene for several hours, it is converted into a white solid

complex (46) of the type  $[\text{IrCl}(\text{L})_2(\text{H})]_2$ . The reaction

also yields a white solid (47) which is tentatively assigned as the

iridium(III) complex  $[\text{IrCl}(\text{L})_2(\text{H})]_2$ .

spectrum  $\nu(\text{Ir-H}) = 1900 \text{ cm}^{-1}$ .



46 [b,c,d]

The infrared spectrum of 46 shows a band at  $1900 \text{ cm}^{-1}$

which is assigned to  $\nu(\text{Ir-H})$  with the hydrogen atom

trans to the chlorine atom. The high field  $\nu(\text{Ir-H})$  band

confirms the presence of an iridium-hydrogen bond; a high

value and the small splittings suggest that the hydrogen atom

is trans to the chlorine atom but cis to three phosphorus

nuclei to which it is equally coupled.

Figure 5-1. Proposed stereochemistries for complexes 45 and 46.



The product 47 results from the cleavage of the chlorine bridge in the complex  $[\text{IrCl}(1,5\text{-C}_8\text{H}_{12})]_2$  by the phosphite ligand. Similar complexes of type  $\text{MCl}[1,5\text{-C}_8\text{H}_{12})\text{L}$  ( $\text{M}=\text{Ir}, \text{Rh}$ ,  $\text{L}$  = tertiary phosphine) have been reported.<sup>39,92</sup> The next step is the displacement of the diene by the ligand  $\text{L}$  to yield 48 as a supposed intermediate, which readily isomerizes to form the more stable iridium(III) complex 45. Finally 46 is formed probably with hydrogen expulsion when product 45 is heated in an inert solvent.

Attempts to reconvert 46 to 45 by addition of hydrogen at one atmosphere to complex 46 failed. Apparently under these conditions the reaction 45 to 46 is irreversible.

c. Isomerization of the iridium(I) complex,  $\text{IrCl}(\text{MePh}_2\text{P})_3$  (3)

On heating complex 3 (see chapter 2, section e) in benzene for several hours, it is converted into a pale cream complex (49) of the same empirical formula. The reaction also yields a white solid (5%) identified tentatively as the iridium(III) complex  $\text{IrHCl}_2(\text{MePh}_2\text{P})_3$  from its infrared spectrum [ $\nu(\text{Ir-H}) = 2250\text{cm}^{-1}$ ].

The infrared spectrum of 49 shows a band at  $2200\text{cm}^{-1}$  which is assigned to  $\nu(\text{Ir-H})$ , with the hydrogen atom possibly trans to the chlorine atom. The high field n.m.r. spectrum confirms the presence of an iridium-hydrogen bond; a 1:3:3:1 quartet,  $J_{\text{P-H}} = 15\text{Hz}$ , is observed at  $28.1\tau$ . The high  $\tau$ -value and the small splittings suggest that the hydrogen atom is trans to the chlorine atom but cis to three phosphorus nuclei to which it is equally coupled.

Figure 5-2 shows the methyl resonances of complex 49, the phosphorus decoupled spectrum between 7-10 $\tau$  and the proposed stereochemistry. The phosphorus decoupled spectrum shows three singlets of equal intensity. This clearly eliminates the possibility that the hydrogen atom is abstracted from a methyl group. Phosphorus decoupling experiments on the methyl resonances indicate that there are three inequivalent phosphorus nuclei, A, B and C, (figure 5-2) around the iridium atom. A large phosphorus-phosphorus coupling constant is observed between two of the phosphorus nuclei, say A and B; thus,  $J_{A-B} = 374\text{Hz}$ . Couplings between phosphorus nuclei A and C, and between B and C are not observed. This large coupling constant suggests that phosphorus nuclei A and B although inequivalent are probably mutually trans, and also cis to phosphorus nucleus C.<sup>91</sup> The inequivalence of  $P_A$  and  $P_B$  is probably due to the fact that a metal-ortho bond exists between one of the phenyl rings of  $P_B$  and the metal.

The decoupling experiments also show  $\delta\nu_{AB} = 2994\text{Hz}$  (the difference in chemical shifts of nuclei  $P_A$  and  $P_B$ ).

The methyl protons attached to phosphorus nuclei  $P_A$  and  $P_B$  belong to  $ABX_3$  (or  $ABY_3$ ) spin systems ( $J_{X-Y}=0$ ) ( $[A=P_A, B=P_B, X=H \text{ on } P_A, Y=H \text{ on } P_B]$ ). However, since  $\frac{J_{A-B}}{\delta\nu_{AB}} = \frac{1}{8}$ , such systems may be approximated to  $AMX_3$  ( $AMY_3$ ) systems ( $M=P_B$ ). The X or Y protons of such systems generally appear as two doublets. The methyl protons (Z) attached to  $P_C$  belong to an  $AX_3$  spin system, the X portion of which appears as a doublet.

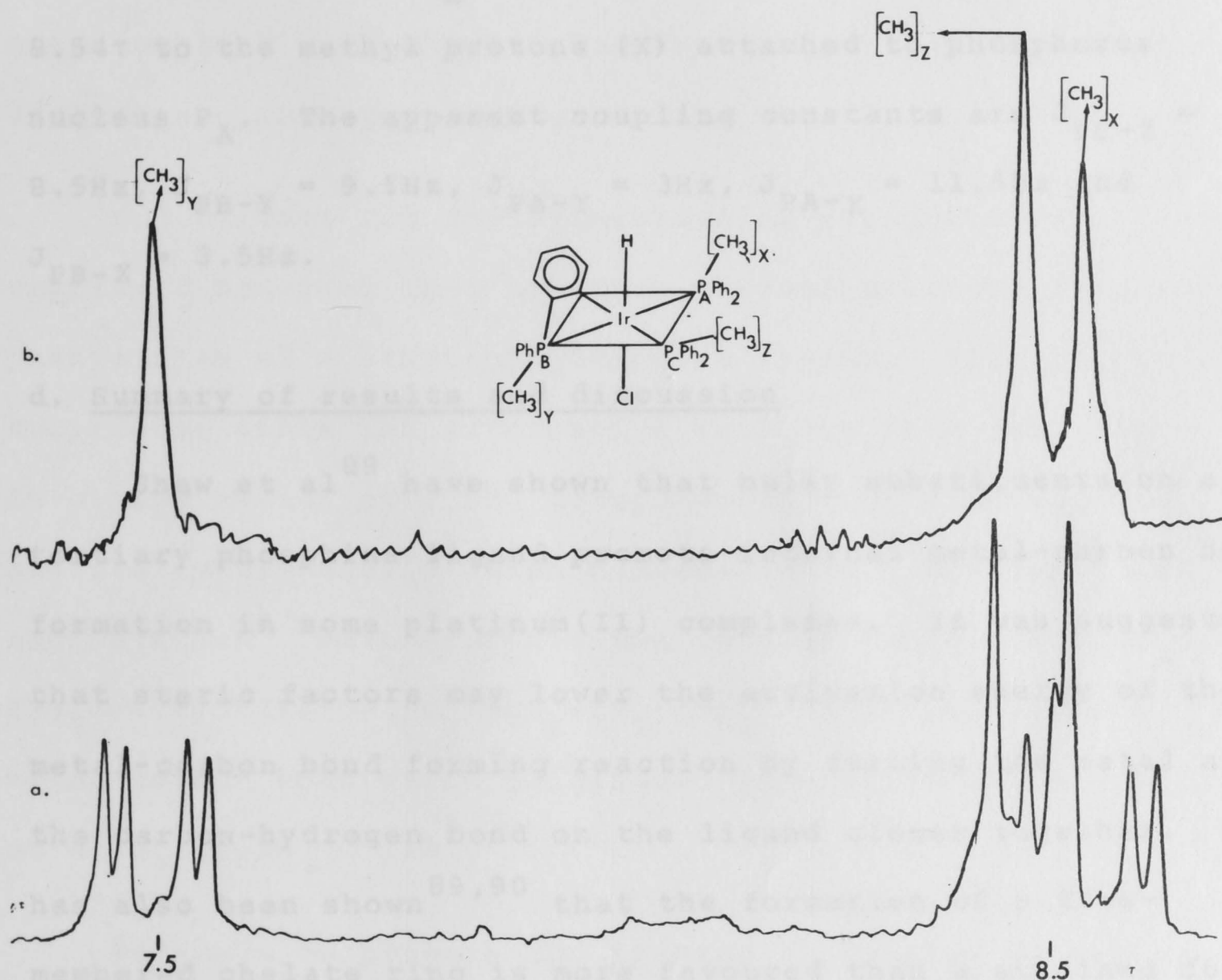
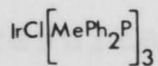


Figure 5-2. a. The methyl resonances of the product obtained from the isomerization of the complex



b. The  $^{31}\text{P}$  decoupled spectrum.



The methyl protons (Z) attached to the phosphorus nucleus  $P_C$  give rise to a doublet ( $J_{P-H} = 8.5\text{Hz}$ ) at  $8.46\tau$ ; these protons do not experience coupling with phosphorus nuclei  $P_A$  or  $P_B$ . The two doublets centred at  $7.51\tau$  are tentatively assigned to the methyl protons (Y) attached to phosphorus nucleus  $P_B$ , and the two doublets centred at  $8.54\tau$  to the methyl protons (X) attached to phosphorus nucleus  $P_A$ . The apparent coupling constants are  $J_{PC-Z} = 8.5\text{Hz}$ ,  $J_{PB-Y} = 9.5\text{Hz}$ ,  $J_{PA-Y} = 3\text{Hz}$ ,  $J_{PA-X} = 11.5\text{Hz}$  and  $J_{PB-X} = 3.5\text{Hz}$ .

#### d. Summary of results and discussion

Shaw et al.<sup>89</sup> have shown that bulky substituents on a tertiary phosphine ligand promote internal metal-carbon bond formation in some platinum(II) complexes. It was suggested<sup>89</sup> that steric factors may lower the activation energy of the metal-carbon bond forming reaction by forcing the metal and the carbon-hydrogen bond on the ligand closer together. It has also been shown<sup>89,90</sup> that the formation of a five-membered chelate ring is more favoured than a strained four- or six-membered ring.

The results from this work lend support to these observations. The isomerization of complex 3 (10 hours) is much slower than that of the triphenylphosphine analogue (1 hour); this would be expected assuming steric factors are important in the rate of isomerization since triphenylphosphine is bulkier than methyldiphenylphosphine. On the other hand attempts to prepare complex  $\text{IrCl}[(\text{PhO})_3\text{P}]_3$  give the iridium-(III) chelate  $\sigma$ -phenyl complex (45a). This clearly shows

that hydrogen migration and metal-ortho-carbon bond formation occur more readily in triphenylphosphite complexes than in triphenylphosphine complexes, owing to the stability of the chelate five-membered ring compared with that of the strained four-membered ring; triphenylphosphine ligands are considered to cause more steric hindrance about the metal atom compared with the triphenylphosphite ligands when these ligands are in a cis-configuration.<sup>9</sup>

N.m.r. data for the isomerization product of the complex 3 confirms that hydrogen migration occurs from a phenyl ring of a triphenylphosphine ligand. This is not surprising since the alternative path for this reaction, involving attack at a CH<sub>3</sub> group, would give rise to less sterically favourable three-membered ring. However Chatt and Davidson<sup>93</sup> have prepared the complex RuH(CH<sub>2</sub>.PMe.CH<sub>2</sub>CH<sub>2</sub>-PMe<sub>2</sub>)<sub>2</sub>(PP) [(PP) = Me<sub>2</sub>P-CH<sub>2</sub>-CH<sub>2</sub>-PMe<sub>2</sub>] which possesses a metal-carbon bond which originated from attack of the metal at a CH<sub>3</sub> group of (PP).

Attempts to prepare the iridium(I) complex of the type IrCl[(PhO)<sub>3</sub>P]L<sub>2</sub> (48) give rise to formation of metal-ortho-carbon bonded complexes 45; on heating in an inert solvent, hydrogen is lost and a second metal-ortho-carbon bond is formed to a second phenyl ring of the triphenylphosphite. These reactions clearly illustrate the importance of stereochemical factors in promoting and directing intramolecular metal-carbon bond formation since the sterically favourable five-membered ring is formed in both reactions.

Table 5-1

N.m.r. and infrared data for the complexes  $\text{IrHCl}[(\text{O}-\text{C}_6\text{H}_4\text{O})(\text{PhO})_2\text{P}]_2\text{L}_2$

Complex when L=	$\nu(\text{Ir-H})^a$ cm <sup>-1</sup>	$\tau(\text{Ir-H})^{b,c}$ $\tau$	$J_t^e$ Hz	$J_c^e$	$\tau(\text{P-CH}_3)^c$ $\tau$	$J_{\text{P-H}}$ Hz
(PhO) <sub>3</sub> P	2080	19.75 (2t)	277.5	18		
Ph <sub>3</sub> P	2127	21.25 (2t)	158	16.5		
Ph <sub>3</sub> As	2150	23.3 (d)		18		
MePh <sub>2</sub> P	2115	20.74 (4d)	157.5	18.0	7.84 (d; 3)	8
				15.0	8.12 (d; 3)	8
Me <sub>2</sub> PhP	2050	20.58 (2t)	156	18	8.3 (d; 6)	10
					8.64 (d; 6)	10
					8.38 (d; 12)	10

a... all spectra were measured in the solid state as nujol mulls.

b... all spectra were measured in CDCl<sub>3</sub>.

c... 2t represents two triplets centred at the  $\tau$ -value listed.

d represents doublet.

4d see results and discussion.

e...  $J_t = J_{\text{P-H}}$  when P is trans to H.

$J_c = J_{\text{P-H}}$  when P is cis to H.



e. Experimental

See Chapter 2, section e for general physical measurements and preparation of the complexes  $\text{IrCl}(\text{MePh}_2\text{P})_3$ ,  $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$  and  $[\text{IrCl}(1,5\text{-C}_8\text{H}_{12})]_2$ .

Hydrogen Abstraction Reactions

A. Preparation of  $\text{IrHCl}[(\text{o-C}_6\text{H}_4)(\text{MePh})\text{P}](\text{MePh}_2\text{P})_2$

The complex chlorotris(methyldiphenylphosphine)iridium-(I) (0.5g) was refluxed in deoxygenated benzene (10 ml) under nitrogen for 10 hours. The dark red solution had become orange at the end of this period. The solution was then cooled and filtered from white solid identified tentatively as the complex  $\text{IrHCl}_2(\text{MePh}_2\text{P})_3$  from its infrared spectrum [ $\nu(\text{Ir-H}) = 2250\text{cm}^{-1}$ ; 5% yield]. The benzene filtrate was evaporated at  $25^\circ$  (15mm) yielding a reddish-brown oil. A pale cream solid was obtained when light petroleum ether (b.p.  $60\text{-}80^\circ$ ; 30 ml) was added to the oil. Recrystallization from tetrahydrofuran/heptane gave pale cream crystals (0.3g) of the product). (64% yield).

[Found: C, 56.5; H, 4.7; Cl, 4.3. Calcd. for  $\text{C}_{39}\text{H}_{39}\text{ClIrP}_3$ : C, 56.8; H, 4.9; Cl, 4.6].

B. Preparation of  $\text{IrHCl}[(\text{o-C}_6\text{H}_4\text{O})(\text{PhO})_2\text{P}][(\text{PhO})_3\text{P}]_2$

To the complex  $[\text{IrCl}(\text{C}_8\text{H}_{14})_2]_2$  (0.2g) suspended in sodium-dried benzene (5 ml) was added dropwise triphenylphosphite (0.46g). The yellow suspension dissolved almost immediately to give a colourless solution. Solvent was removed at  $25^\circ$  (15 mm) and the residual oil dissolved in

sodium-dried ether (5 ml). The solution deposited white crystals after several hours at 0°. Two recrystallizations from diethyl ether gave 0.4g (77%) of white crystals of the product. M.P. 146-147°.

[Found: C, 56.0; H, 3.8; Cl, 2.8; P, 7.9; mol.wt. (CHCl<sub>3</sub>) 1149. Calcd. for C<sub>54</sub>H<sub>45</sub>ClIrO<sub>9</sub>P<sub>3</sub>: C, 56.0; H, 3.9; Cl, 3.1; P, 8.0; mol.wt. 1158.]

### C. Preparation of RhCl[(PhO)<sub>3</sub>P]<sub>3</sub>

This was carried out as above (B), using the complex [RhCl(C<sub>8</sub>H<sub>14</sub>)<sub>2</sub>]<sub>2</sub> (1 mol. propn.) and triphenylphosphite (6 mol. propn.). The oil, after recrystallization from methanol or ether gave yellow crystals of RhCl[(PhO)<sub>3</sub>P]<sub>3</sub> identical with those obtained by treating either [RhCl(CO)<sub>2</sub>]<sub>2</sub> or [RhCl(1,5-C<sub>8</sub>H<sub>12</sub>)]<sub>2</sub> with triphenylphosphite.<sup>97,98</sup>

### D. Preparation of complexes IrHCl[(o-C<sub>6</sub>H<sub>4</sub>O)(PhO)<sub>2</sub>P]L<sub>2</sub>;

L = Ph<sub>3</sub>P, Ph<sub>3</sub>As, MePh<sub>2</sub>P, Me<sub>2</sub>PhP

To a solution of [IrCl(1,5-C<sub>8</sub>H<sub>12</sub>)]<sub>2</sub> (0.3g; 1 mol. propn.) in hexane (30 ml) and dichloromethane (10 ml) was added dropwise triphenylphosphite (0.28g; 1 mol. propn.). The solution was refluxed for 1 hour. After this time dichloromethane was evaporated off at 25° (15 mm.). To the remaining solution, ligand L (2.5 mol. propn.) was added and solution refluxed for 1/2-2 hours. White solid precipitated out during the final period of refluxing. The solid was filtered and crystallization from tetrahydrofuran/heptane gave white crystals of the products.

Analyses of the products:

When L=	%C	%H	%Cl	Mol. Wt.
Ph <sub>3</sub> P	c. 61.04	4.26	3.24	
	f. 61.28	4.30	3.20	
MePh <sub>2</sub> P	c. 56.32	4.40	3.78	938
	f. 56.17	4.58	3.70	887
Ph <sub>3</sub> As	c. 56.38	3.94	3.08	
	f. 56.18	3.96	3.21	
Me <sub>2</sub> PhP	c. 50.15	4.58	4.35	814
	f. 50.10	4.69	4.19	780

In the above preparation, the intermediate  $\text{IrCl}(1,5\text{-C}_8\text{H}_{12})\text{-}[(\text{PhO})_3\text{P}]$  was isolated and identified by its n.m.r. spectrum. Before addition of the ligand L, the solution was evaporated at 25° (15 mm) yielding an orange solid which upon recrystallization from dichloromethane/petroleum spirit (b.p. 40-60°) gave orange crystals of the complex  $\text{IrCl}(1,5\text{-C}_8\text{H}_{12})[(\text{PhO})_3\text{P}]$ . N.m.r. in deuteriochloroform : Ph:2.6-3τ (area 15),

$(-\text{CH}_2^-)_4$  : 8.1τ(m)

olefinic protons : 4.6τ(m,2)

and 6.75τ(m,2).

E. Preparation of complexes  $\text{IrCl}[(\text{o-C}_6\text{H}_4\text{O})_2(\text{PhO})_2\text{P}]_2\text{L}_2$ ;

L = Ph<sub>3</sub>P, MePh<sub>2</sub>P, Me<sub>2</sub>PhP.

The complex  $\text{IrHCl}[(\text{o-C}_6\text{H}_4\text{O})_2(\text{PhO})_2\text{P}]_2$  (0.5g),

(L = Ph<sub>3</sub>P, MePh<sub>2</sub>P, Me<sub>2</sub>PhP) was refluxed in toluene/heptane (1:1)



under nitrogen for 10 hours. When the solution was cooled to 0°C white crystals of the products precipitated out. These were filtered and recrystallization from hot benzene/heptane gave beautiful white crystals of the products.

Analyses of the products:

When L=	%C	%H	%Cl	mol.wt.
Ph <sub>3</sub> P	c. 61.16	4.09	3.34	
	f. 62.14	4.20	2.98	
MePh <sub>2</sub> P	c. 56.44	4.19	3.79	937
	f. 56.76	4.24	3.65	892
Me <sub>2</sub> PhP	c. 50.28	4.34	4.36	813
	f. 50.34	4.42	4.27	775

## CHAPTER 6

FINAL DISCUSSION

In Chapter 1 brief mention was made of the factors which influence oxidative addition reactions. The tendency for  $d^8$  complexes to undergo oxidative addition reactions depends markedly on the nature of the central metal ion and the ligands attached to it. This tendency increases upon descending a triad (Co, Rh, Ir) and is enhanced by ligands which increase electron density at the central metal.

Nyholm<sup>99,100</sup> has pointed out that the ease with which  $M(x) \longrightarrow M(x+2)$  (i.e.  $d^8 \longrightarrow d^6$ ) valency change occurs depends on the energy required to promote an electron from a  $nd$  orbital to a  $(n+1)p$  orbital. For the vertical sequence Co, Rh, and Ir comparative data are difficult to obtain; however, for the somewhat similar promotion process  $(n)d^{10} \longrightarrow nd^9(n+1)p^1$  for  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Hg^{2+}$  the promotion energies are in the order,  $Zn^{2+} > Cd^{2+} > Hg^{2+}$ , i.e. 1st row > 2nd row > 3rd row.<sup>99</sup> Therefore by comparison it should be easier to oxidize Ir(I) to Ir(III) than it is to oxidize Rh(I) to Rh(III). The promotion energy increases as the formal positive charge of the metal atom increases and thus, the nature of the attached ligands should affect the promotion energy. Ligands which reduce the formal positive charge on the metal atom (i.e. increase the electron density on the metal atom) have been shown to enhance the oxidation from  $M(x) \longrightarrow M(x+2)$ . Thus, triphenylphosphine should be a better ligand than carbon monoxide for promoting oxidative addition reactions; since carbon monoxide is a better

$\pi$ -bonding ligand than triphenylphosphine and should therefore decrease the electron density (or increase the formal positive charge) on the metal atom.<sup>101,102,103</sup>

The energy of dissociation of the bond in the addend molecule (XY) (X-Y bond) and the energy of formation of X and Y to the metal must also be considered to be involved in the oxidation of a  $d^8$  complex to a  $d^6$  complex by addition of molecule XY.

Therefore, the expected reactivity trends for complexes  $\text{IrCl}(\text{Ph}_3\text{P})_3$  (1),  $\text{RhCl}(\text{Ph}_3\text{P})_3$  (23),  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$  (11) and  $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$  (50) to undergo oxidative addition reactions would be  $\text{IrCl}(\text{Ph}_3\text{P})_3 > \text{RhCl}(\text{Ph}_3\text{P})_3 > \text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$  and  $\text{IrCl}(\text{Ph}_3\text{P})_3 > \text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2 > \text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ .

The failure of complex 50 to activate hydrogen is in contrast to the ability of the iridium analogue (11) to give reversible hydrogen activation and a cis-dihydride iridium(III) product. Hydrogen adds to complex 23 reversibly yielding a five-coordinate di-hydride product whereas its addition to complex 1 is irreversible and the product obtained is a six-coordinate iridium(III) complex. The difference of reactivity in these reactions may be ascribed to (i) the lower promotional energy for Ir(I) to Ir(III) system compared with the Rh systems and (ii) the somewhat increased strength of the Ir-H bonds compared to Rh-H. The greater reactivity of complex 1 to undergo addition reactions compared with its rhodium analogue 23 is borne out by the fact that complex 1 readily isomerizes in solution to give a hydrido-iridium(III)- $\sigma$ -bonded aryl complex,<sup>36</sup> the hydrogen atom being extracted from a triphenylphosphine ligand, whereas



complex 23 does not isomerize similarly. Again this difference may be due to the lower promotional energies for  $\text{Ir(I)} \longrightarrow \text{Ir(III)}$  and the stronger Ir-H bond.

The reactions of silicon hydrides including triphenylsilane and complex 1 are very similar to those with complex 23; both systems give stable Rh(III) and Ir(III) five-coordinate adducts. In contrast, complex 11 does not add triphenylsilane.<sup>16</sup> Similarly, diphenylacetylene, phenylacetylene and dimethyl acetylene dicarboxylate react readily with complex 1 yielding stable iridium(III) products whereas no isolatable adducts are obtained in their reactions with complex 11.<sup>31</sup>

Wilkinson et al<sup>66</sup> have suggested that the factors which govern the stabilities of the acyl derivatives,  $\text{MX}_2(\text{CO.R}^1)(\text{PR}_3^2)_2\text{L}[\text{M}=\text{Ir,Rh}]$  towards dissociation of  $\text{R}^1\text{COX}$  depend on the nature of X,  $\text{R}^1$ ,  $\text{R}^2$  and L. Acetyl chloride adds to trans- $\text{RhCl}(\text{CO})(\text{Et}_2\text{PhP})_2$  to give the acyl complex,  $\text{RhCl}_2(\text{CO.Me})(\text{CO})(\text{Et}_2\text{PhP})_2$ <sup>104</sup> while the complex  $\text{RhClI}(\text{Me})(\text{CO})(\text{Bu}_3^{\text{n}}\text{P})_2$  absorbs carbon monoxide to give the compound  $\text{RhClI}(\text{CO.Me})(\text{CO})(\text{Bu}_3^{\text{n}}\text{P})_2$ .<sup>70</sup> However acetyl chloride does not add to trans- $\text{RhCl}(\text{CO})(\text{Ph}_3\text{P})_2$ , while addition of carbon monoxide to the complexes  $\text{RhCl}_2(\text{CO.R})(\text{Ph}_3\text{P})_2$  [R=Me or Et] results in spontaneous loss of  $\text{RCOCl}$ .<sup>66</sup> It was therefore suggested<sup>66</sup> that the greater  $\pi$ -acidity of triphenylphosphine in the latter complex is stabilising the I oxidation state in the rhodium series, while the former complexes (containing  $\text{Et}_2\text{PhP}$  and  $\text{Bu}_3^{\text{n}}\text{P}$ ) are stable, because of the lower  $\pi$ -acidity and higher polarisability of the aliphatic phosphines. In contrast, the analogous iridium complexes,  $\text{IrX}_2(\text{CO.R})(\text{CO})(\text{Ph}_3\text{P})_2$  can

be isolated.<sup>104</sup> The addition of acid chlorides to complex 1 give stable alkyl-iridium(III)-carbonyl complexes with the loss of 1 mole of triphenylphosphine. However the reaction of acyl chlorides and complex 23 give in most cases the acyl complexes  $\text{RhCl}_2(\text{CO}\cdot\text{R})(\text{Ph}_3\text{P})_2$ . Although these products are coordinatively unsaturated, only in the cases where  $\text{R}=\text{Me}$  or  $\text{Ph}$ , it is possible to isolate alkyl-rhodium(III)-carbonyl complexes. This difference reflects the generally higher stabilities of alkyl complexes of the third-row transition elements.<sup>75</sup>

The results outlined in this thesis therefore support the observed trend that ligands which increase the electron density at the central metal enhance the tendency of a  $d^8$  complex to undergo oxidative addition, i.e.  $\text{Ph}_3\text{P} > \text{CO}$ . This observation is borne out by the fact that the complex  $\text{IrCl}(\text{Ph}_3\text{P})_3$  is a better nucleophile than complex  $\text{IrCl}(\text{CO})(\text{Ph}_3\text{P})_2$ .

14. P. S. Piper, D. W. Lavel and G. Wilkinson, *Naturwissenschaften*, 1956, 41, 127.

15. P. G. A. Stone, *New Pathways in Organometallic Chemistry*, Edited by K. A. V. Ebsworth, A. G. Macdonald, R. C. Sherpe, Camb. Univ. Press, 1962, 202.

16. J. P. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, 1965, 87, 184.

17. W. R. R. Graham and A. J. Oliver, *Inorg. Chem.*, 1971, 10, 3.

18. R. M. Hazeldine, R. G. Parish and G. J. Parker, *J. Chem. Soc. (B)*, 1969, 663.

19. J. Chatt, C. Eaborn and P. H. Kapoor, *J. Chem. Soc. (A)*, 1970, 601.

20. W. Jett, F. B. Simeon, J. A. J. Thompson and W. R. R. Graham, *Inorg. Chem.*, 1966, 5, 2117.

References

1. J. P. Collman, Accounts Chem. Res., 1968, 1, 136.
2. J. P. Collman and W. R. Roper, Advances in Organometallic Chem., 1968, 7, 53.
3. L. Vaska, Accounts Chem. Res., 1968, 1, 335.
4. J. Halpern, Accounts Chem. Res., 1970, 3, 386.
5. R. S. Nyholm and M. L. Tobe, Experientia Suppl., 1964, 9, 112.
6. P. B. Chock and J. Halpern, J. Amer. Chem. Soc., 1966, 88, 3511.
7. J. F. Harrod, D. F. R. Gilson and R. Charles, Canad. J. Chem., 1969, 47, 2205.
8. J. F. Harrod and C. A. Smith, Canad. J. Chem., 1970, 48, 870.
9. J. A. Osborn, F. H. Jardine, F. H. Young and G. Wilkinson, J. Chem. Soc.(A), 1966, 1711.
10. D. N. Lawson, J. A. Osborn and G. Wilkinson, J. Chem. Soc.(A), 1966, 1733.
11. B. L. Shaw and J. M. Jenkins, Proc. Chem. Soc., 1963, 279.
12. A. P. Ginsberg, "Transition Metal Chemistry", Edited by R. L. Carlin, 1965, 1, 111.
13. B. L. Shaw and J. M. Jenkins, J. Chem. Soc.(A), 1965, 6789.
14. T. S. Piper, D. M. Lemal and G. Wilkinson, Naturwissenschaften, 1956, 43, 129.
15. F. G. A. Stone, "New Pathways in Inorganic Chemistry" Edited by E. A. V. Ebsworth, A. G. Maddock, A. G. Sharpe, Camb. Univ. Press, 1968, 283.
16. J. F. Harrod and A. J. Chalk, J. Amer. Chem. Soc., 1965, 87, 16.
17. W. A. G. Graham and A. J. Oliver, Inorg. Chem., 1971, 10, 1.
18. R. N. Haszeldine, R. U. Parish and D. J. Parry, J. Chem. Soc.(A), 1969, 683.
19. J. Chatt, C. Eaborn and P. N. Kapoor, J. Chem. Soc.(A), 1970, 881.
20. W. Jetz, P. B. Simons, J. A. J. Thompson and W. A. G. Graham, Inorg. Chem., 1966, 5, 2217.



21. J. D. Cotton, S. A. R. Knox and F. G. A. Stone, Chem. Comm., 1967, 965.
22. W. Jetz and W. A. G. Graham, J. Amer. Chem. Soc., 1967, 89, 2773.
23. D. J. Cardin, S. A. Keppie, B. M. Kingston and M. F. Lappert, Chem. Comm., 1967, 1035.
24. M. C. Baird, J. Inorg. Nucl. Chem., 1967, 29, 367.
25. F. de Charentenay, J. A. Osborn and G. Wilkinson, J. Chem. Soc.(A), 1968, 787.
26. K. W. Muir and J. A. Ibers, Inorg. Chem., 1970, 9, 440.
27. R. C. Taylor, J. F. Young and G. Wilkinson, Inorg. Chem., 1966, 5, 20.
28. J. Chatt, R. S. Coffey and B. L. Shaw, J. Chem. Soc. (A), 1965, 7391.
29. A. L. Smith and N. C. Angelotti, Spectrochem. Acta, 1959, 15, 412.
30. J. M. Jenkins and B. L. Shaw, J. Chem. Soc.(A), 1966, 1407.
31. J. P. Collman and J. W. Kang, J. Amer. Chem. Soc., 1967, 89, 844.
32. J. P. Collman and C. T. Sears Jr., Inorg. Chem., 1968, 7, 27.
33. A. J. Chalk, Chem. Comm., 1969, 1207.
34. L. H. Sommer, J. E. Lyons and H. Fujimoto, J. Amer. Chem. Soc., 1969, 91, 7051.
35. J. Chatt, C. Eaborn and S. Ibekwe, Chem. Comm., 1966, 700.
36. M. A. Bennett and D. L. Milner, J. Amer. Chem. Soc., 1969, 91, 6983.
37. J. F. Young, Advances in Inorg. Chem and Radio Chem., 1968, 11, 92.
38. B. L. Shaw and E. Singleton, J. Chem. Soc.(A), 1967, 1683.
39. G. Winkhaus and H. Singer, Chem. Ber., 1966, 99, 3610.
40. F. L. Bowden and A. B. P. Lever, Organometallic Chem. Rev. Sect.A, 1968, 3, 227.
41. M. L. H. Green, "Organometallic Compounds - The transition elements", Vol. 2, 1968, 288.
42. W. Hubel, "Organic Synthesis via metal carbonyl", Edited by I. Wender and P. Pino, Vol.1, 1968, 273.

43. G. N. Schrauzer, Angew. Chem. Int. Ed. English, 1964, 3, 185.
44. G. N. Schrauzer, Advances in Organometallic Chem., 1964, 2, 27.
45. L. S. Meriwether, M. F. Leto, E. C. Colthup and G. W. Kennerly, J. Org. Chem., 1962, 27, 3930.
46. R. G. Guy and B. L. Shaw, Advances in Inorg. Chem. and Radio Chem., 1962, 4, 77.
47. M. J. Grogan and K. Nakamoto, J. Amer. Chem. Soc., 1966, 88, 5454.
48. J. Chatt, B. L. Shaw and A. A. Williams, J. Chem. Soc. (A), 1969, 3269.
49. G. W. Parshall and F. N. Jones, J. Amer. Chem. Soc., 1965, 87, 5356.
50. K. Kahanishi, "Infrared Absorption Spectroscopy" Holden Day, San Francisco, 1962, 8.
51. C. K. Brown and G. Wilkinson, Chem. Comm., 1971, 70.
52. G. E. Coates and C. Parkin, J. Chem. Soc. (A), 1962, 3220.
53. B. Clarke, M. Green and F. G. A. Stone, J. Chem. Soc. (A), 1970, 951.
54. J. T. Mague and G. Wilkinson, J. Chem. Soc. (A), 1966, 1736.
55. J. P. Collman, J. W. Kang, W. F. Little and M. F. Sullivan, Inorg. Chem., 1968, 7, 1298.
56. J. Chatt, G. A. Rowe and A. A. Williams, Pro. Chem. Soc., 1957, 208.
57. J. Chatt, R. G. Guy, L. A. Duncanson and D. T. Thompson, J. Chem. Soc. (A), 1963, 5170.
58. J. Chatt, L. A. Duncanson and R. G. Guy, J. Chem. Soc. (A), 1961, 827.
59. G. R. Davies, W. Hewertson, R. H. B. Mais and P. G. Owston, Chem. Comm., 1967, 423.
60. J. O. Glanville, J. M. Stewart and S. O. Grim, J. Organometallic Chem., 1967, 7, P9.
61. R. Nast, Abs. Internat. Conf. Coord. Chem., London, Chem. Soc. (London) Spec. Publ., 1959, 13, 103.
62. J. T. Mague and G. Wilkinson, Inorg. Chem., 1968, 7, 542.
63. J. T. Mague, Inorg. Chem., 1970, 9, 1617.

64. J. Blum, E. Oppenheimer and E. D. Bergmann, J. Amer. Chem. Soc., 1967, 89, 2338.
65. K. Ohno and T. Tsuji, J. Amer. Chem. Soc., 1968, 90, 99.
66. M. C. Baird, J. T. Mague, J. A. Osborn and G. Wilkinson, J. Chem. Soc.(A), 1967, 1347.
67. T. Tsuji and K. Ohno, J. Amer. Chem. Soc., 1966, 88, 3452.
68. J. Chatt, N. P. Johnson and B. L. Shaw, J. Chem. Soc. (A), 1967, 604.
69. A. J. Deeming and B. L. Shaw, J. Chem. Soc.(A), 1969, 1128.
70. R. F. Heck, J. Amer. Chem. Soc., 1964, 86, 2796.
71. I. C. Douek and G. Wilkinson, J. Chem. Soc.(A), 1969, 2604.
72. F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, 2nd Ed. Wiley, New York, NY 1967, pp. 578-609.
73. B. L. Booth, R. N. Haszeldine and N. P. Woffenden, J. Chem. Soc.(A), 1970, 1979 and references cited therein.
74. R. F. Heck, "Inorganic Reaction Mechanisms", pp. 181-219, "Advances in Chemistry" Series No. 49, Amer. Chem. Soc., Washington D.C., 1966.
75. G. W. Parshall and J. J. Mrowca, Advances in Organometallic Chem., 1968, 7, 157.
76. J. F. Harrod and A. J. Chalk, Advances in Organometallic Chem., 1967, 6, 119.
77. R. F. Heck, Advances in Organometallic Chem., 1966, 4, 243.
78. C. W. Bird, Chem. Rev., 1962, 62, 283.
79. J. R. Dyer, "Applications of Absorption Spectroscopy of organic compounds", pp. 81-82.
80. L. H. Slaugh and R. D. Mullineaux, J. Organometallic Chem., 1968, 13, 469.
81. F. H. Jardine, J. A. Osborn, G. Wilkinson and J. F. Young, Chem. and Ind., 1965, 560.
82. D. M. Blake and M. Kubota, J. Amer. Chem. Soc., 1971, 93, 1368.
83. D. M. Blake, S. A. Smith and M. Kubota, Inorg. Chem., 1971, 10, 1430.



84. G. W. Parshall, Accounts Chem. Res., 1970, 3, 139.
85. W. Keim, J. Organometallic Chem., 1968, 14, 179.
86. G. W. Parshall, W. H. Knott and R. A. Schunn, J. Amer. Chem. Soc., 1969, 91, 4990.
87. E. W. Ainscough and S. D. Robinson, Chem. Comm., 1970, 863.
88. J. M. Guss and R. Masson, Chem. Comm., 1971, 58.
89. A. J. Cheney, B. E. Mann, B. L. Shaw and R. N. Slade, Chem. Comm., 1970, 1176.
90. E. W. Ainscough and S. D. Robinson, Chem. Comm., 1971, 130.
91. J. F. Nixon and A. Pidcock, Annual Rev. N.M.R. Spectroscopy, 1969, 2, 345.
92. S. O. Grim and R. A. Ferrence, Inorg. Chem. Acta, 1970, 4, 277.
93. J. Chatt and J. M. Davidson, J. Chem. Soc.(A), 1965, 843.
94. R. Adams and L. Ulich, J. Amer. Chem. Soc., 1920, 42, 599.
95. Coll. Org. Syn. Vol. 111, pp. 727 and 733.
96. E. Eliel and J. Freeman, J. Amer. Chem. Soc., 1952, 74, 925.
97. L. Vallarino, J. Chem. Soc., 1957, 2473.
98. L. M. Haines, Inorg. Chem., 1970, 9, 1517.
99. R. S. Nyholm and K. Vrieze, J. Chem. Soc., 1965, 5337.
100. R. S. Nyholm, "Tilden Lecture", Proc. Chem. Soc., 1961, 273.
101. E. W. Abel, M. A. Bennett and G. Wilkinson, J. Chem. Soc., 1959, 2325.
102. W. A. G. Graham, Inorg. Chem., 1968, 7, 320.
103. J. Chatt and S. A. Butter, Chem. Comm., 1967, 501.
104. J. Chatt and B. L. Shaw, J. Chem. Soc.(A), 1966, 1437.