ALKYL GROUP REARRANGEMENTS OF SIX COORDINATE ALKYL IRIDIUM(III) COMPLEXES

by

Geoffrey Thomas Crisp

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The work described in this Thesis is the candidate's own, except where otherwise stated. It was carried out in the Research School of Chemistry, The Australian National University, from 1978 to 1981 during the tenure of a Commonwealth Postgraduate Research Award and Supplement from The Australian National University.

Geoffrey Crisp

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ABBREVIATIONS

AIBN	azobisisobutyronitrile
Bu	butyl
Bu^t	tertiary butyl
CIDNP	chemically induced dynamic nuclear polarisation
Cp	η^5-cyclopentadienyl
δ	chemical shift
DMF	dimethylformamide
DMG	dimethylglyoximato
dmpe	1,2-bis(dimethylphosphino)ethane
DMSO	dimethylsulphoxide
dppe	1,2-bis(diphenylphosphino)ethane
esr	electron spin resonance
Et	ethyl
IR	infrared
Me	methyl
mnt	maleonitriledithiolate
Mp	melting point
nmr	nuclear magnetic resonance
nr	no reaction
ν(CO)	carbon-oxygen stretching vibrational mode, etc.
Ph	phenyl
Pr	propyl
TFA	trifluoroacetic acid

ABSTRACT

This work is concerned with the branched- to linear-alkyl group rearrangement of monoalkyl and dialkyl iridium(III) complexes.

Alkyl iridium(III) complexes of the type, $IrRClI(CO)L_2$ (R = primary and secondary alkyl, L = $PPhMe_2$, PMe_3), are obtained by addition of alkyl iodides to $IrCl(CO)L_2$. Dissolution of *sec*-alkyl iridium(III) complexes in protic solvents (alcohols, water, acids), causes a quantitative *sec*- to *n*-alkyl group rearrangement. Kinetic data and deuterium labelling studies suggest that the mechanism for the rearrangement involves a rate determining loss of iodide (*trans* to the alkyl group), followed by a series of reversible β-hydride migrations and finally, re-entry of iodide *trans* to the rearranged alkyl group.

Substituted-alkyl iridium(III) complexes, $IrR'ClX(CO)L_2$ (R' = electronegatively-substituted alkyl; X = Br, I; L = PPh_2Me, $PPhMe_2$, PMe_3), are also obtained by addition of alkyl halides to $IrCl(CO)L_2$, but do not show any interconversion between the *sec*- and *n*-alkyl isomers.

Alkyl iridium(I) complexes, $IrR''(CO)(PMe_3)_2$ (R" = methyl, trimethylsilylmethyl, phenyl), are obtained by reaction of alkyl-lithium with $IrCl(CO)(PMe_3)_2$. Oxidative addition of alkyl halides, RX, to $IrR''(CO)(PMe_3)_2$ gives dialkyl iridium(III) complexes, $IrR''RX(CO)(PMe_3)_2$, which can undergo *sec*- to *n*-alkyl group rearrangements in benzene/methanol. For the isomerization of *sec*-alkyl complexes containing the bulky trimethylsilylmethyl group reductive elimination of alkane and alkene is competitive with formation of the expected linear alkyl complex. An intermediate, present only during the *sec* to *n*-alkyl group rearrangement, is observed for the methyl and trimethylsilylmethyl complexes.

CHAPTER ONE

Introduction

General.

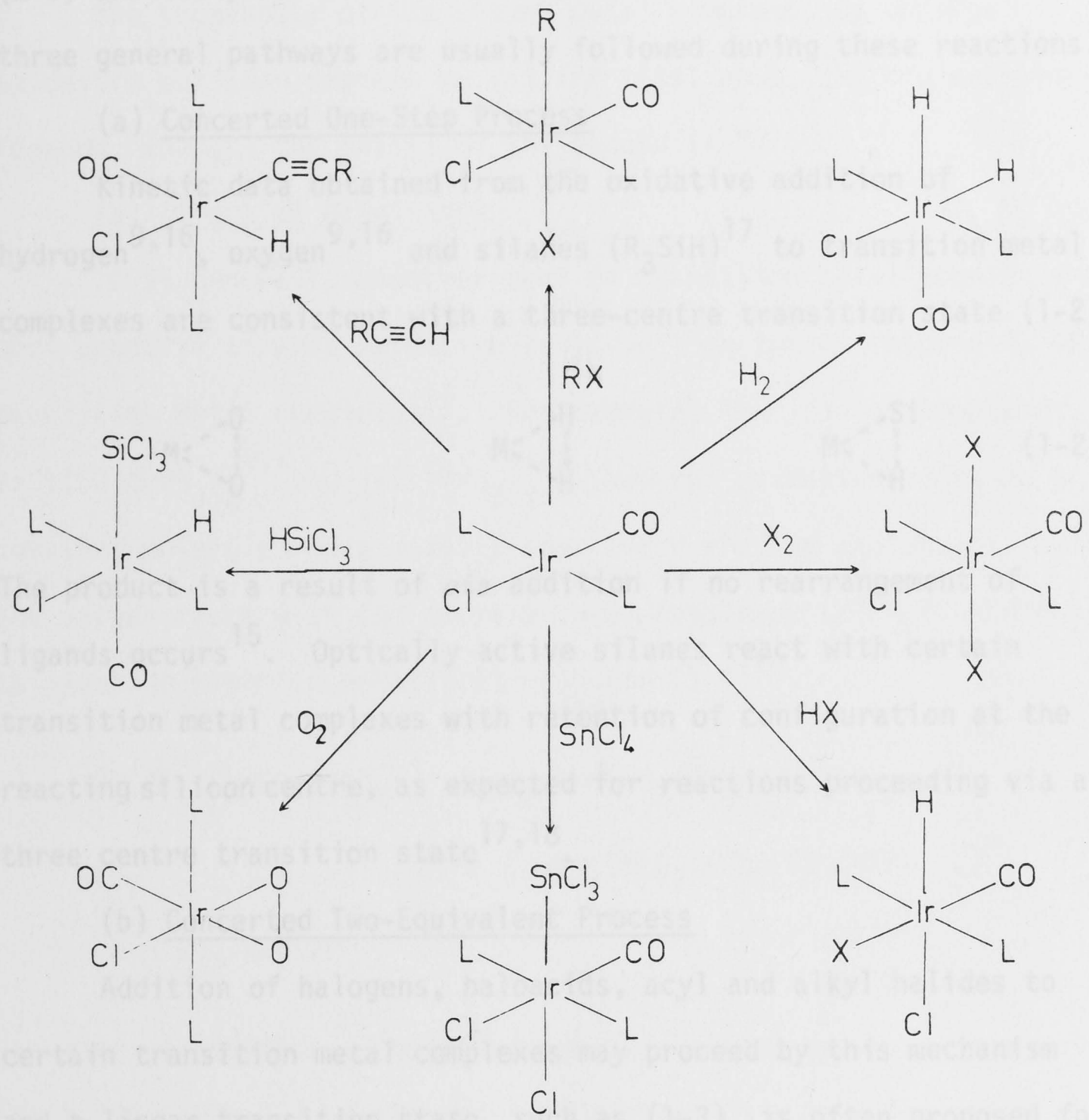
Transition metal complexes have been used in organic synthesis for both stoichiometric and catalytic transformations, some of which are inaccessible to non-metal systems[1-4]. Functional groups may be added to, or removed from, organic molecules under mild conditions and often in a stereoselective manner.

The transition-metal induced reactions that are relevant to this Thesis include decarbonylation of acyl halides[5], hydrogenation[6] and hydroformylation[7] of olefins, and cross-coupling reactions of Grignard reagents with organic halides[8]. These reactions frequently involve the oxidative addition of a covalent molecule (X-Y) to a low-valent transition metal complex. The effect of such an addition is to cleave the (X-Y) bond to form two new bonds to the metal atom and, as a result, to increase the oxidation state and coordination number of the metal by two (1-1).

$$X\text{-}Y \;+\; M^{n} \longrightarrow \begin{matrix} X \\ \diagdown \\ M^{n+2} \\ \diagup \\ Y \end{matrix} \qquad (1\text{-}1)$$

n = oxidation state

This description, although adequate for the reactions discussed in this Thesis, does not include all known examples of oxidative additions. For a more detailed discussion of the scope and mechanism of these reactions a number of review articles are available[9-13]. The range of covalent molecules which can undergo oxidative addition to transition metal complexes is shown in Figure 1 (using the metal complex, $IrCl(CO)L_2$, where L = various tertiary phosphines).



R = alkyl, aryl, acyl

X = Cl, Br, I

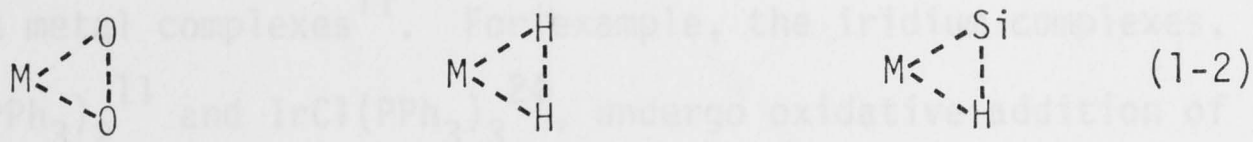
L = tertiary phosphine

Figure 1. Oxidative Addition of Covalent Molecules to $IrCl(CO)L_2$[14].

The mechanism of oxidative addition depends on the addend (X-Y) and the particular metal complex[11,13,15]. Nevertheless, three general pathways are usually followed during these reactions.

(a) Concerted One-Step Process

Kinetic data obtained from the oxidative addition of hydrogen[9,16], oxygen[9,16] and silanes (R_3SiH)[17] to transition metal complexes are consistent with a three-centre transition state (1-2).

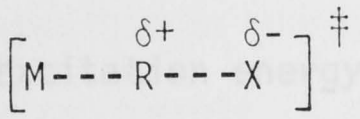


(1-2)

The product is a result of *cis* addition if no rearrangement of ligands occurs[15]. Optically active silanes react with certain transition metal complexes with retention of configuration at the reacting silicon centre, as expected for reactions proceeding via a three centre transition state[17,18].

(b) Concerted Two-Equivalent Process

Addition of halogens, haloacids, acyl and alkyl halides to certain transition metal complexes may proceed by this mechanism and a linear transition state, such as (1-3), is often proposed for these reactions[15,19]. The addition of such addends can involve ionic intermediates and, for alkyl halides, should involve stereochemical inversion at the reacting carbon centre[13,15].



(1-3)

(c) Succession of One-Equivalent Processes (Radicals)

Participation of alkyl radicals during addition of alkyl halides to transition metal complexes is well established[20-23]. The main characteristics of this pathway are the influence of radical

initiators and scavengers on the rate of oxidative addition and racemization of the reacting carbon centre.

The propensity of transition metal complexes to undergo oxidative addition depends on (a) the metal atom, (b) the ancillary ligands, and (c) the nature of the addend (X-Y).

(a) Effect of Metal Atom

It is generally observed that 5d transition metal complexes are more reactive towards oxidative addition than the corresponding 4d transition metal complexes[11]. For example, the iridium complexes, $IrCl(CO)(PPh_3)_2$[11] and $IrCl(PPh_3)_3$[24], undergo oxidative addition of covalent molecules more readily than their rhodium analogues. Hydrogen and oxygen react with the isostructural complexes $[M(Ph_2PCH{=}CHPPh_2)_2]^+$ to give the expected metal(III) products (1-4)[25].

$$[M(Ph_2PCH{=}CHPPh_2)_2]^+ + H_2 \longrightarrow [MH_2(Ph_2PCH{=}CHPPh_2)_2]^+$$
$$+ O_2 \longrightarrow [M(O_2)(Ph_2PCH{=}CHPPh_2)_2]^+ \qquad (1\text{-}4)$$

M = Co, Rh, Ir

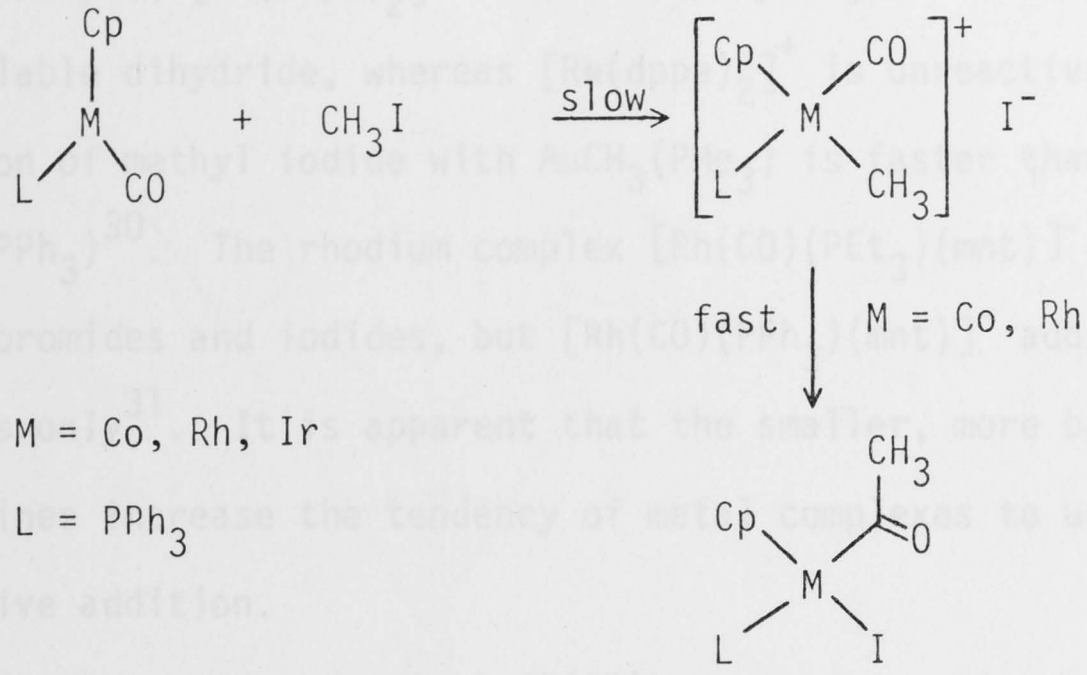
The rate of addition of both hydrogen and oxygen to $[M(Ph_2PCH{=}CHPPh_2)_2]^+$ decreases in the order Co > Ir > Rh, which correlates with the lowest electronic excitation energy for the three complexes (1-5).

$$\text{Co} \quad 13.5; \quad \text{Ir} \quad 19.1; \quad \text{Rh} \quad 24.7 \quad \times 10^3 \text{cm}^{-1} \qquad (1\text{-}5)$$

Since the excitation energy is associated with a d to d transition, the rate of oxidative addition parallels the ease with which an electron can be removed from the metal d orbital.

Alkyl halides react with $CpM(CO)(PPh_3)$ to give neutral acyl complexes when M=Co or Rh, and cationic alkyl complexes when M=Ir (Scheme 1)[26]. The effect of varying the metal atom on the rate of

methyl iodide addition is Ir > Rh > Co, whereas for ethyl iodide addition the order is Ir > Co > Rh.



Scheme 1. Reaction of Methyl Iodide with $CpM(CO)(PPh_3)$.

Structural effects are also important in determining the relative reactivity of different metal complexes towards oxidative addition. For example, tetrahedral complexes are less reactive than square planar complexes, probably because greater ligand reorganization is required in the former compared to the latter[19]. Thus, $RhCl(PPh_3)_3$, shown by x-ray diffraction studies to be square planar (with slight distortions toward tetrahedral geometry)[27], reacts with hydrogen and oxygen[25], whereas $CoCl(PPh_3)_3$, thought to be tetrahedral from spectroscopic properties[28], is unreactive to hydrogen and oxygen[25].

(b) Effect of Ancillary Ligands

Irrespective of the mechanism by which an oxidative addition occurs, the net result is to increase the formal oxidation state of the metal. Therefore, an increase in the electron density on the metal atom should increase the propensity of the metal complex to undergo oxidative addition[19].

The electronic and steric properties of tertiary phosphine ligands can have a dramatic effect on the reactivity of a metal complex. As an example, $[Rh(dmpe)_2]^+$ reacts with hydrogen reversibly to give an isolable dihydride, whereas $[Rh(dppe)_2]^+$ is unreactive[29]. The reaction of methyl iodide with $AuCH_3(PMe_3)$ is faster than with $AuCH_3(PPh_3)$[30]. The rhodium complex $[Rh(CO)(PEt_3)(mnt)]^-$ reacts with alkyl bromides and iodides, but $[Rh(CO)(PPh_3)(mnt)]^-$ adds alkyl iodides only[31]. It is apparent that the smaller, more basic phosphines increase the tendency of metal complexes to undergo oxidative addition.

Complexes of the type $IrCl(CO)L_2$ provide a unique opportunity to monitor both the electronic and steric effects of tertiary phosphine ligands on the rate of such additions. The $\nu(CO)$ stretching frequency gives a good indication of changes in electron density at the metal atom. With the accepted mode of bonding of CO to a transition metal[14], an increase in electron density on the metal atom will increase the electron donation from filled metal d orbitals into the π^* orbitals of the CO ligand. This, in turn, will lower the CO bond order and so lower the $\nu(CO)$ stretching frequency. The steric size of phosphine ligands can be estimated from the ligand cone angle (θ), defined by a conical surface (Figure 2) that can just enclose the van der Waals radii of all ligand atoms assuming a constant M-P bond length of 2.28 Å[32]. This correlates well with the degree of substitution of CO by L in $Ni(CO)_4$.

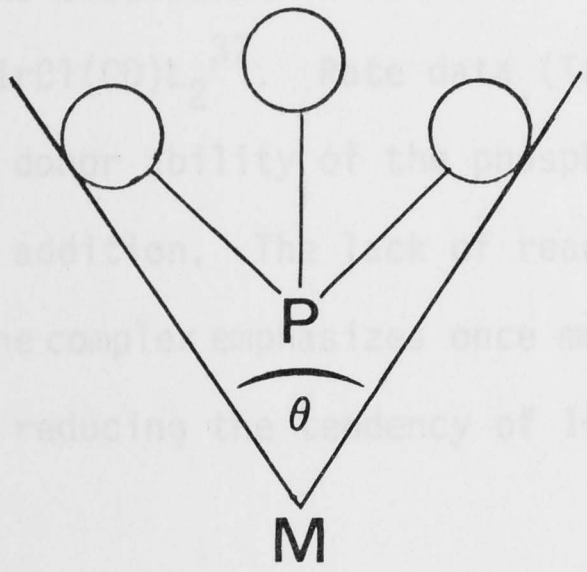


Figure 2. Definition of Ligand Cone Angle (θ).

The extent of protonation of $IrCl(CO)L_2$ by benzoic acid (1-6) provides a quantitative measure of the effect of L on the reactivity of these complexes[33-35].

$$IrCl(CO)L_2 + PhCO_2H \overset{K}{\rightleftharpoons} IrHCl(O_2CPh)(CO)L_2 \qquad (1\text{-}6)$$

As shown in Column 1, Table 1, the extent of protonation decreases in the order, $PMe_3 > PPhMe_2 > PPh_2Me > PPh_3$, but it is not clear whether this sequence results from electronic or steric effects, since the most basic phosphine, PMe_3, is also the smallest, whilst PPh_3 is the least basic, but is also the bulkiest. The importance of steric hindrance in reducing the reactivity of $IrCl(CO)L_2$ toward oxidative addition is shown by Column 2 in Table 1, where the iridium complex with $L=PBu^t{}_2R$ is unreactive toward benzoic acid. The lower $\nu(CO)$ for $IrCl(CO)(PBu^tPr_2)_2$ compared to that for $IrCl(CO)(PPhMe_2)_2$, and the larger ligand cone angle (θ) for PBu^tPr_2 compared to that for

$PPhMe_2$ (Table 2), shows that the reluctance of $IrCl(CO)(PBu^tPr_2)_2$ to protonate (Column 2, Table 1) is steric and not electronic in origin.

Use of para-substituted triphenylphosphine ligands provides a measure of the electronic influence of L on the rate of methyl iodide addition to $IrCl(CO)L_2$[37]. Rate data (Table 3) show that increasing the electron donor ability of the phosphine ligand increases the rate of oxidative addition. The lack of reactivity of the tri-o-tolylphosphine complex emphasizes once more the effect of steric hindrance in reducing the tendency of $IrCl(CO)L_2$ to undergo oxidative addition.

TABLE 1

Ratio Ir(III)/Ir(I) for (1-6)

Column 1		Column 2	
L	Ratio	L	Ratio
PPh_3	0.02	$PPhMe_2$	0.79
PPh_2Me	0.19	PBu^tMe_2	0.33
$PPhMe_2$	2.0	PBu^tEt_2	0.07
PMe_3	7.3	PBu^tPr_2	0.01
		$PBu^t{}_2R$	nr

nr = no reaction

TABLE 2

CO Stretching Frequency and Ligand Cone Angle (θ) of $IrCl(CO)L_2$

L	$\nu(CO)cm^{-1}$	θ[32]
$PPhMe_2$	1960[36]	122
PBu^tPr_2	1930[34]	149

TABLE 3

Second Order Rate Constants at 25°C in Benzene for

$IrCl(CO)L_2 + CH_3I \longrightarrow Ir(CH_3)ClI(CO)L_2$ [37]

L	Rate M^{-1} S^{-1}
$(p\text{-}FC_6H_4)_3P$	8.54×10^{-5}
PPh_3	2.67×10^{-3}
$(p\text{-}CH_3C_6H_4)_3P$	1.32×10^{-2}
$(p\text{-}CH_3OC_6H_4)_3P$	2.53×10^{-2}
$(o\text{-}CH_3C_6H_4)_3P$	nr

nr = no reaction

(c) Effect of Addend

Oxidative addition is generally favoured by addends with high electron affinities[19]. For example, alkyl halides with electronegative substituents in the α or β positions are more reactive than the analogous simple alkyl halides[38]. Silanes, R_3SiH, bearing electronegative groups (R=Cl, OEt) will add reversibly to $IrCl(CO)(PPh_3)_2$ to give octahedral, hydrido(silyl)iridium(III) adducts (1-7), whereas trialkyl- or triaryl-silanes do not react under the same conditions[39].

$$IrCl(CO)(PPh_3)_2 + R_3SiH \rightleftharpoons IrHCl(SiR_3)(CO)(PPh_3)_2 \qquad (1\text{-}7)$$

A similar trend occurs for the reaction of alk-1-ynes with $IrCl(CO)(PPh_3)_2$, where ethyl propiolate ($HC{\equiv}CCO_2Et$) reacts to give a stable hydridoacetylide, $IrHCl(C_2CO_2Et)(CO)(PPh_3)_2$, but propyne ($CH_3C{\equiv}CH$) does not[40].

Formation of a carbon-metal δ-bond is of crucial importance to the use of transition metal complexes in organic synthesis. There are a variety of methods available for forming metal-carbon bonds,

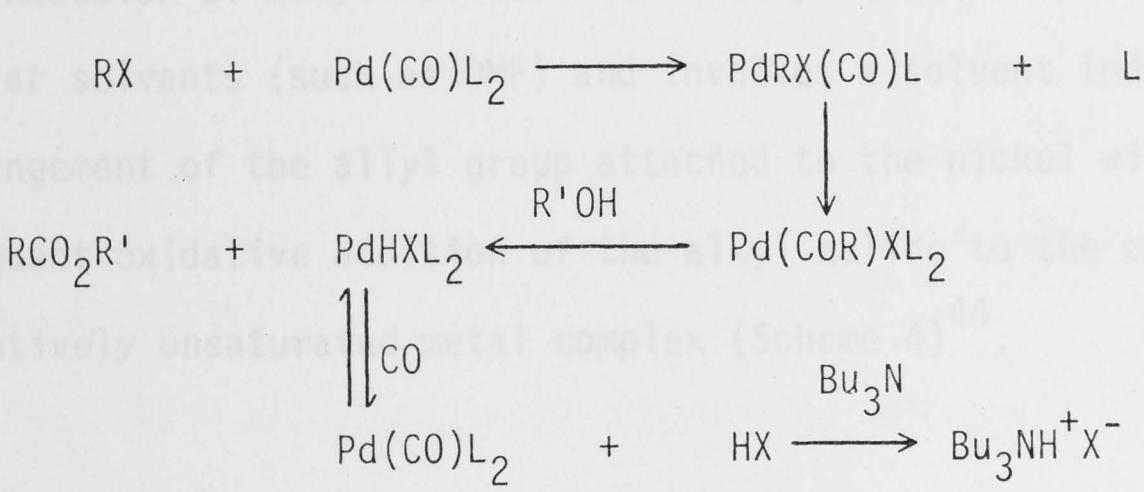
including addition of olefins to metal-hydride complexes, decarbonylation of metal-acyl complexes and oxidative addition of organic halides to low-valent metal complexes[41]. Some examples of the last method are shown in Schemes 2-4.

The Pd(0)-induced alkoxycarbonylation of aromatic and vinylic halides proceeds as shown in (1-8)[42].

$$RX + CO + R'OH + Bu_3N \xrightarrow{Pd(0)} RCO_2R' + Bu_3NH^+X^- \quad (1\text{-}8)$$

R = aryl, substituted vinyl, X = Br, I; R = $PhCH_2$, X = Cl.

The proposed mechanism for (1-8) involves the addition of the organic halide to $Pd(CO)L_2$, followed by alkyl-group migration to give a palladium-acyl intermediate, and finally solvolysis by alcohol to give the organic product (Scheme 2)[42].

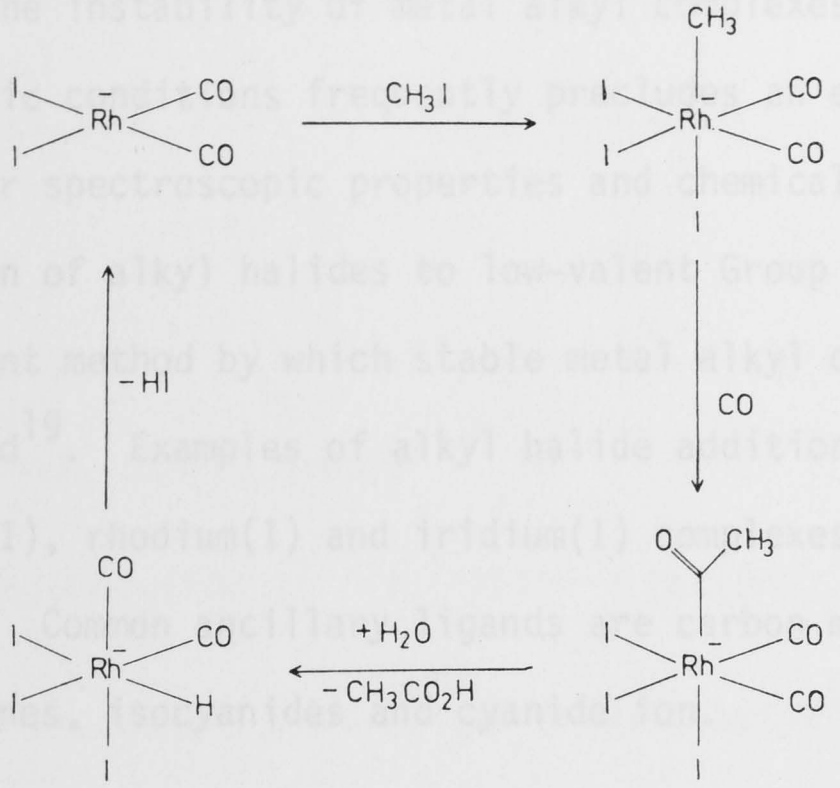


L = PPh_3

Scheme 2. Mechanism for Pd(0)-Induced Alkoxycarbonylation of Organic Halides.

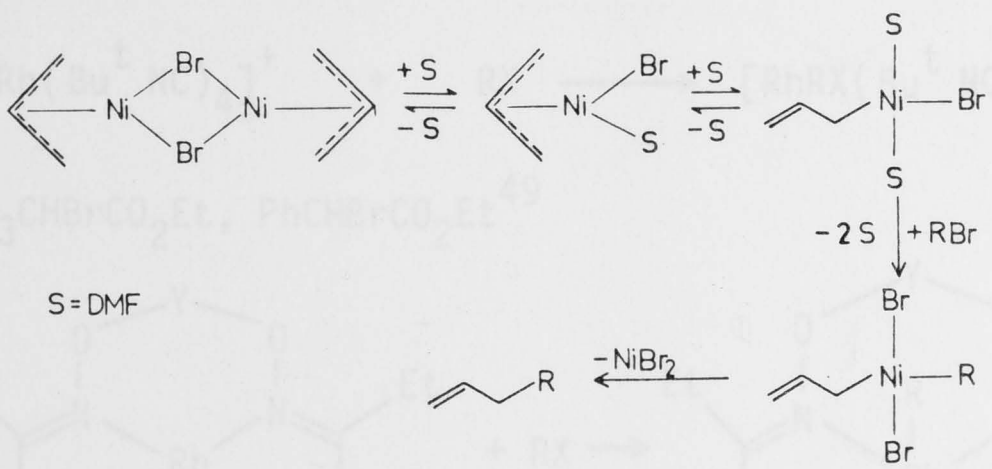
Carbonylation of methanol to acetic acid is catalysed by low-valent rhodium complexes, the key step in the reaction being the oxidative addition of methyl iodide to $[RhI_2(CO)_2]^-$ (Scheme 3)[43].

$$HI + CH_3OH \rightleftharpoons CH_3I + H_2O$$



Scheme 3. Mechanism for the Carbonylation of Methanol to Acetic Acid by $[RhI_2(CO)_2]^-$.

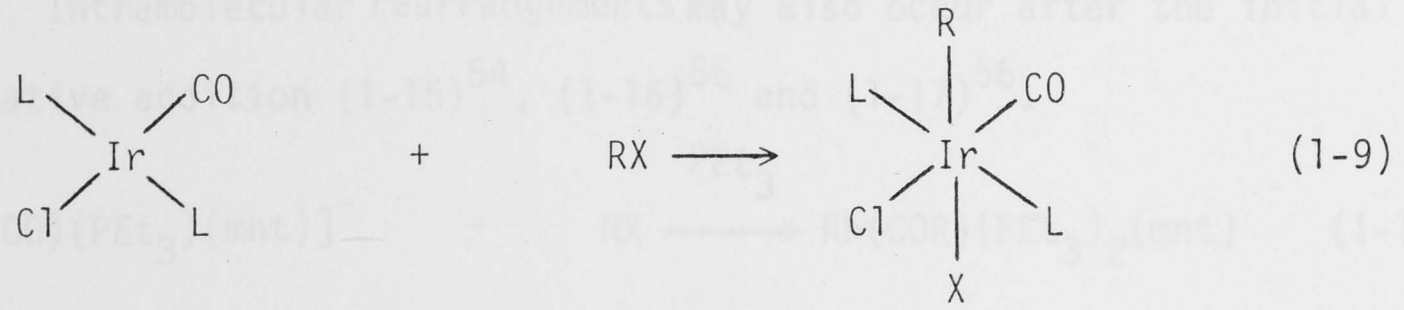
Reaction of alkyl halides with π-allyl nickel halides occurs in polar solvents (such as DMF) and involves a solvent induced π to σ rearrangement of the allyl group attached to the nickel with subsequent oxidative addition of the alkyl halide to the co-ordinatively unsaturated metal complex (Scheme 4)[44].



Scheme 4. Mechanism for Reaction of Alkyl Bromide with π-Allyl Nickel Bromide.

Alkyl Halide Addition.

The instability of metal alkyl complexes formed under catalytic conditions frequently precludes an extensive investigation of their spectroscopic properties and chemical reactivity. Oxidative addition of alkyl halides to low-valent Group 8 complexes is an important method by which stable metal alkyl complexes can be prepared[19]. Examples of alkyl halide addition to neutral, d^8, cobalt(I), rhodium(I) and iridium(I) complexes are shown in (1-9)-(1-11). Common ancillary ligands are carbon monoxide, tertiary phosphines, isocyanides and cyanide ion.



(1-9)

L = PMe_3; X = I, R = methyl, ethyl, propyl, *iso*-propyl[45]

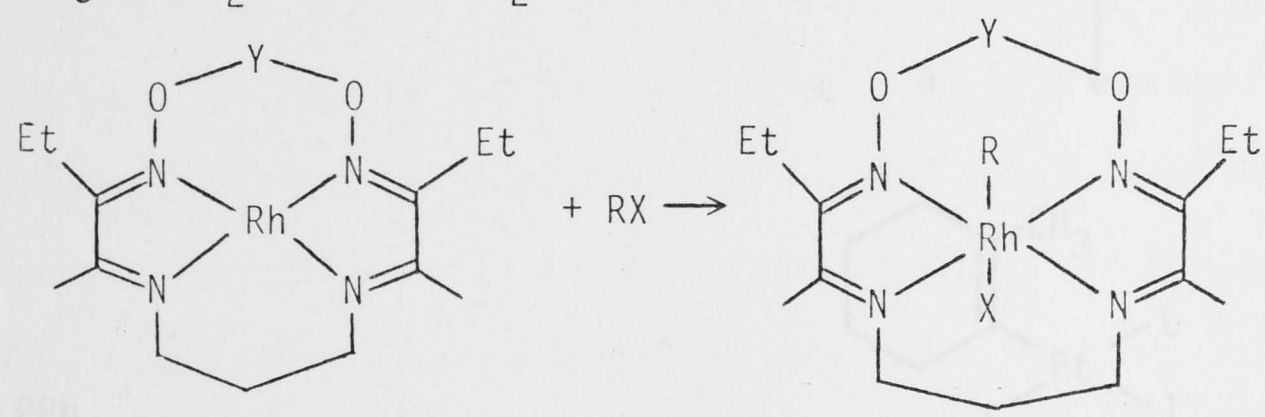
L = PMe_3; RX = bromocyclohexane, *cis*- and *trans*-1-bromo-2-fluoro-cyclohexane[46]

L = $PPhMe_2$; RX = methyl(Cl,Br,I), $ClCH_2CO_2Me$, $ClCH_2CN$[47]

L = PPh_2Me, $PPhMe_2$, PMe_3; RX = $CH_3CHBrCO_2Et$[48]

$$[Rh(Bu^tNC)_4]^+ + RX \longrightarrow [RhRX(Bu^tNC)_4]^+ \qquad (1\text{-}10)$$

RX = $CH_3CHBrCO_2Et$, $PhCHBrCO_2Et$[49]



(1-11)

X = I, R = methyl, ethyl, propyl, butyl

X = Br, R = butyl, *iso*-propyl[50]

Y = BF_2

Reaction of alkyl halides with anionic metal complexes is well established (1-12)-(1-14).

$$[IrI_2(CO)_2]^- + CH_3I \longrightarrow [Ir(CH_3)I_3(CO)_2]^- \quad (1\text{-}12)$$

(ref 51)

$$Co(CN)_5I^{3-} + RI \longrightarrow Co(CN)_5R^{3-} + Co(CN)_5I^{3-} \quad (1\text{-}13)$$

R = methyl, ethyl, propyl[52]

$$Co(DMG)_2(PBu_3)^- + RCl \longrightarrow CoR(DMG)_2(PBu_3) + Cl^- \quad (1\text{-}14)$$

R = methyl, ethyl, propyl, *iso*-propyl, butyl[53].

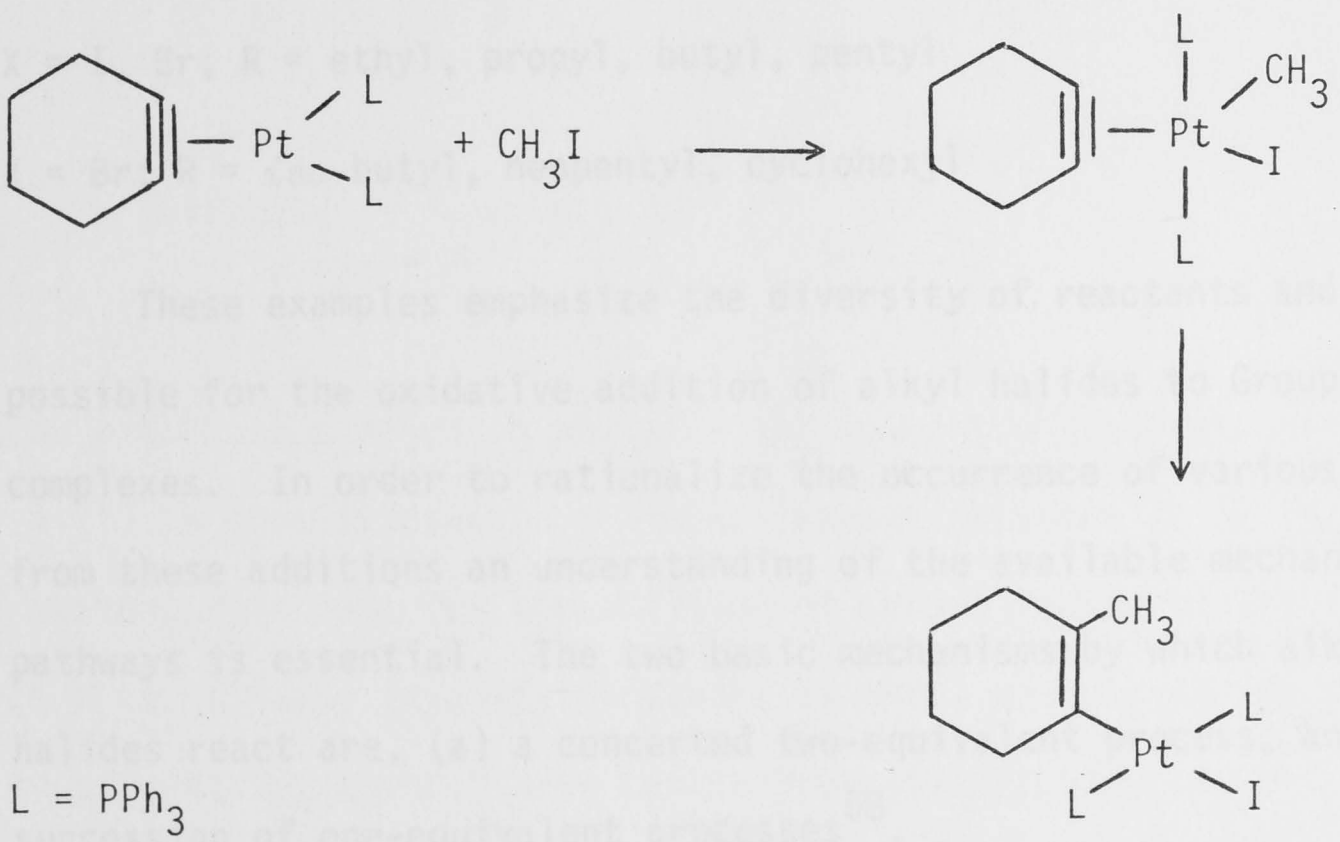
Intramolecular rearrangements may also occur after the initial oxidative addition (1-15)[54], (1-16)[55] and (1-17)[56].

$$[Rh(CO)(PEt_3)(mnt)]^- + RX \xrightarrow{PEt_3} Rh(COR)(PEt_3)_2(mnt) \quad (1\text{-}15)$$

mnt = maleonitriledithiolate

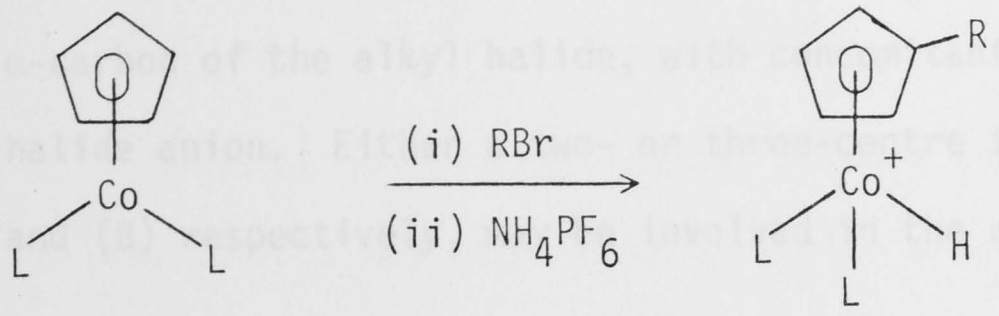
X = I; R = methyl, ethyl, propyl, *iso*-butyl, *iso*-propyl

X = Br; R = ethyl, butyl, propyl



(1-16)

L = PPh_3



(1-17)

L = PMe_3; R = *iso*-propyl, *tert*-butyl

Not all reactions of RX with Group 8 complexes give products containing metal-carbon bonds as shown by (1-18)[57] and (1-19)[20].

$$PtL_3 + RX \longrightarrow PtX_2L_2 \qquad (1\text{-}18)$$

L = $P(C_6H_{11})_3$, $PPhMe_2$, PEt_3

X = I, R = $CH_3CHC_2H_5$

X = Br, R = $CH_3CHC_2H_5$, CH_3CHPh, CH_3CHCO_2Et

$$ML_3 + RX \longrightarrow MRXL_2 + MHXL_2 + MX_2L_2 \qquad (1\text{-}19)$$

M = Pd, Pt; L = PEt_3

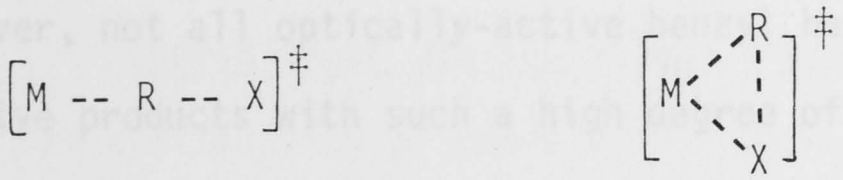
X = I, Br; R = ethyl, propyl, butyl, pentyl

X = Br; R = *iso*-butyl, neopentyl, cyclohexyl

These examples emphasize the diversity of reactants and products possible for the oxidative addition of alkyl halides to Group 8 metal complexes. In order to rationalize the occurrence of various products from these additions an understanding of the available mechanistic pathways is essential. The two basic mechanisms by which alkyl halides react are, (a) a concerted two-equivalent process, and (b) a succession of one-equivalent processes[58].

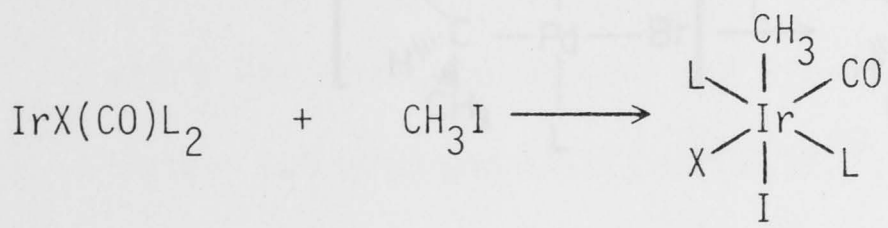
(a) Concerted Two-Equivalent Process

This pathway involves a nucleophilic attack of the metal on the α-carbon of the alkyl halide, with concomitant displacement of the halide anion. Either a two- or three-centre transition state, (A) and (B) respectively, may be involved in the reaction (1-20)[19].



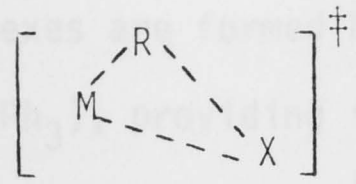
(A) (B) (1-20)

Transition state (A) resembles that of a classical S_N2 process and should result in stereochemical inversion at the reacting carbon centre, whereas transition state (B) should result in a retention of configuration at the reacting carbon. Evidence for reactions proceeding via (A) comes from the addition of reactive alkyl halides (such as methyl iodide and benzyl bromide) to d^8 and d^{10} metal complexes[19]. For example, kinetic data from the reaction of methyl iodide with $IrX(CO)L_2$ (1-21) support a bimolecular pathway with a polar transition state[16,59].



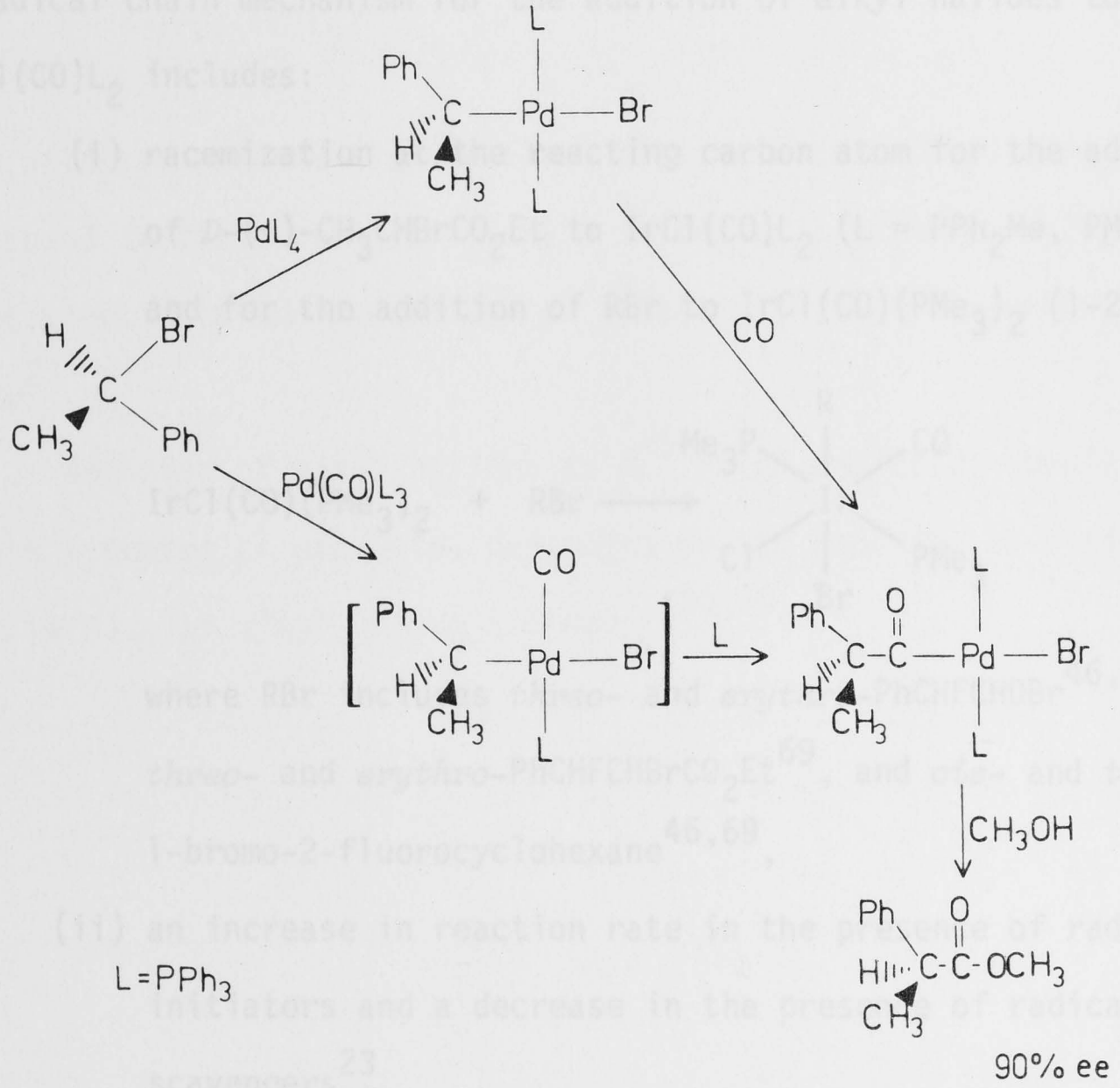
(1-21)

The effect of changes in pressure and solvent on the rate of reaction (1-21) is consistent with a linear transition state as in (A)[60]. However, rate data for the addition of methyl iodide to $IrCl(CO)L_2$ (L = substituted triphenylphospnine ligands) are claimed to support an asymmetric, polar, three centre transition state, as in (1-22)[37,61].



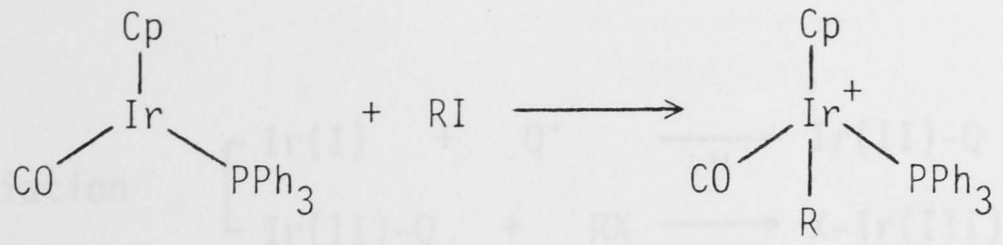
(1-22)

Addition of optically-active primary and secondary benzyl halides to PdL_4 may occur with inversion of configuration at the reacting carbon with up to 90% stereospecificity (Scheme 5)[62-65]. However, not all optically-active benzyl halides react with PdL_4 to give products with such a high degree of stereospecificity and a nucleophilic exchange process is believed to be the major cause of low optical yields in these cases[64].



Scheme 5. Reaction of Optically Active Benzyl Halides with Pd(0) Complexes.

Cationic complexes are formed by addition of methyl and benzyl iodide to $CpIr(CO)(PPh_3)$, providing further evidence for a nucleophilic displacement mechanism (1-23)[66].

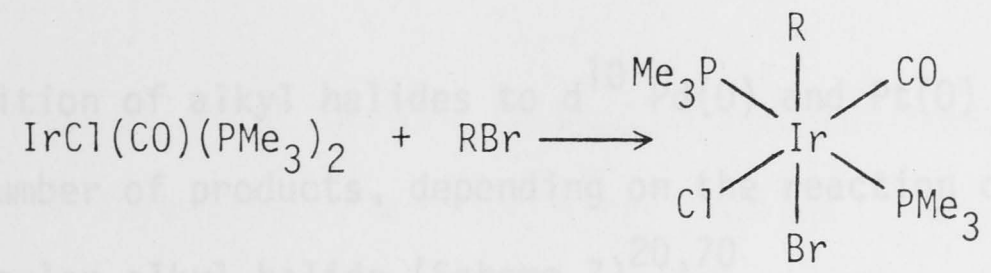


(1-23)

(b) Succession of One-Equivalent Processes

The availability of one-electron pathways for the transition-metal induced reduction of alkyl halides is well established.[58] Both radical chain[67] and non-chain[68] mechanisms have been proposed for the reaction of alkyl halides with Group 8 complexes. Evidence in favour of a radical chain mechanism for the addition of alkyl halides to $IrCl(CO)L_2$ includes:

(i) racemization at the reacting carbon atom for the addition of *D*-(+)-$CH_3CHBrCO_2Et$ to $IrCl(CO)L_2$ (L = PPh_2Me, PMe_3)[69], and for the addition of RBr to $IrCl(CO)(PMe_3)_2$ (1-24).



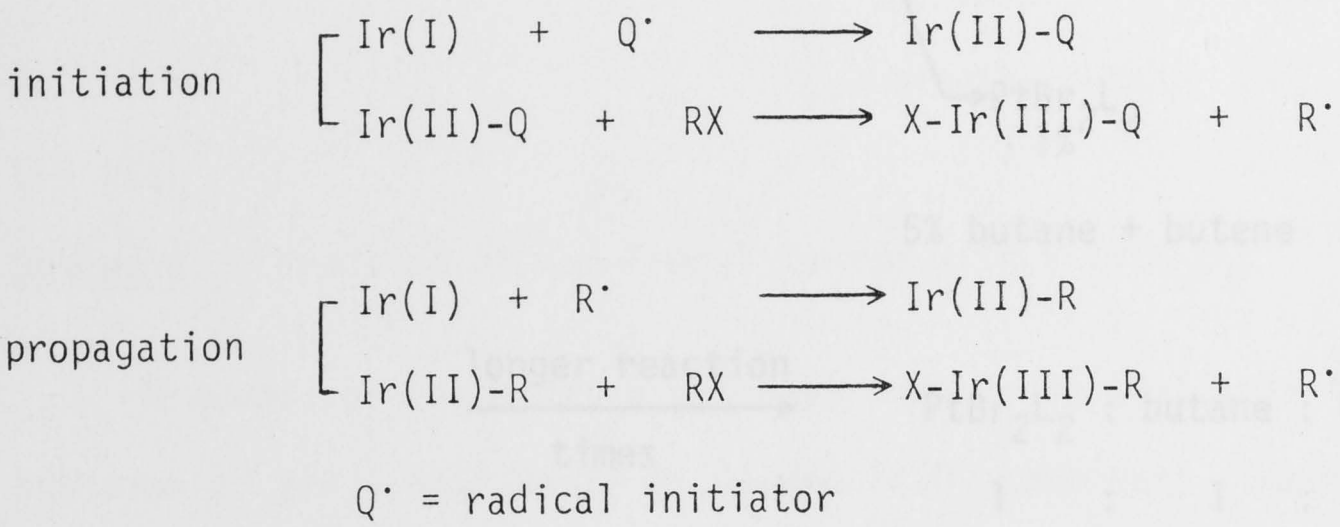
(1-24)

where RBr includes *threo*- and *erythro*-PhCHFCHDBr[46,69], *threo*- and *erythro*-$PhCHFCHBrCO_2Et$[69], and *cis*- and *trans*-1-bromo-2-fluorocyclohexane[46,69],

(ii) an increase in reaction rate in the presence of radical initiators and a decrease in the presence of radical scavengers[23].

The initiating step of this radical chain mechanism is variable, but the propagation sequence is constant and involves the generation of alkyl radicals (Scheme 6)[67]. It should be noted that the para-

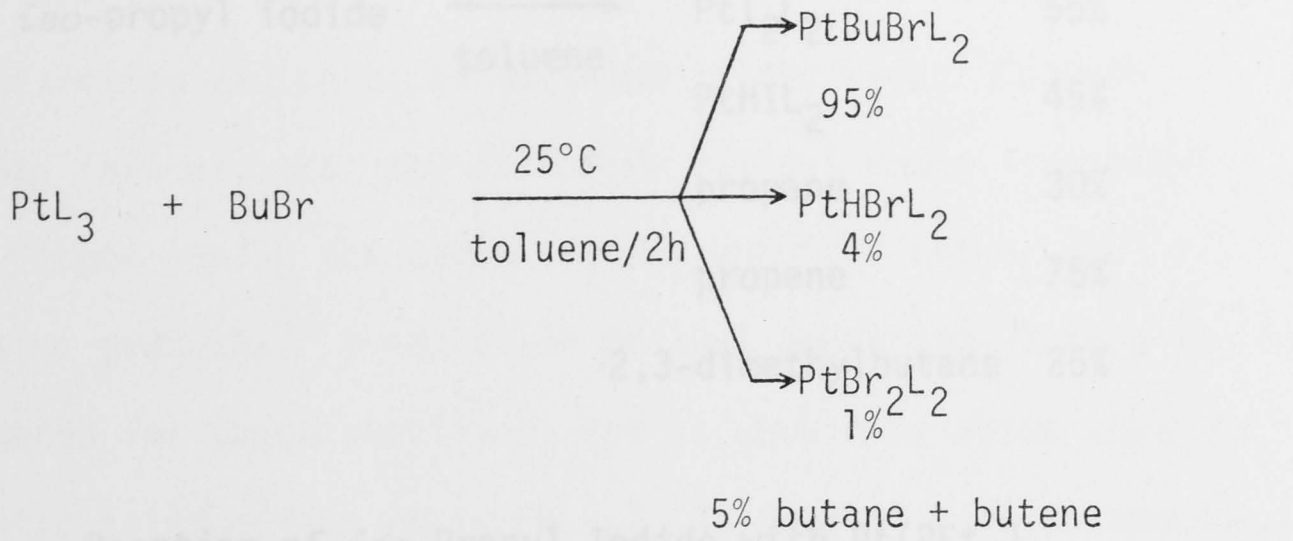
magnetic intermediate [Ir(II)-R] resulting from radical capture, is postulated rather than the alternative [Ir-X]$^{\cdot}$, resulting from halogen abstraction.



Scheme 6. Radical-Chain Mechanism for the Addition of RX to $IrCl(CO)L_2$.

The relative reactivities of alkyl halides with $IrCl(CO)(PMe_3)_2$ decrease in the order - tertiary > secondary > primary, which is consistent with the generation of radicals in the rate-determining step[23].

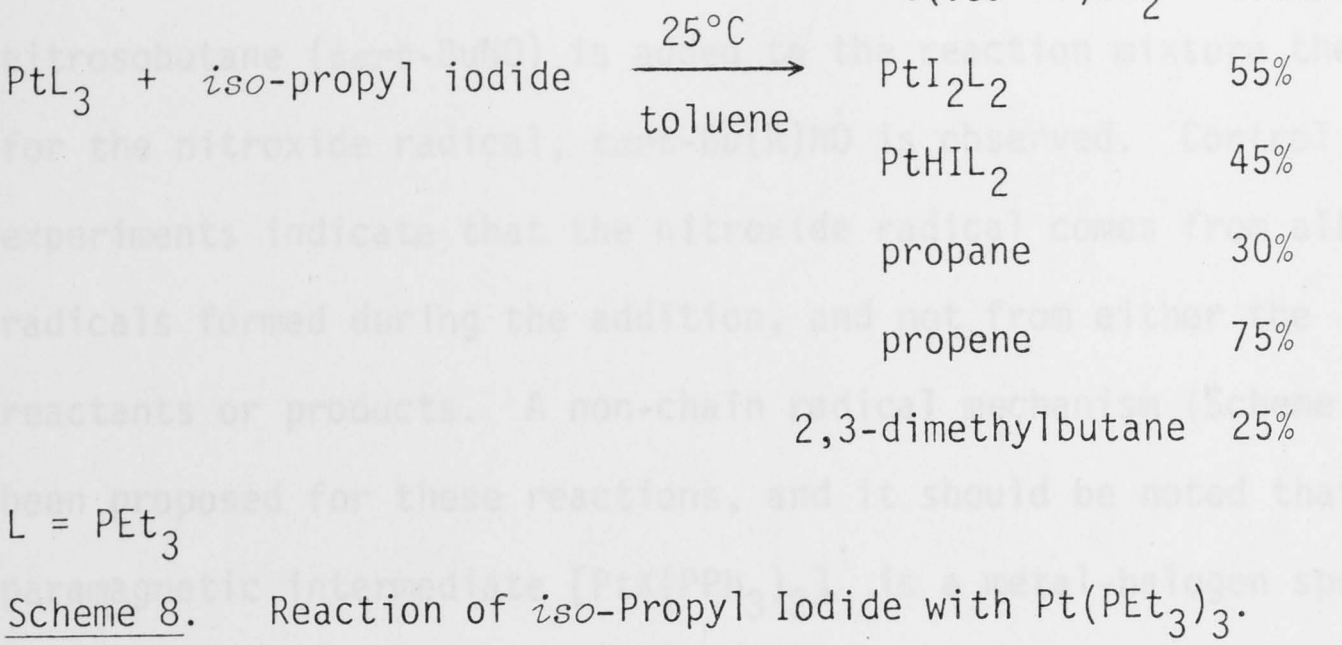
Addition of alkyl halides to d^{10} Pd(0) and Pt(0) complexes gives a number of products, depending on the reaction conditions and the particular alkyl halide (Scheme 7)[20,70].



Scheme 7. Reaction of 1-Bromobutane with $Pt(PEt_3)_3$.

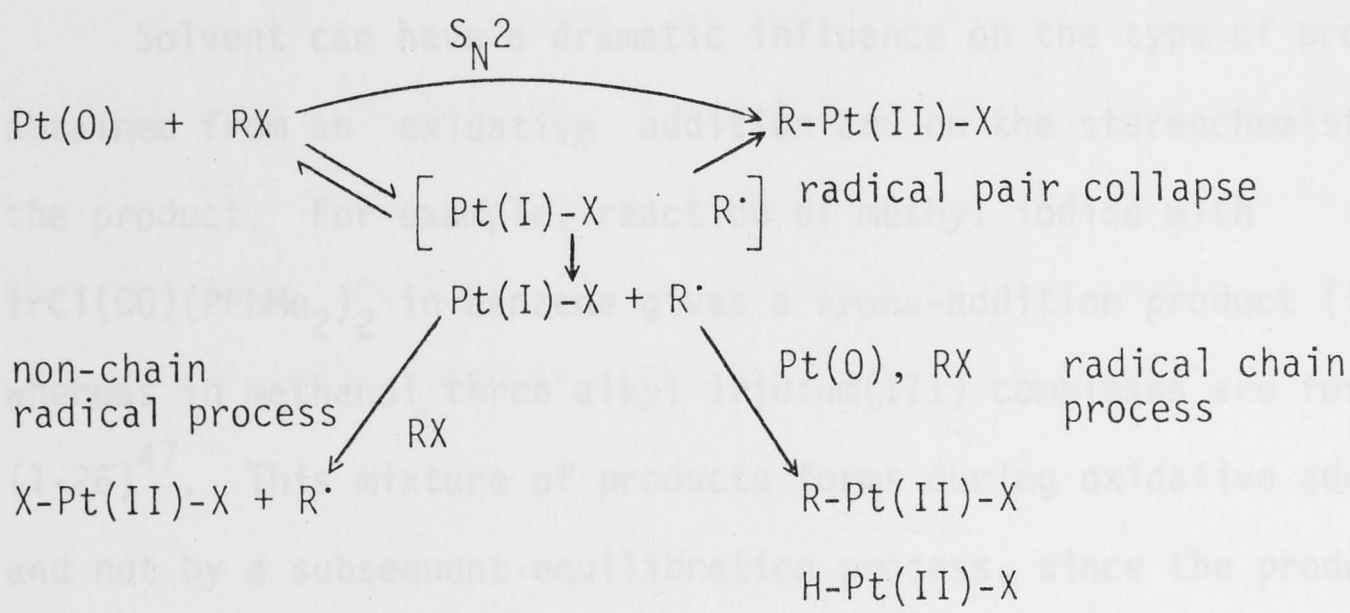
Radical scavengers, which react with the Pt(0) complex, cause reaction rates to decrease and detailed mechanistic studies support a radical chain mechanism for the addition of alkyl halides to $Pt(PEt_3)_3$.

Addition of alkyl halides to Pt(0) complexes does not always result in the formation of a metal alkyl complex. For example, reaction of *iso*-propyl iodide with $Pt(PEt_3)_3$ gives a number of products (Scheme 8)[70]. Pronounced CIDNP enhancements occur in the propane and *iso*-propyl iodide resonances, which is consistent with the diffusive encounter of *iso*-propyl radicals. Rate of formation of dihalide, PtI_2L_2, is unaffected by radical scavengers.



Scheme 8. Reaction of *iso*-Propyl Iodide with $Pt(PEt_3)_3$.

A number of competitive pathways seem to be available for the addition of alkyl halides to Pt(0) and Pd(0) complexes (Scheme 9)[67]. The expected adduct, $PtRXL_2$, and the hydride complex, $PtHXL_2$, may arise from a radical chain process. The dihalide, PtX_2L_2, may result from a non-chain radical process, since its formation is unaffected by radical scavengers. Addition of very reactive alkyl halides, such as methyl and benzyl halides, may proceed by an S_N2 mechanism or by the formation and collapse of a tightly held radical pair.



Scheme 9. Mechanistic Pathways for the Addition of Alkyl Halides to Pt(0).

The reaction of alkyl halides, such as methyl and ethyl iodide and benzyl bromide, with $Pt(PPh_3)_3$ can be monitored by esr and spin trapping can be used to detect alkyl radicals[68, 71, 72]. When *tert*-

nitrosobutane (*tert*-BuNO) is added to the reaction mixture the signal for the nitroxide radical, *tert*-Bu(R)NO· is observed. Control experiments indicate that the nitroxide radical comes from alkyl radicals formed during the addition, and not from either the reactants or products. A non-chain radical mechanism (Scheme 10) has been proposed for these reactions, and it should be noted that the paramagnetic intermediate $[PtX(PPh_3)_2]^{\cdot}$ is a metal-halogen species, in contrast to the metal-alkyl species proposed for the iridium system[67].

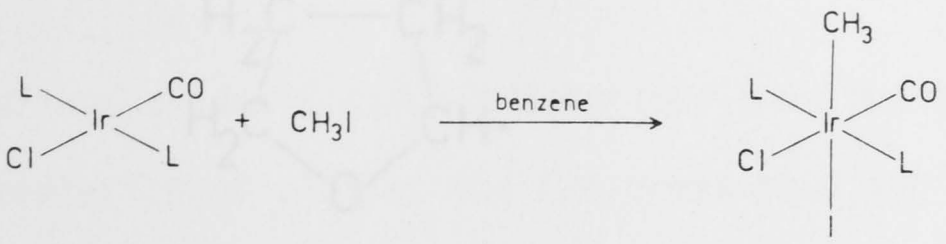
$$Pt(PPh_3)_3 \rightleftharpoons Pt(PPh_3)_2 + PPh_3$$

$$Pt(PPh_3)_2 + RX \overset{\text{slow}}{\rightleftharpoons} PtX(PPh_3)_2 + R^{\cdot}$$

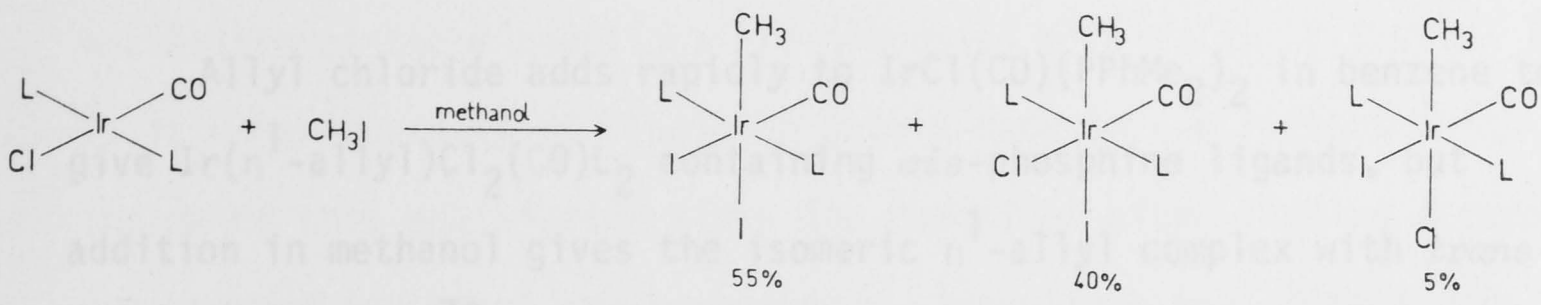
$$PtX(PPh_3)_2 + R^{\cdot} \xrightarrow{\text{fast}} Pt(R)X(PPh_3)_2$$

Scheme 10. Non-Chain Radical Mechanism for the Addition of RX to $Pt(PPh_3)_3$.

Solvent can have a dramatic influence on the type of product obtained from an oxidative addition and on the stereochemistry of the product. For example, reaction of methyl iodide with $IrCl(CO)(PPhMe_2)_2$ in benzene gives a *trans*-addition product (1-25), whereas in methanol three alkyl iridium(III) complexes are formed (1-26)[47]. This mixture of products forms during oxidative addition and not by a subsequent equilibration process, since the product from the benzene reaction is recovered unchanged after being heated in methanol for 20 minutes. The addition is believed to occur through an ion pair, such as $[Ir(CH_3)Cl(CO)L_2]^+I^-$, which, in polar solvents, may separate, leading to halide exchange between I^- and unreacted $IrCl(CO)L_2$.



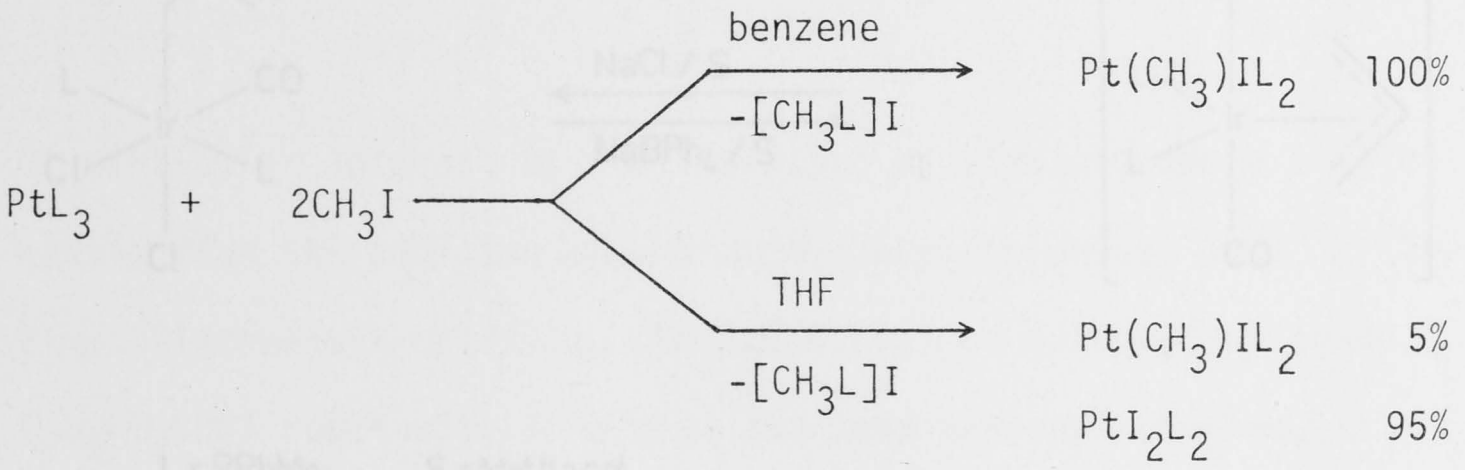
(1-25)



L = $PPhMe_2$

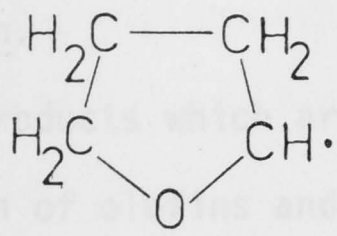
(1-26)

The mechanism for addition of methyl iodide to $Pt(PPh_3)_3$, outlined in Scheme 10, is believed to involve free radicals. The products, however, are solvent dependent, since in benzene only $Pt(CH_3)I(PPh_3)_2$ is obtained, whereas in tetrahydrofuran the major product is $PtI_2(PPh_3)_2$ (Scheme 11)[72,73]. The solvent effect can be interpreted if it is assumed that the methyl radical abstracts a hydrogen atom from tetrahydrofuran to generate the radical shown (1-27). This bulky radical will combine less readily with $PtI(PPh_3)_2$ than the methyl radical, so that abstraction of a second halogen from methyl iodide becomes a favourable process (1-28).



L = PPh_3

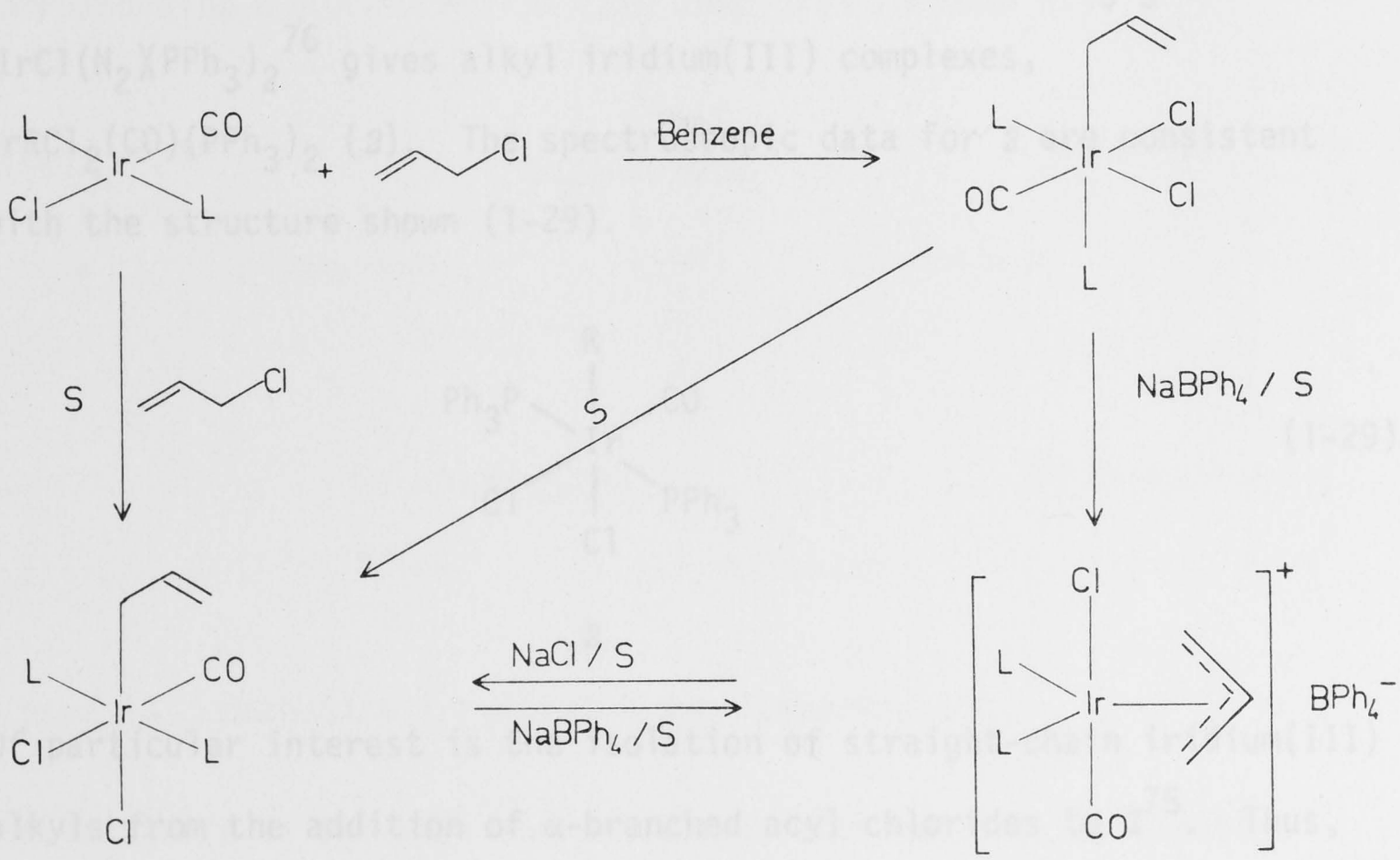
Scheme 11. Solvent Dependence of CH_3I Addition to $Pt(PPh_3)_3$.



(1-27)

$$PtI(PPh_3)_2 + CH_3I \longrightarrow PtI_2(PPh_3)_2 + CH_3\cdot \qquad (1\text{-}28)$$

Allyl chloride adds rapidly to $IrCl(CO)(PPhMe_2)_2$ in benzene to give $Ir(\eta^1\text{-allyl})Cl_2(CO)L_2$ containing *cis*-phosphine ligands, but addition in methanol gives the isomeric η^1-allyl complex with *trans*-phosphine ligands[74]. This rearrangement presumably occurs by halide dissociation from the η^1-allyl complex to give a cationic η^3-allyl intermediate (Scheme 12). Such intermediates are isolated by the addition of $NaBPh_4$ to $Ir(\eta^1\text{-allyl})Cl_2(CO)L_2$ in methanol, and subsequent reaction with sodium halide generates the η^1-allyl again.

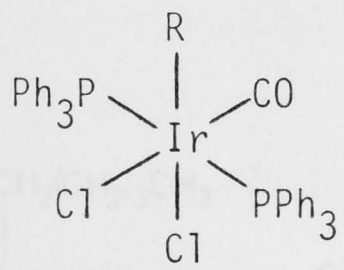


Scheme 12. Reaction of Allyl Chloride with $IrCl(CO)(PPhMe_2)_2$.

Acyl Halide Addition.

The various products which are derived from the hydrogenation and hydroformylation of olefins and the cross-coupling reactions of Grignard reagents with organic halides depend on the position of equilibrium between isomeric alkyl metal intermediates. The mechanisms of these reactions are discussed more fully in Chapter 3. It is experimentally difficult to obtain data on the factors which influence this equilibrium since the reactions often involve a complex sequence of additions, rearrangements, insertions and eliminations, all of which depend on the reaction conditions. Therefore systems in which isolable metal alkyl complexes are found to undergo alkyl group rearrangement and which are amenable to mechanistic investigation are clearly useful. An example of such a system is the addition of acyl halides to $IrClL_3$ (L = various tertiary phosphines).

Reaction of acyl chlorides, (RCOCl), with $IrCl(PPh_3)_3$ (*1*)[75] or $IrCl(N_2)(PPh_3)_2$[76] gives alkyl iridium(III) complexes, $IrRCl_2(CO)(PPh_3)_2$ (*2*). The spectroscopic data for *2* are consistent with the structure shown (1-29).



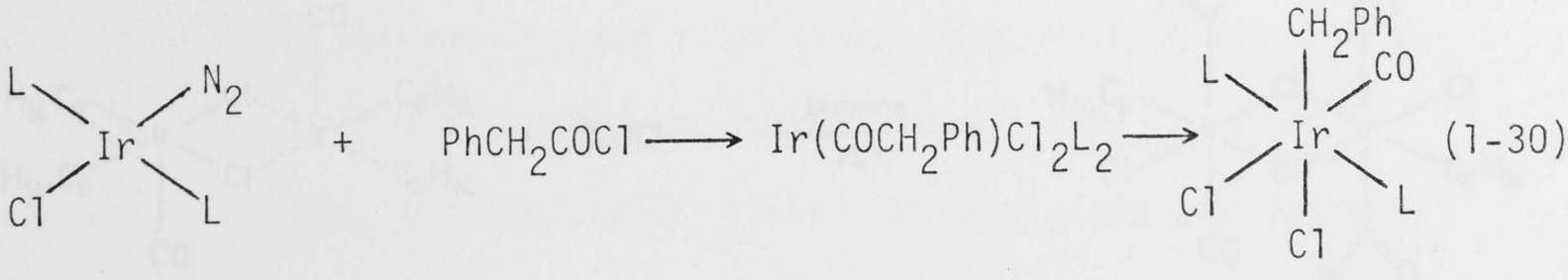
(1-29)

2

Of particular interest is the isolation of straight-chain iridium(III) alkyls from the addition of α-branched acyl chlorides to *1*[75]. Thus, 2-methylpropanoyl chloride, $(CH_3)_2CHCOCl$, or butanoyl chloride, $C_2H_5CH_2COCl$ react with *1* to give the same *n*-propyl complex, $Ir(CH_2CH_2CH_3)Cl_2(CO)(PPh_3)_2$. Similarly, addition of 2-methylbutanoyl chloride, $CH_3CH_2CH(CH_3)COCl$, 2-ethylbutanoyl chloride,

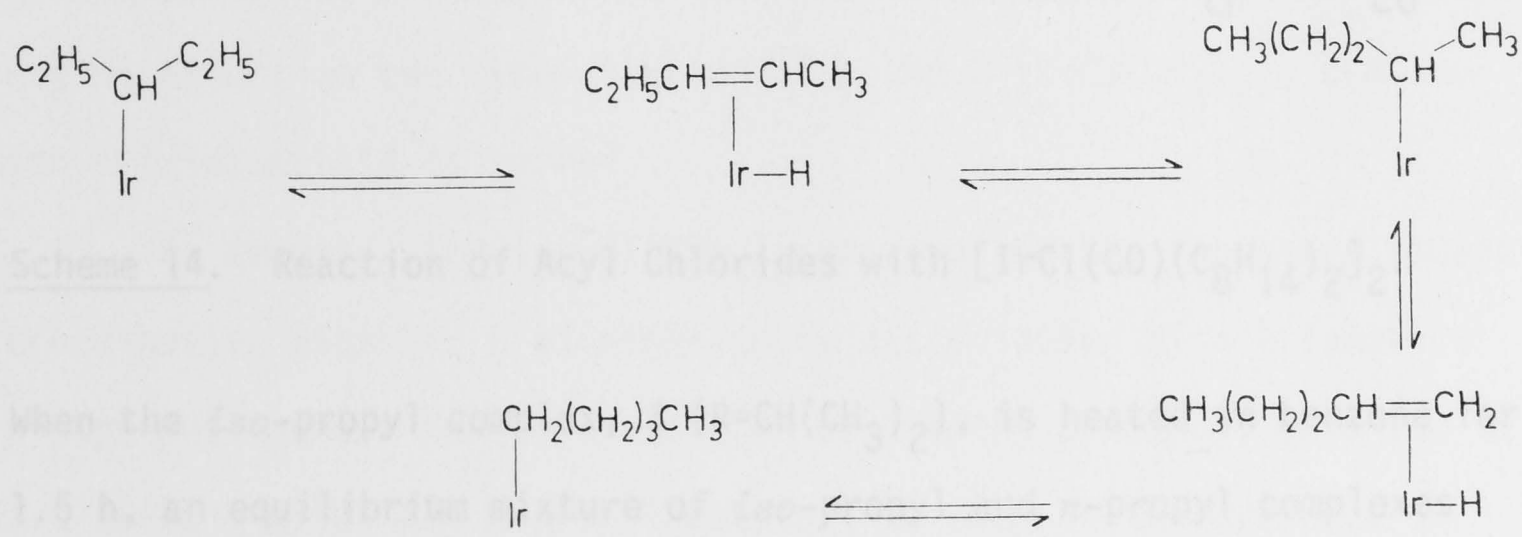
$(CH_3CH_2)_2CHCOCl$ and 2-phenylpropanoyl chloride, $PhCH(CH_3)COCl$ to *1* gives the *n*-butyl, *n*-pentyl and 2-phenethyl iridium(III) complexes, respectively.

Reaction of acyl chlorides with *1* is presumed to give an intermediate iridium(III) acyl complex which undergoes alkyl group migration to generate the alkyl iridium(III) product. In some cases an intermediate acyl complex can be isolated (1-30)[76].



L=PPh_3

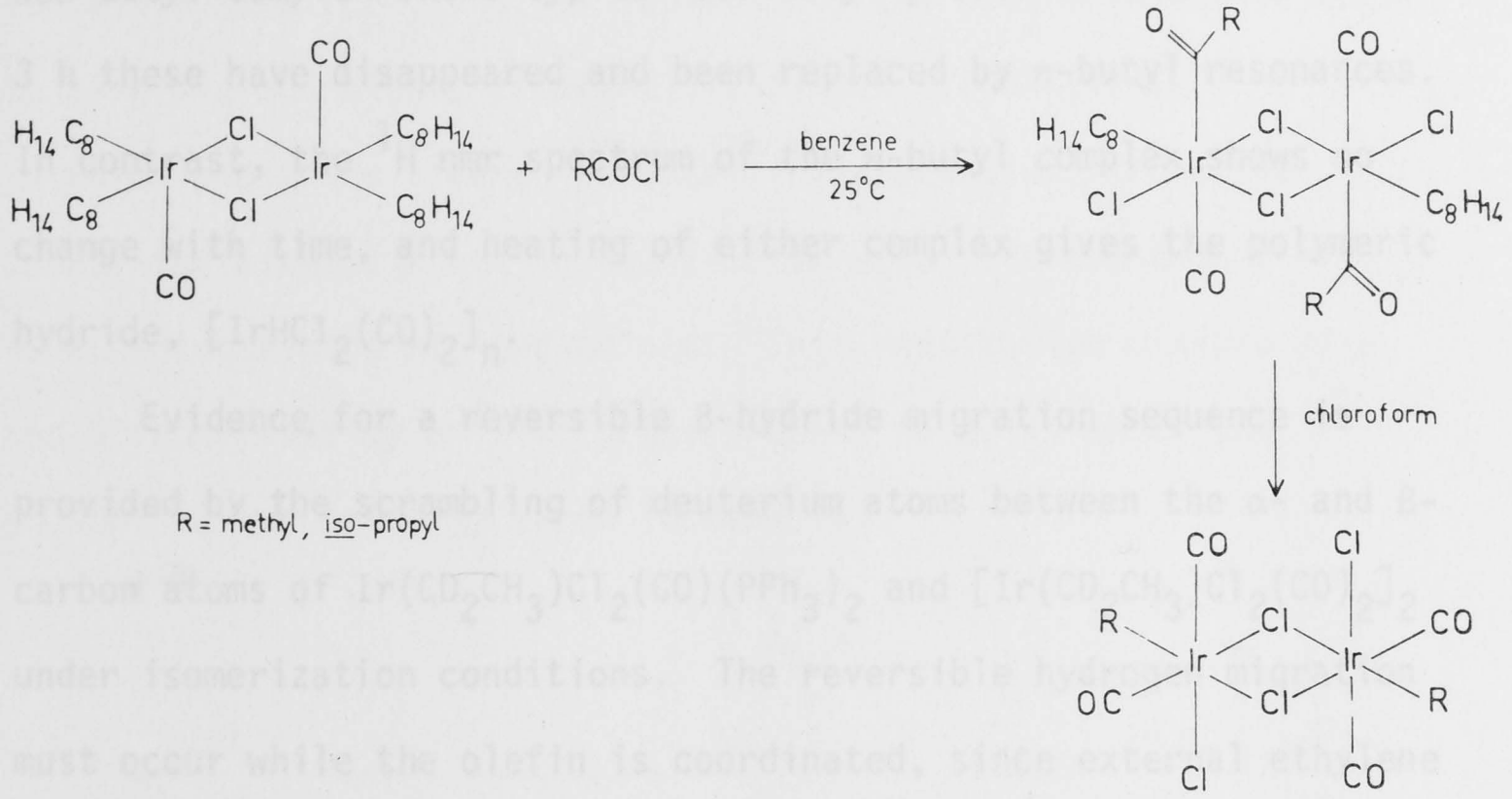
Sec-alkyl iridium(III) complexes are believed to undergo a series of reversible β-hydride migrations which give the corresponding *n*-alkyl iridium(III) complexes (Scheme 13)[75].



Scheme 13. Mechanism for Alkyl Group Isomerization.

The existence of *sec*-acyl and *sec*-alkyl intermediates, presumably formed by the addition of α-branched acyl chlorides to *1*, could not be confirmed spectroscopically. However, acyl chlorides react with $[IrCl(CO)(C_8H_{14})_2]_2$ in benzene to give *sec*-alkyl complexes,

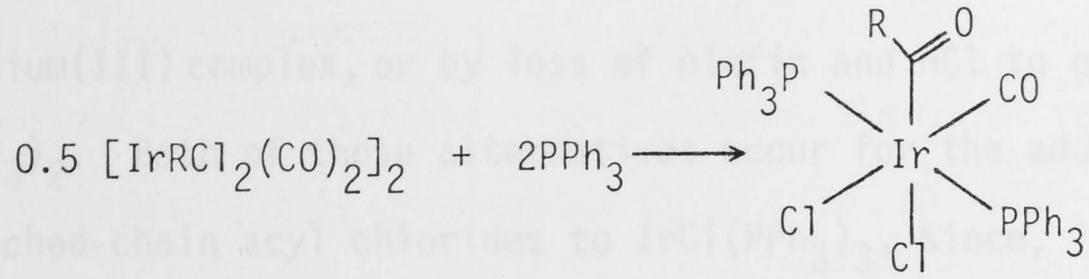
$[IrRCl_2(CO)_2]_2$ (*3*), and *sec*-acyl precursors can be detected in this case (Scheme 14)[75]. It should also be noted that *sec*-alkyl complexes can be isolated from the addition of $PhCH(CF_3)COCl$ to $IrCl(N_2)(PPh_3)_2$, since β-elimination is suppressed[77].



Scheme 14. Reaction of Acyl Chlorides with $[IrCl(CO)(C_8H_{14})_2]_2$.

When the *iso*-propyl complex, *3* ($R=CH(CH_3)_2$), is heated in benzene for 1.5 h, an equilibrium mixture of *iso*-propyl and *n*-propyl complexes (ca.2:3) is obtained[75]. The *n*-propyl complex, *3* ($R=CH_2CH_2CH_3$), prepared by reacting butanoyl chloride with $[IrCl(CO)(C_8H_{14})_2]_2$, also isomerizes when heated in benzene for 1.5 h to give the same equilibrium mixture. Both complexes decompose on prolonged heating, giving the polymeric hydride, $[IrHCl_2(CO)_2]_n$, presumably with elimination of propene. Addition of two equivalents of triphenylphosphine to the dimeric alkyl complex, *3* ($R=CH_2CH_2CH_3$, $CH(CH_3)_2$) gives monomeric $Ir(COR)Cl_2(CO)(PPh_3)_2$ without alkyl group

isomerization (1-31).



(1-31)

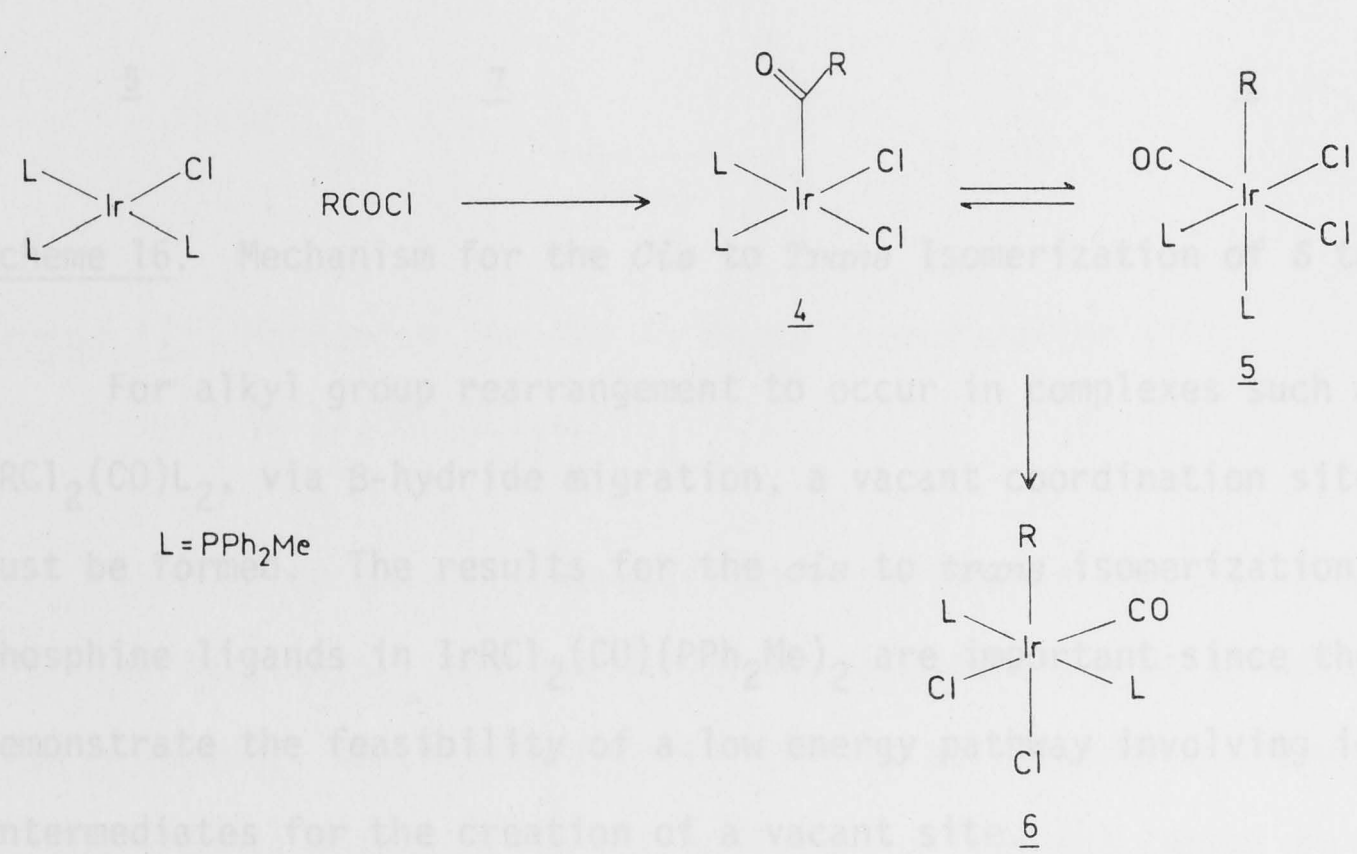
Reaction of pentanoyl and 2-methylbutanoyl chloride with $[IrCl(CO)(C_8H_{14})_2]_2$ gives the expected *n*- and *sec*-alkyl complexes, *3* (R = $CH_2CH_2C_2H_5$, $CH(CH_3)C_2H_5$). A freshly prepared solution of the *sec*-butyl complex shows typical *sec*-butyl proton resonances, but after 3 h these have disappeared and been replaced by *n*-butyl resonances. In contrast, the ^1H nmr spectrum of the *n*-butyl complex shows no change with time, and heating of either complex gives the polymeric hydride, $[IrHCl_2(CO)_2]_n$.

Evidence for a reversible β-hydride migration sequence is provided by the scrambling of deuterium atoms between the α- and β-carbon atoms of $Ir(CD_2CH_3)Cl_2(CO)(PPh_3)_2$ and $[Ir(CD_2CH_3)Cl_2(CO)_2]_2$ under isomerization conditions. The reversible hydrogen migration must occur while the olefin is coordinated, since external ethylene has no effect on the isomerization of *2* and *3* ($R=CH(CH_3)_2$), i.e. no ethyl iridium(III) is formed.

The complex, $IrRCl_2(CO)(PPh_3)_2$ can provide the necessary vacant coordination site for β-elimination by dissociation of a triphenylphosphine ligand. However, addition of 2-methylpropanoyl chloride to $IrCl(PPh_3)_3$ gives the *n*-propyl complex, *2*, even in the presence of an excess of triphenylphosphine (kinetic data could not be obtained for the reaction). The dimeric alkyl complex, $[IrRCl_2(CO)_2]_2$, may dissociate by cleavage of the chloride bridge to give a coordinatively unsaturated intermediate. A reasonable formulation of the olefin-hydride intermediate formed during the isomerization of $IrRCl_2(CO)(PPh_3)_2$ would be $IrHCl_2(CO)(olefin)(PPh_3)$. Steric

congestion may be relieved by either formation of a linear alkyl iridium(III) complex, or by loss of olefin and HCl to give $IrCl(CO)(PPh_3)_2$. Both of these alternatives occur for the addition of branched-chain acyl chlorides to $IrCl(PPh_3)_3$, since, in addition to the *n*-alkyl complex, $IrRCl_2(CO)(PPh_3)_2$, up to 30% of $IrCl(CO)(PPh_3)_2$ is also formed.

Acyl chlorides react with $IrCl(PPh_2Me)_3$, or with a solution containing $[IrCl(C_8H_{14})_2]_2$ (1 equivalent) and PPh_2Me (4 equivalents), to give six-coordinate iridium(III) alkyls, $IrRCl_2(CO)(PPh_2Me)_2$ (*5*), in which phosphine ligands are *cis*[78]. In solution, these six-coordinate alkyls, *5*, are in equilibrium with five-coordinate acyls, *4*, also containing *cis* phosphines. This equilibrium mixture of *4* and *5* isomerizes by a first order process to *6*, in which the phosphines are mutually *trans* (Scheme 15).

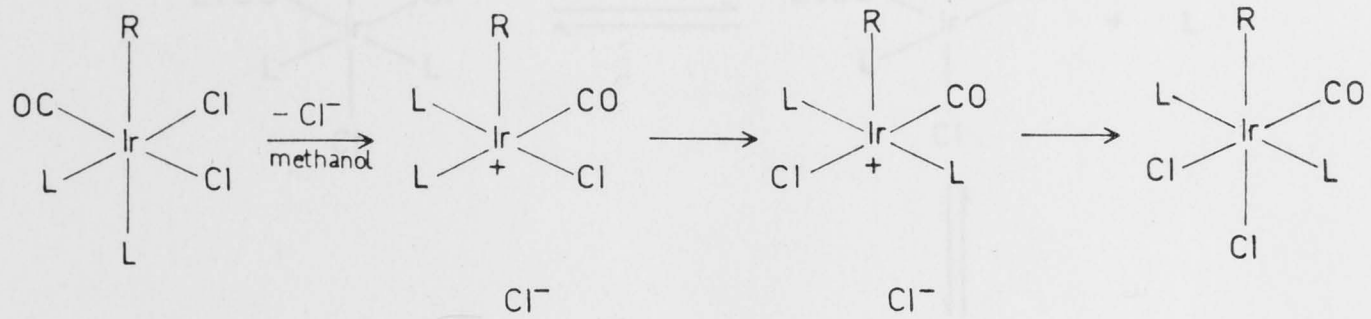


Scheme 15. Reaction of Acyl Chlorides with $IrCl(PPh_2Me)_3$.

Reaction of either *n*-butanoyl or 2-methylpropanoyl chloride with $IrCl(PPh_2Me)_3$ gives the same *n*-propyl iridium(III) complex. Attempts to detect spectroscopically the 2-methylpropanoyl or *iso*-propyl

iridium(III) intermediates were inconclusive. The *cis* to *trans* isomerization of phosphine ligands occurs slowly at room temperature in chloroform and is accelerated by addition of methanol. The rate also increases in the presence of $LiClO_4$ and decreases in the presence of LiCl.

The mechanism for this isomerization is believed to involve a rate-determining loss of Cl^- from *5*, followed by a rapid rearrangement of the resulting five coordinate cation, *7*, and subsequent reentry of Cl^- to generate *6* (Scheme 16).



5 7 6

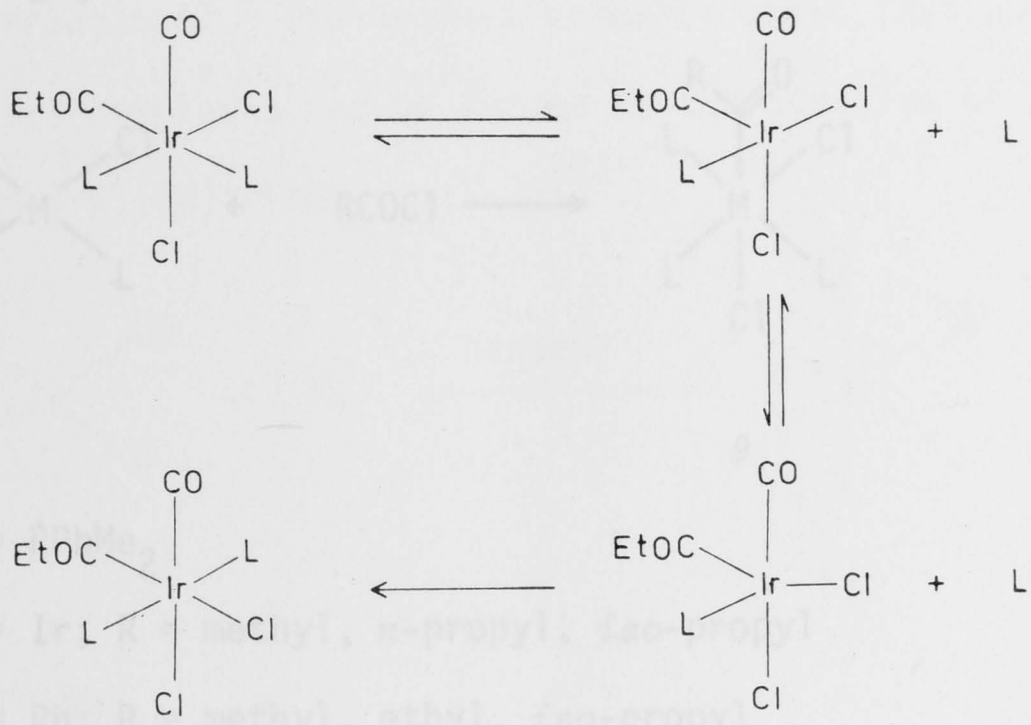
Scheme 16. Mechanism for the *Cis* to *Trans* Isomerization of *5* to *6*.

For alkyl group rearrangement to occur in complexes such as $IrRCl_2(CO)L_2$, via β-hydride migration, a vacant coordination site must be formed. The results for the *cis* to *trans* isomerization of phosphine ligands in $IrRCl_2(CO)(PPh_2Me)_2$ are important since they demonstrate the feasibility of a low energy pathway involving ionic intermediates for the creation of a vacant site.

Despite the smaller size and increased basicity of PPh_2Me relative to PPh_3, the addition of 2-methylpropanoyl chloride to $IrCl(PPh_2Me)_3$ still gives the *n*-propyl iridium(III) complex. The *n*-alkyl complexes appear to be the thermodynamically favoured isomer in these systems, regardless of the nature of the substituents on

phosphorus. However, mechanisms for acyl halide additions and subsequent alkyl group rearrangements have not been fully developed for these systems, so it is difficult to predict what effect changes in the ancillary ligands will have on these reactions.

Cis to *trans* isomerization of phosphine ligands also occurs in chloroform solution for the acyl complex, $Ir(COEt)Cl_2(CO)L_2$ (*8*) (L = PPh_2Me, $PPhMe_2$, $AsPhMe_2$, $P(OMe)_2Ph$)[79]. Kinetic data for the rearrangement, which is slowed by the addition of L, are consistent with the mechanism shown (Scheme 17).

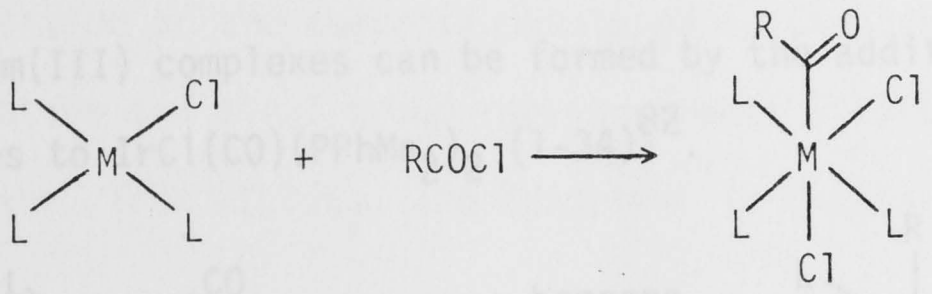


Scheme 17. Mechanism for *Cis* to *Trans* Isomerization of L in $Ir(COEt)Cl_2(CO)L_2$.

The *cis* to *trans* isomerizations described in Schemes 16 and 17 are clearly similar, and yet different rate determining steps have been proposed. Whether this difference is attributed to the nature of the organic moiety or to the influence of solvent cannot be ascertained without further experiments. It would be informative, therefore, to determine the effect on the rate of isomerization of (i) adding methanol to a chloroform solution of the acyl complex, *8* and, (ii) adding PPh_2Me to a chloroform solution of the alkyl complex, *5*. It is conceivable that both rearrangements proceed via different rate determining steps which are independent of the solvent or,

alternatively, that two independent mechanisms are operating, one in protic solvents and another in aprotic solvents. This also emphasizes the point that the creation of a vacant coordination site in a coordinatively saturated complex may occur by different mechanisms, depending on the solvent.

Reaction of straight chain and α-branched acyl chlorides with $MCl(PPhMe_2)_3$ (M=Rh, Ir) gives six-coordinate acyl metal complexes, $M(COR)Cl_2L_3$ (*9*), (1-32)[80]. Addition of acetyl chloride to $RhCl(PPhMe_2)_3$ has been reported independently[81].



(1-32)

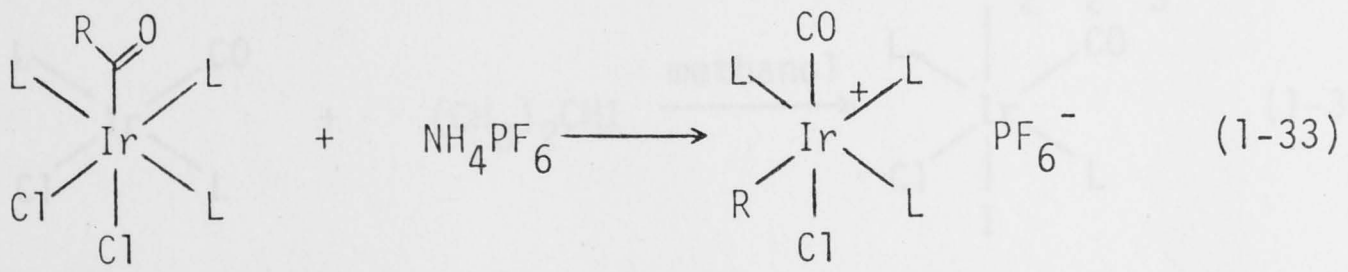
9

L = $PPhMe_2$

M = Ir; R = methyl, *n*-propyl, *iso*-propyl

M = Rh; R = methyl, ethyl, *iso*-propyl

In contrast to the complexes containing PPh_3, *2*, and PPh_2Me, *6*, the various complexes *9* contain three rather than two phosphine ligands, and do not readily rearrange to σ-alkyls. However, when R is a straight chain alkyl, addition of NH_4PF_6 induces loss of Cl^-, thereby providing a pathway for alkyl migration (1-33).

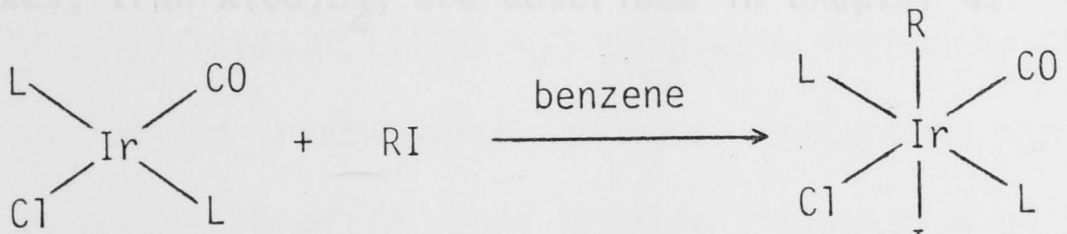


(1-33)

Addition of NH_4PF_6 has no effect on the branched acyl complex, *9*

($R=CH(CH_3)_2$), so it would be interesting to know if migration and/or alkyl isomerization would take place in the presence of a stronger electrophile, such as $AgPF_6$. These observations emphasize the necessity of a vacant coordination site for alkyl group rearrangement.

It would be advantageous to be able to prepare *sec*-alkyl iridium(III) complexes directly, instead of via acyl halide addition, since it is difficult to separate factors which influence alkyl group migration from carbon monoxide to metal from those influencing alkyl group rearrangement. Preliminary evidence shows that *sec*-alkyl iridium(III) complexes can be formed by the addition of *sec*-alkyl iodides to $IrCl(CO)(PPhMe_2)_2$ (1-34)[82].



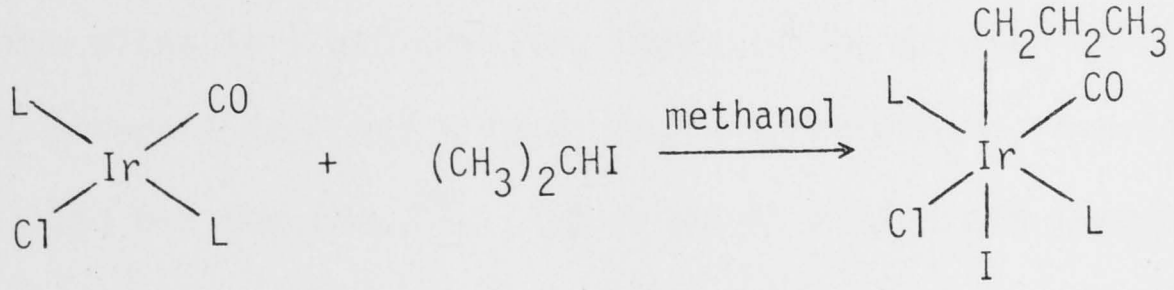
(1-34)

10

L = $PPhMe_2$

R = ethyl, *n*-propyl, *iso*-propyl, cyclohexyl

When *10* ($R=CH(CH_3)_2$) is heated in benzene at 45°C for 20 h a mixture of products, consisting of the *n*-propyl complex, *10*, as well as the dichloride and diiodide analogues, is obtained. Reaction of *iso*-propyl iodide with $IrCl(CO)(PPhMe_2)_2$ in methanol gives only the *n*-propyl iridium(III) complex (1-35).



(1-35)

L = $PPhMe_2$

As part of a general investigation of the mechanism of this alkyl group rearrangement the preparation and properties of alkyl iridium(III) complexes have been studied. In the context of exploring the scope of this rearrangement, an extensive series of complexes of the type, $IrRX_2(CO)L_2$, have been prepared by the addition of alkyl halides to $IrX(CO)L_2$. The synthesis and spectroscopic properties of these complexes are described in Chapter 2. On the basis of kinetic data and deuterium labelling experiments, a mechanism for alkyl group rearrangement is proposed in Chapter 3. In an extension of the concepts developed in Chapters 2 and 3, the preparation and alkyl group rearrangements of dialkyl iridium(III) complexes, $IrRR"X(CO)L_2$, are described in Chapter 4.

CHAPTER TWO

Preparation and Characterization of Alkyl Iridium(III) Complexes

Introduction.

Vaska's complex, $IrCl(CO)(PPh_3)_2$, reacts with only a few alkyl halides, namely methyl iodide[83], allyl iodide[83] and benzyl chloride[84]. Replacing phenyl groups with methyls on the phosphine ligand substantially increases the reactivity of the metal complex, enabling a wider series of alkyl iridium(III) complexes to be prepared[23,69].

This chapter describes the preparation, characterization and properties of iridium(III) alkyl complexes formed by the addition of alkyl halides to iridium(I) precursors. Attention has been focussed on those complexes which would provide information on the alkyl group rearrangement described at the conclusion of Chapter One.

The principal methods used for elucidating the stereochemistry of the oxidative adducts are far-infrared spectroscopy and ^1H and ^{31}P nmr spectroscopy. The stereochemistry of methyl-substituted tertiary phosphine ligands may be assigned from the proton resonance of the PCH_3 group. The methyl resonance for two phosphine ligands in a mutually *trans* position is usually a 1:2:1 triplet due to "virtual coupling" with both phosphorus nuclei, whereas two phosphine ligands in mutually *cis* positions usually give rise to 1:1 doublets[85]. These two situations are limiting cases to the general spin system $X_nAA'X'_n$ (where A is P and X is H, and n=3 for PPh_2Me, n=6 for $PPhMe_2$, and n=9 for PMe_3)[86]. The A and A' nuclei are chemically equivalent but magnetically inequivalent (see Appendix for a more detailed discussion of this system).

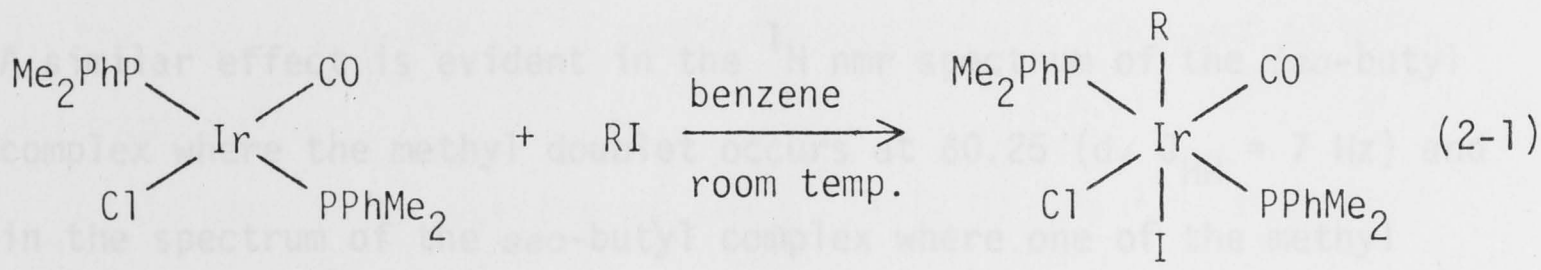
Results.

I. Oxidative Addition of Alkyl Halides to $IrCl(CO)L_2$

It is convenient to discuss these reactions in terms of the phosphine ligand (L) attached to the metal atom.

(A) $L = PPhMe_2$

Addition of primary and secondary alkyl iodides to $IrCl(CO)(PPhMe_2)_2$ (*11b*) in benzene at room temperature gives $IrRClI(CO)(PPhMe_2)_2$ (*10a-g*) in high yield (2-1). Addition of *n*-propyl or *iso*-propyl bromide to *11b* under similar conditions gives only starting material, although benzyl bromide reacts with *11b* to give the expected adduct, $Ir(CH_2C_6H_5)BrCl(CO)(PPhMe_2)_2$. Alkyl iodides also react with $IrI(CO)(PPhMe_2)_2$ to give the expected adduct, $IrRI_2(CO)(PPhMe_2)_2$ (R=*n*-propyl and *iso*-propyl).



(2-1)

11b *10a-g*

R = (a) ethyl, (b) propyl, (c) *iso*-propyl, (d) butyl, (e) *iso*-butyl, (f) *sec*-butyl, (g) octyl.

Analytical and spectroscopic data for *10a-g* appear in Tables 4-6. Solution infrared spectra of *10a-g* (Table 5) show one $\nu(CO)$ band in the range 2010-2040 cm^{-1}, whereas in Nujol mulls two such bands are occasionally observed, probably owing to solid state splitting. The far-infrared spectra show one $\nu(IrCl)$ at ca.300 cm^{-1} assignable to Cl *trans* to CO[47].

In the ^1H nmr spectrum of each of the complexes *10a-g* (Table 6) the PCH_3 ligand resonance appears as two triplets ($^2J_{PH} + {}^4J_{PH}$ = 8 Hz)

owing to coupling to two chemically equivalent phosphorus nuclei.

The $^{31}P\{^{1}H\}$ nmr spectra of *10a-g* (Table 5) show a singlet resonance due to the equivalent phosphine ligands. The chemical shift of the secondary alkyl complexes, *10c* and *10f* , is about 3 ppm to higher field than that in the primary alkyl complexes, *10a,b,d, e,g*. The spectroscopic data are consistent with the stereochemistry shown in (2-1).

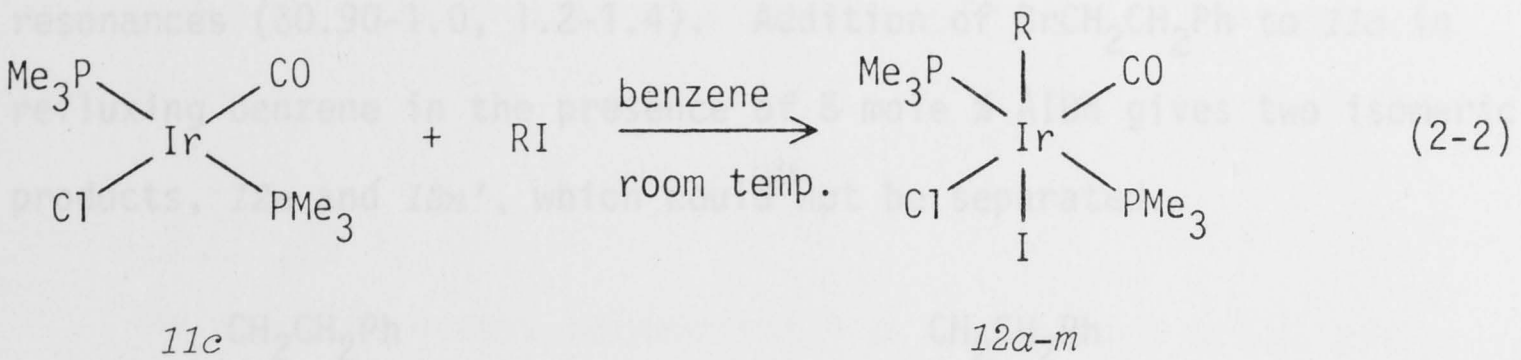
Although the resonances for the methyl (δ0.80,t,J_{HH} = 7 Hz) and methylene (δ1.23,sextet,J_{HH} = 7 Hz, $^{3}J_{PH}$ = 7 Hz) protons of the ethyl complex are unexceptional, the methyl triplet of the *n*-propyl complex (δ0.14,t,J_{HH} = 7 Hz) is ca. 0.65 ppm to higher field than that in the ethyl complex and the methylene protons give rise to a complex multiplet at δ1.00. In the ^{1}H nmr spectrum of the *n*-butyl complex the protons of the methyl group and one of the methylene groups also occur at unexpectedly high field (δ0.27, m). A similar effect is evident in the ^{1}H nmr spectrum of the *iso*-butyl complex where the methyl doublet occurs at δ0.25 (d, J_{HH} = 7 Hz) and in the spectrum of the *sec*-butyl complex where one of the methyl groups occurs at δ0.18 (t, J_{HH} = 7 Hz).

An attempt was made to react the analogous rhodium complex, $RhCl(CO)(PPhMe_2)_2$, with ethyl and *iso*-propyl iodide under similar conditions to (2-1), but no reaction was observed. This result is consistent with the trends in reactivity of Group 8 complexes discussed on page 4[67].

(b) L = PMe_3

$IrCl(CO)(PMe_3)_2$ (*11c*) reacts with straight chain and branched alkyl iodides to give $IrRClI(CO)(PMe_3)_2$ (*12a-m*) in high yield (2-2). The ethyl[38,45], propyl[45] and *iso*-propyl[38,45] complexes have been prepared previously. Reaction of *tert*-butyl iodide with *11c* gives

the diiodide adduct, $IrClI_2(CO)(PMe_3)_2$. Analytical and spectroscopic data for *12a-m* appear in Tables 7-9.



(2-2)

11c *12a-m*

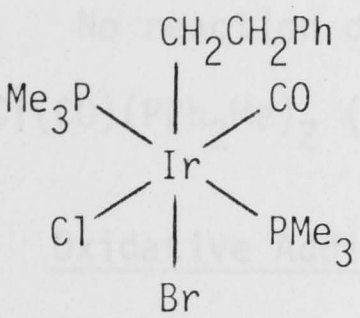
R = (a) ethyl, (b) propyl, (c) *iso*-propyl, (d) butyl, (e) *sec*-butyl, (f) *iso*-butyl, (g) neopentyl, (h) 2-methylbutyl, (i) 3-methylbutyl, (j) 3-pentyl, (k) octyl, (l) 2-octyl, (m) cyclohexyl.

Infrared spectra for the various complexes *12a-m* (Table 8) show one ν(CO) band in the region 2010-2030 cm^{-1} and a ν(IrCl) band ca. 300 cm^{-1} assignable to Cl trans to CO[47]. These PMe_3-containing complexes have an additional band, compared to their $PPhMe_2$ analogues, in the region 270-280 cm^{-1}, which is tentatively assigned to a PC_3 deformation[87].

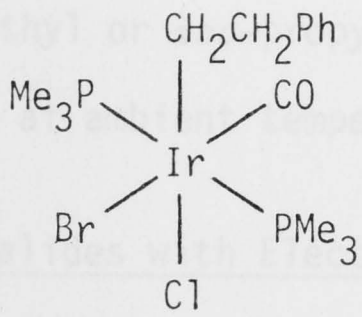
In the ^1H nmr spectra of *12a-m* (Table 9) the PCH_3 resonance is a triplet ($^2J_{PH} + {}^4J_{PH}$ = 8 Hz), which reduces to a singlet on ^{31}P decoupling. There is no upfield shift of the protons on C(3) and C(4) for *12a-m*, as in the $PPhMe_2$-containing complexes, *10a-g*. Although coupling between the methylene protons of the neopentyl complex and the phosphorus nuclei is ca. 7 Hz, for the secondary alkyl complexes the coupling between the methine protons and the phosphorus nuclei is not observed. The α-methylene protons of most of the primary alkyl complexes appear under the PCH_3 resonance.

Reaction of alkyl bromides with *11c* occurs only in the presence of a radical initiator. For example, *iso*-propyl and *sec*-butyl bromide react with *11c* in refluxing benzene in the presence of catalytic amounts of AIBN to give a mixture of iridium(III) products which were not completely identified. The solution infrared spectra of these

mixtures show only one ν(CO) band at 2030 cm^{-1} and the ^1H nmr spectra show a number of broad PCH_3 resonances (δ1.6-2.2) and broad alkyl resonances (δ0.90-1.0, 1.2-1.4). Addition of $BrCH_2CH_2Ph$ to *11c* in refluxing benzene in the presence of 5 mole % AIBN gives two isomeric products, *12n* and *12n'*, which could not be separated.



12n

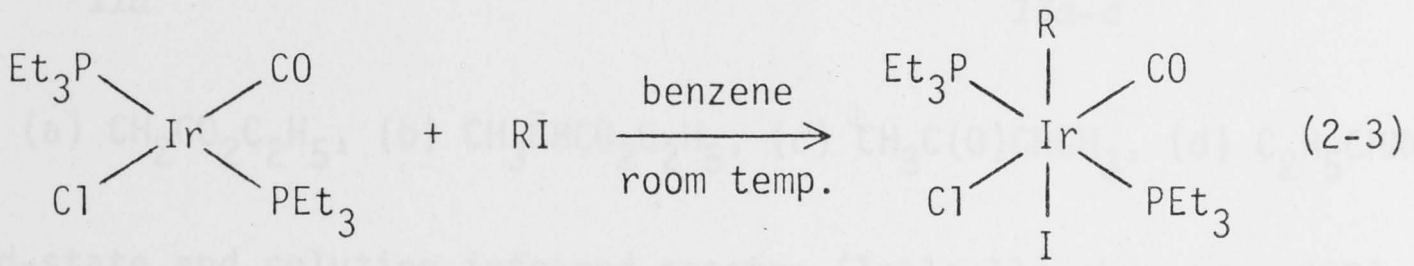


12n'

The ^1H nmr spectrum of this mixture exhibits two triplets (δ1.78,1.84, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz) for the PCH_3 resonances, as well as resonances at δ2.04 (m,$IrCH_2CH_2Ph$) and δ2.80 (m,$IrCH_2CH_2Ph$). The $^{31}P\{^1H\}$ nmr spectrum shows two singlets at δ-35.82 and δ-41.25. These data are consistent with the isomers shown in *12n* and *12n'*. The oxidative addition of alkyl bromides to *11c* was not investigated further as *sec*-alkyl complexes were not readily accessible by this method.

(C) L = PEt_3

Ethyl and *n*-propyl iodide react with $IrCl(CO)(PEt_3)_2$ to give $IrRClI(CO)(PEt_3)_2$ (2-3)



(2-3)

R = ethyl, propyl

No reaction occurs with *iso*-propyl or neopentyl iodide. For the ethyl complex the infrared spectrum shows a ν(CO) band at 2010 cm^{-1}

and a ν(IrCl) band at 305 cm^{-1}, and the $^{31}P\{^{1}H\}$nmr spectrum consists of a singlet at δ-21.41. The *n*-propyl complex could only be obtained as a dark oil, with a ν(CO) band at 2020 cm^{-1}, and a ^{31}P resonance at δ-21.31.

(D) L = PPh_2Me

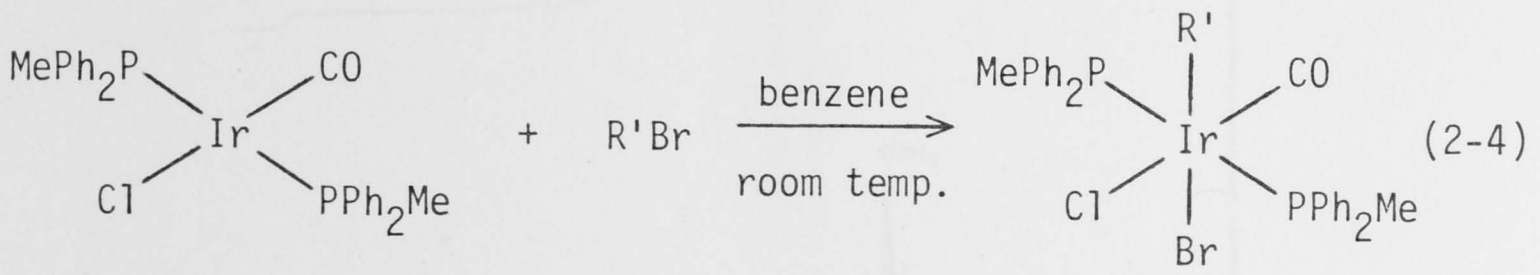
No reaction occurs between ethyl or *iso*-propyl iodide and $IrCl(CO)(PPh_2Me)_2$ (*11a*) in benzene at ambient temperature.

II. Oxidative Addition of Alkyl Halides with Electronegative Substituents to $IrCl(CO)L_2$

Alkyl halides with electronegative substituents react with $IrCl(CO)L_2$ (L = PPh_2Me, $PPhMe_2$, PMe_3) at ambient temperature to give the expected iridium(III) alkyls in high yield. These reactions are conveniently classified according to the phosphine ligand (L).

(A) L = PPh_2Me

Substituted alkyl bromides (R'Br) react with $IrCl(CO)(PPh_2Me)_2$ (*11a*) to give $IrR'BrCl(CO)(PPh_2Me)_2$ (*13a-d*) (2-4). Analytical and spectroscopic data for complexes *13a-d* appear in Tables 10-12.



(2-4)

11a *13a-d*

R' = (a) $CH_2CO_2C_2H_5$, (b) $CH_3CHCO_2C_2H_5$, (c) $CH_3C(O)CHCH_3$, (d) $C_2H_5CHNO_2$

Solid-state and solution infrared spectra (Table 11) show one ν(CO) band between 2030 and 2060 cm^{-1} and, where appropriate, a ν(C=O) band ca. 1700 cm^{-1}. Far-infrared spectra show a ν(IrCl) band ca. 300 cm^{-1}, assignable to a Cl trans to CO[47].

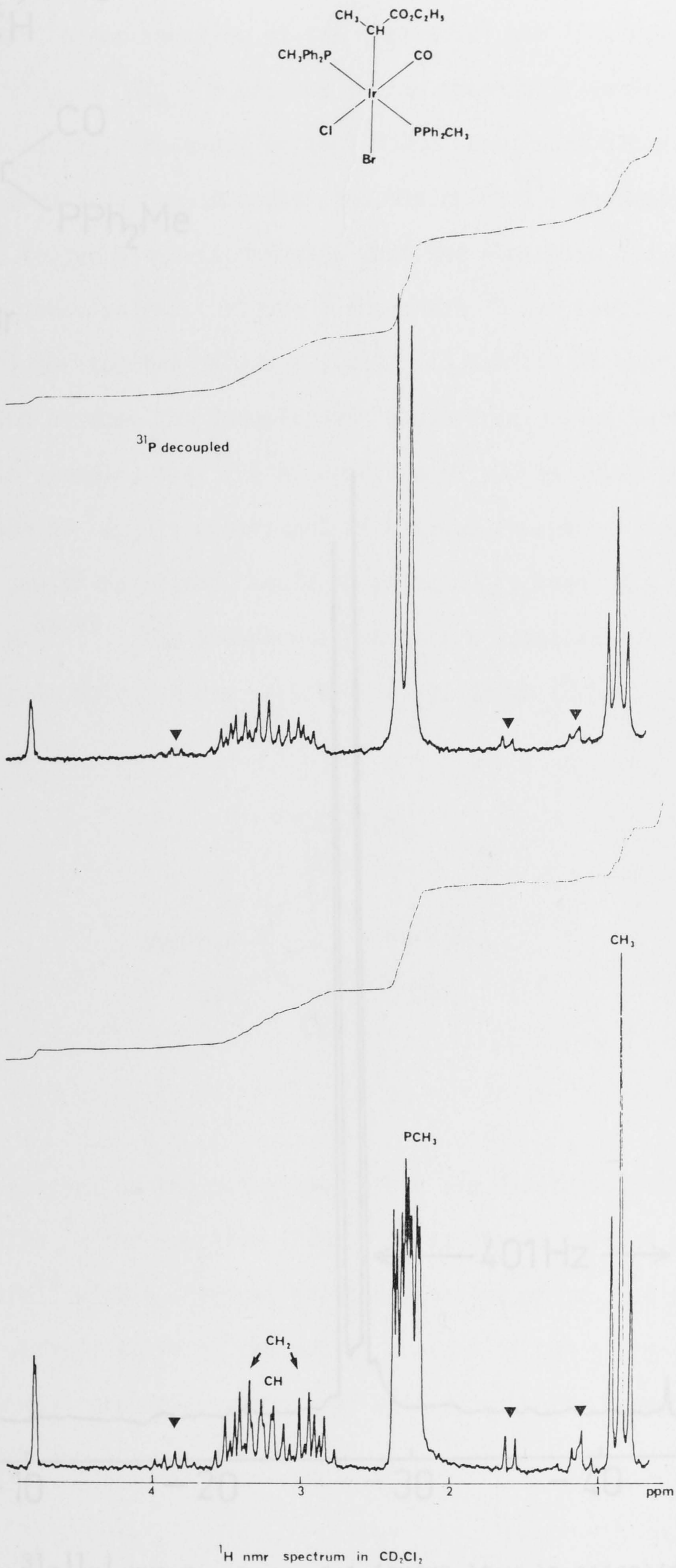
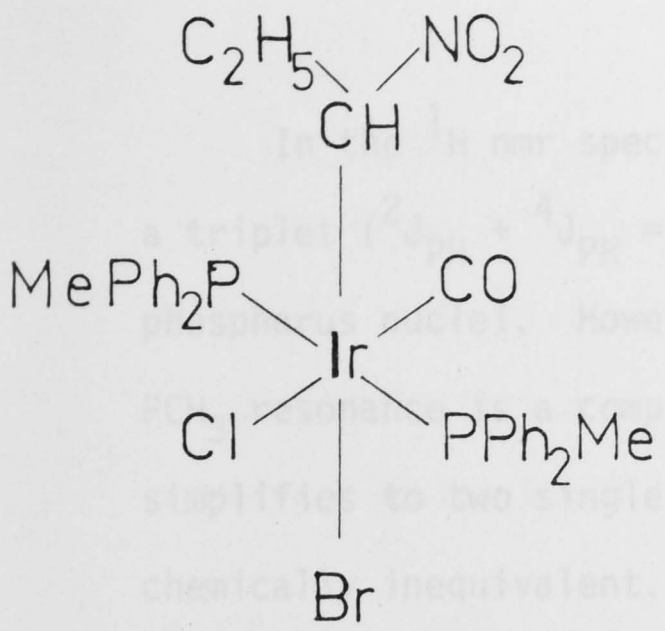


Figure 3. ^{1}H NMR Spectrum of $Ir(CH(CH_3)CO_2Et)BrCl(CO)(PPh_2Me)_2$.

▼ Impurities.



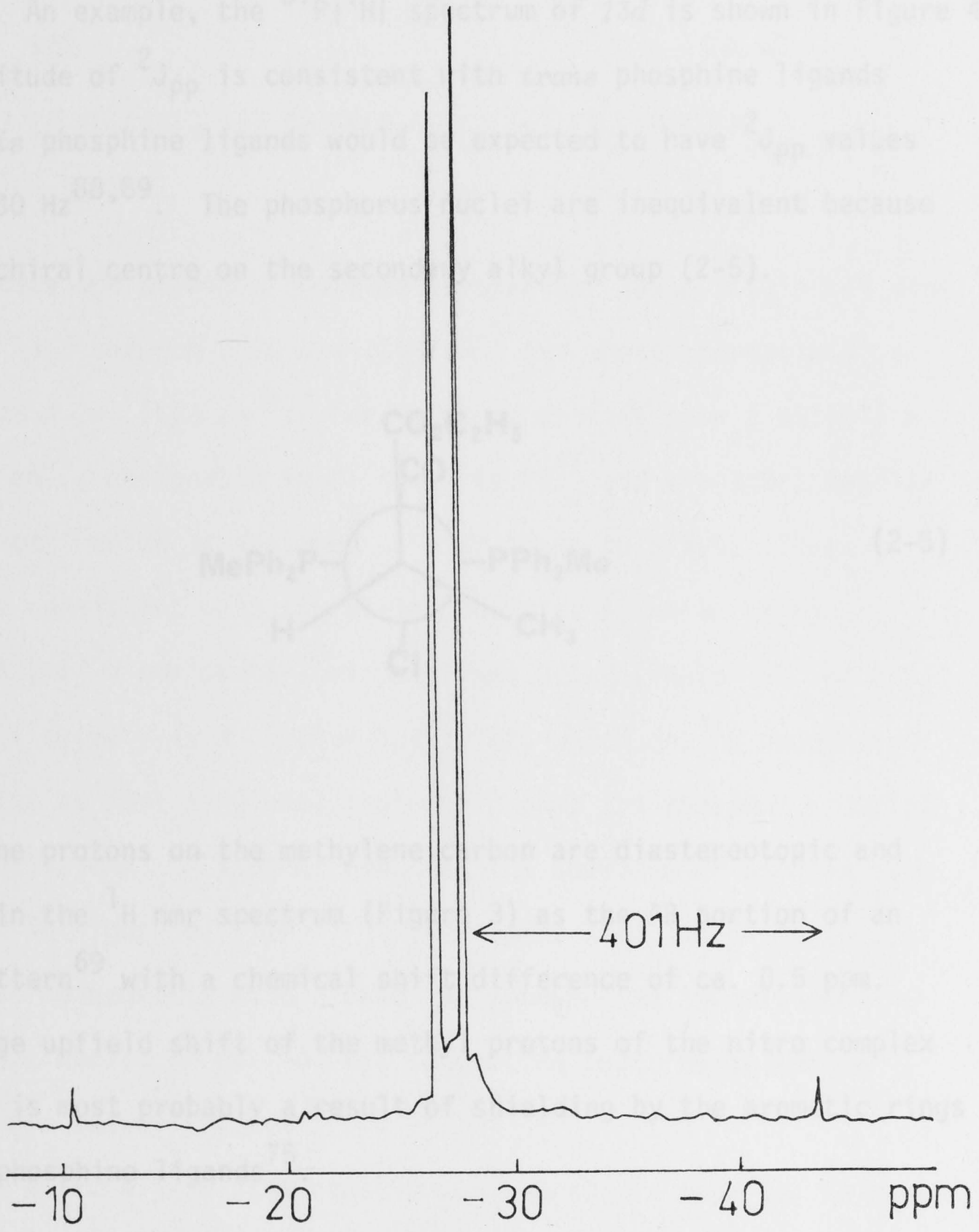
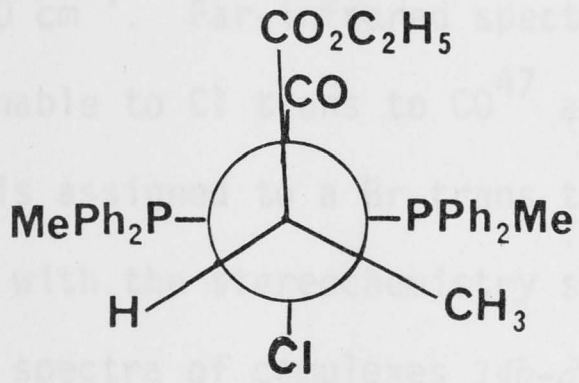


Figure 4. $^{31}P\{^{1}H\}$ NMR Spectrum of $Ir(CH(NO_2)C_2H_5)BrCl(CO)(PPh_2Me)_2$.

In the ^{1}H nmr spectrum of *13a* (Table 12) the PCH_3 resonance is a triplet ($^{2}J_{PH} + {}^{4}J_{PH}$ = 8 Hz) due to the chemically-equivalent phosphorus nuclei. However, in the ^{1}H nmr spectra of *13b-d*, the PCH_3 resonance is a complex multiplet, which on ^{31}P decoupling simplifies to two singlets, showing that the phosphine nuclei are chemically inequivalent. Figure 3 shows the ^{1}H nmr spectrum of *13b*. The $^{31}P\{^{1}H\}$ nmr spectra of *13b-d* (Table 11) exhibit AB quartets with the coupling between the inequivalent phosphorus nuclei being ca. 400 Hz. An example, the $^{31}P\{^{1}H\}$ spectrum of *13d* is shown in Figure 4. The magnitude of $^{2}J_{PP}$ is consistent with *trans* phosphine ligands since *cis* phosphine ligands would be expected to have $^{2}J_{PP}$ values ca. 10-30 Hz[88,89]. The phosphorus nuclei are inequivalent because of the chiral centre on the secondary alkyl group (2-5).

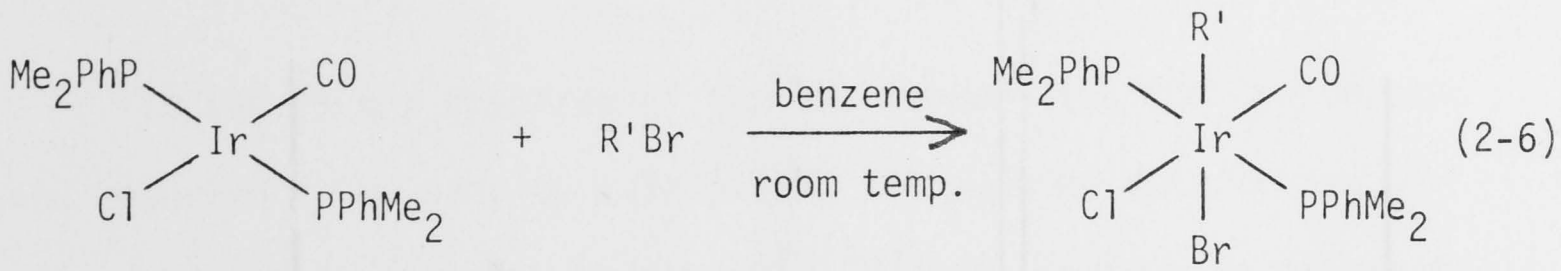


(2-5)

The protons on the methylene carbon are diastereotopic and appear in the ^{1}H nmr spectrum (Figure 3) as the AB portion of an ABX_3 pattern[69] with a chemical shift difference of ca. 0.5 ppm. The large upfield shift of the methyl protons of the nitro complex (δ0.16) is most probably a result of shielding by the aromatic rings of the phosphine ligands[75].

(B) L = $PPhMe_2$

Addition of substituted alkyl bromides (R'Br) to IrCl(CO)$(PPhMe_2)_2$ (*11b*) gives IrR'BrCl(CO)$(PPhMe_2)_2$ (*14a-d*) in high yield (2-6). Analytical and spectroscopic data for the complexes *14a-d* appear in Tables 13-15.



(2-6)

11b *14a-d*

R' = (a) $CH_2CO_2C_2H_5$, (b) $CH_3CHCO_2C_2H_5$, (c) $CH_3C(O)CHCH_3$, (d) $C_2H_5CHNO_2$

Solid-state and solution infrared spectra for *14a-d* (Table 14) show a ν(CO) band between 2030 and 2050 cm^{-1} and where appropriate, a ν(C=O) band ca. 1700 cm^{-1}. Far-infrared spectra show a ν(IrCl) at ca. 300 cm^{-1}, assignable to Cl trans to CO[47] and a ν(IrBr) band at ca. 180 cm^{-1} which is assigned to a Br trans to alkyl. These data are consistent with the stereochemistry shown in (2-6).

In the ^1H nmr spectra of complexes *14b-d* (Table 15) the PCH_3 resonance appears as a complex multiplet, which on ^{31}P decoupling simplifies to four singlets, indicating that the phosphorus nuclei are inequivalent. A typical example, the spectrum of complex *14d*, is shown in Figure 5. The $^{31}P\{^1H\}$ nmr spectra of *14b-d* (Table 14) appear as AB quartets with a coupling between the inequivalent phosphorus nuclei of ca. 400 Hz, suggesting that the phosphine ligands are mutually *trans*[88,89].

In a closely related reaction $CH_3CHBrNO_2$ is reported to react with IrBr(CO)$(PPhMe_2)_2$ in benzene at ambient temperature to give two isomeric products in which the phosphine ligands are claimed to be mutually *cis* (2-7)[90].

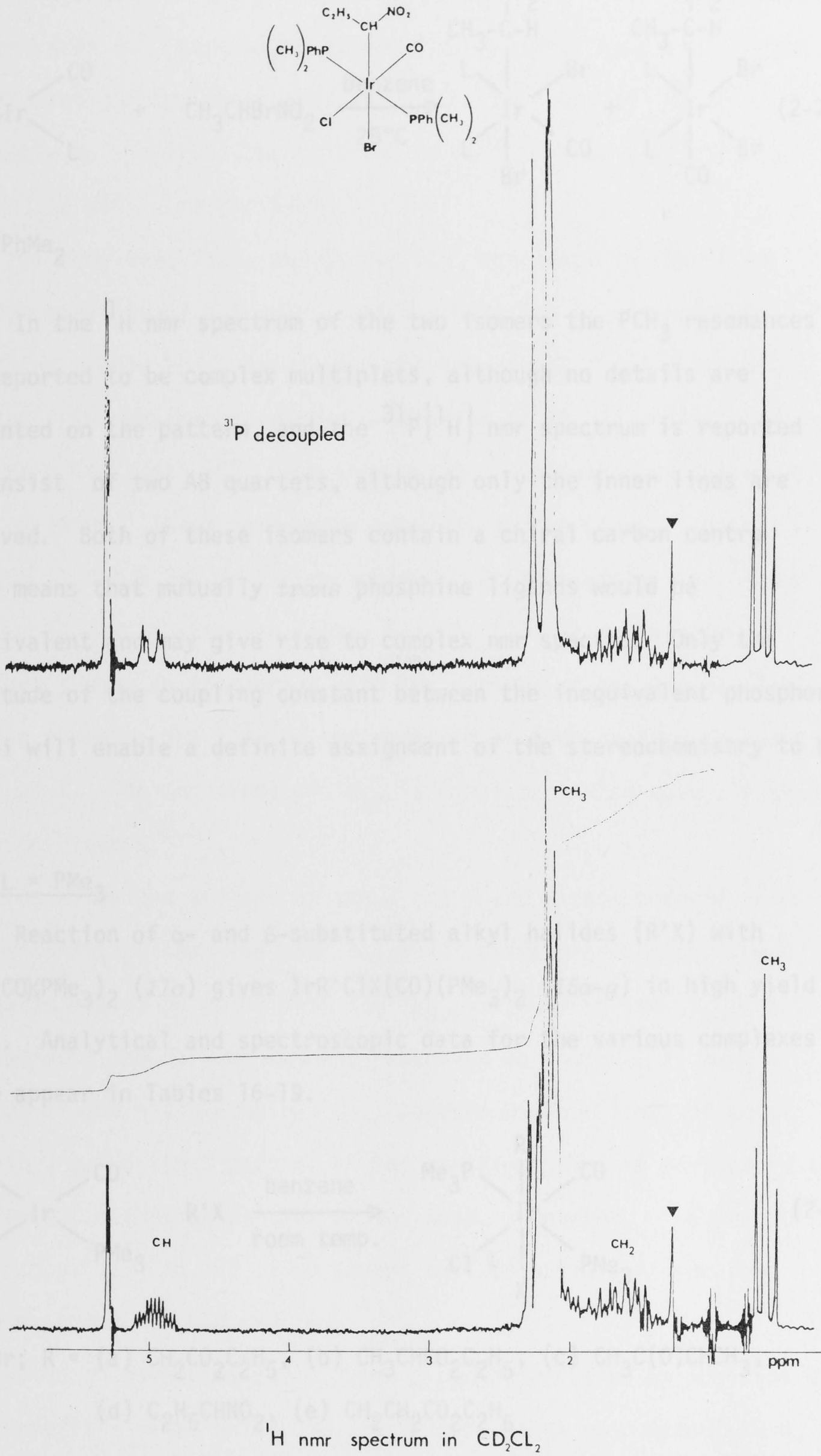
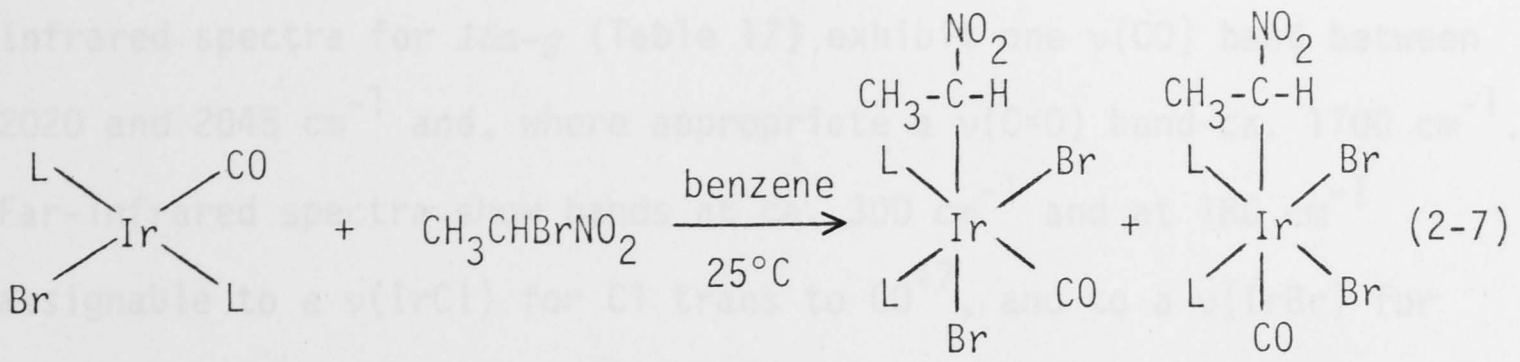


Figure 5. ^{1}H NMR Spectrum of $Ir(CH(C_2H_5)NO_2)BrCl(CO)(PPhMe_2)_2$. ▼ impurity.



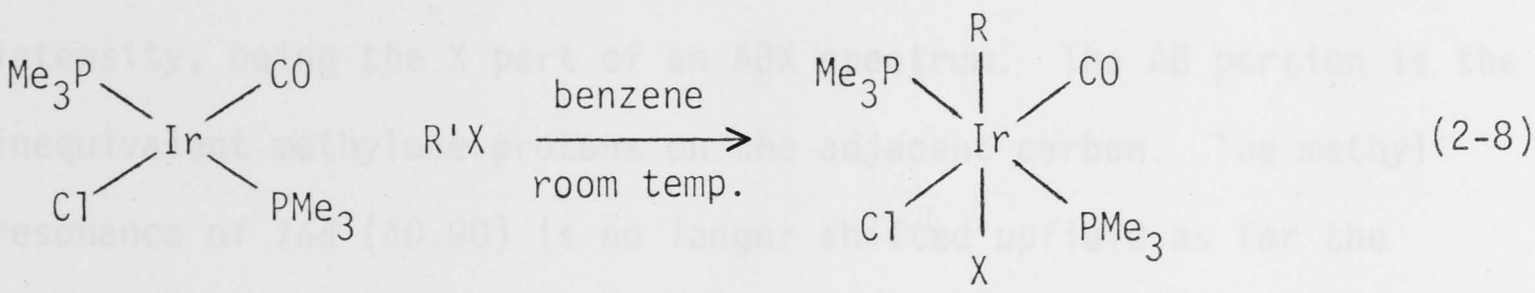
(2-7)

L = $PPhMe_2$

In the ^1H nmr spectrum of the two isomers the PCH_3 resonances are reported to be complex multiplets, although no details are presented on the pattern, and the $^{31}P\{^1H\}$ nmr spectrum is reported to consist of two AB quartets, although only the inner lines are observed. Both of these isomers contain a chiral carbon centre which means that mutually *trans* phosphine ligands would be inequivalent and may give rise to complex nmr spectra. Only the magnitude of the coupling constant between the inequivalent phosphorus nuclei will enable a definite assignment of the stereochemistry to be made.

(C) L = PMe_3

Reaction of α- and β-substituted alkyl halides (R'X) with $IrCl(CO)(PMe_3)_2$ (*11c*) gives $IrR'ClX(CO)(PMe_3)_2$ (*15a-g*) in high yield (2-8). Analytical and spectroscopic data for the various complexes *15a-g* appear in Tables 16-19.



(2-8)

X = Br; R = (a) $CH_2CO_2C_2H_5$, (b) $CH_3CHCO_2C_2H_5$, (c) $CH_3C(O)CHCH_3$, (d) $C_2H_5CHNO_2$, (e) $CH_2CH_2CO_2C_2H_5$

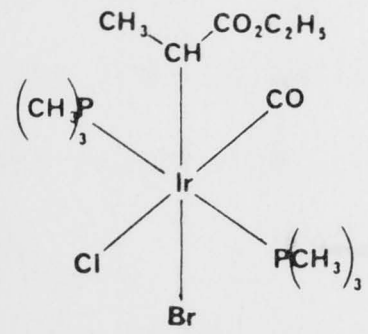
X = I; R = (f) $CH_3CHCO_2C_2H_5$, (g) CH_2CH_2CN

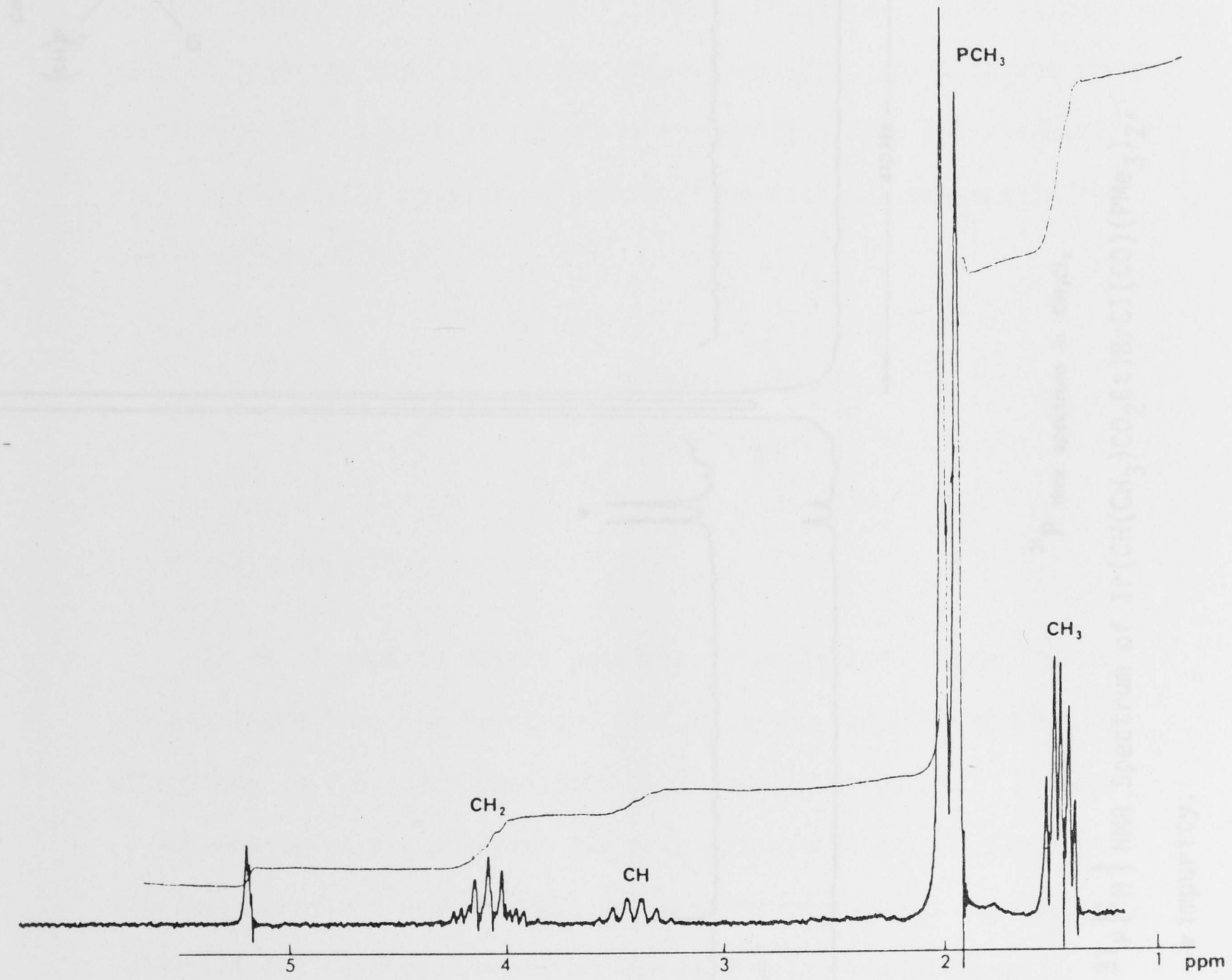
Infrared spectra for *15a-g* (Table 17) exhibit one ν(CO) band between 2020 and 2045 cm^{-1} and, where appropriate a ν(C=O) band ca. 1700 cm^{-1}. Far-infrared spectra show bands at ca. 300 cm^{-1} and at 180 cm^{-1} assignable to a ν(IrCl) for Cl trans to CO[47], and to a ν(IrBr) for Br trans to alkyl, respectively.

For complexes *15a,e* and *g*, the PCH_3 resonance in the ^1H nmr spectrum consists of a triplet, which simplifies to a singlet on ^{31}P decoupling (Table 18). The ^1H nmr spectra of *15b,d* and *f* exhibit a "doublet" PCH_3 resonance, with a separation of 10 Hz, whereas *15c* exhibits a "triplet" PCH_3 resonance, with a separation of the outer peaks of 10 Hz. These resonances simplify to two closely spaced singlets (1.0-1.5 Hz) on ^{31}P decoupling. As an example, the ^1H nmr spectrum of *15b* is shown in Figure 6. The $^{31}P\{^1H\}$ nmr spectra of *15b,d* and *f* show an AB quartet with $^2J_{PP}$ values of ca. 410 Hz (Table 19). An example, the $^{31}P\{^1H\}$ nmr spectrum of complex *15b*, is shown in Figure 7. The magnitude of $^2J_{PP}$ is consistent with mutually *trans* phosphine ligands[88,89].

The methylene protons of *15b,d* and *f* are diastereotopic, and it is interesting that the chemical shift difference between these protons decreases on going from *13b* ($\delta_{H-H'}$ = 0.5) to *15b* ($\delta_{H-H'}$ = 0.1), cf. Figures 3 and 6. The methine resonance in the $^1H\{^{31}P\}$ nmr spectrum of the nitro complex, *15c*, appears as four lines of equal intensity, being the X part of an ABX spectrum. The AB portion is the inequivalent methylene protons on the adjacent carbon. The methyl resonance of *15d* (δ0.90) is no longer shifted upfield as for the analogous complexes *13d* and *14d*.

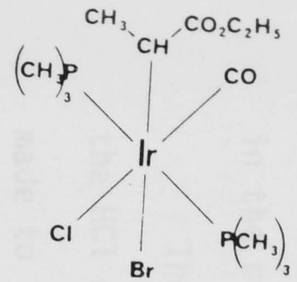
Although complexes *15a-d,f* and *g* can be prepared by addition of the appropriate alkyl halide to *11c* in benzene at room temperature, $BrCH_2CH_2CO_2C_2H_5$ reacts with *11c* only on being refluxed in benzene with 5 mole % AIBN. The bromide, $BrCH_2CH_2CN$, reacts with *11c* to give

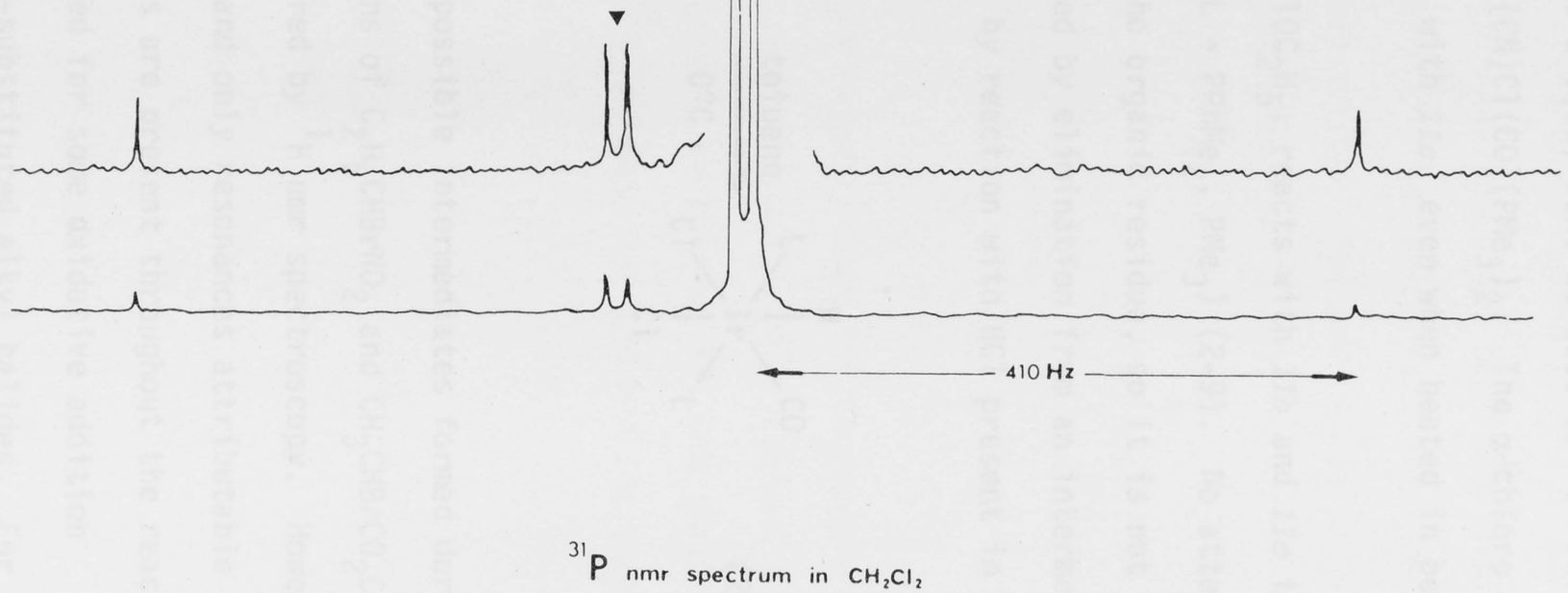




^{1}H nmr spectrum in CD_2Cl_2

Figure 6. ^{1}H NMR Spectrum of $Ir(CH(CH_3)CO_2Et)BrCl(CO)(PMe_3)_2$.



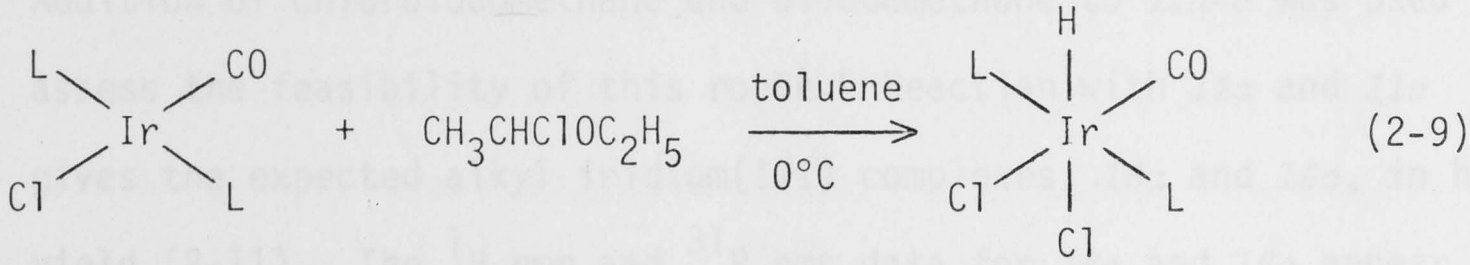


^{31}P nmr spectrum in CH_2Cl_2

Figure 7. $^{31}P\{^{1}H\}$ NMR Spectrum of $Ir(CH(CH_3)CO_2Et)BrCl(CO)(PMe_3)_2$.
▼ impurity.

an iridium(III) complex whose ^1H nmr suggests that no alkyl group is present. The infrared spectrum shows a weak ν(CN) band at 2180 cm^{-1} (well below the normal ν(CN) position of 2240 cm^{-1} for RCN complexes[91]) in addition to a ν(CO) band at 2050 cm^{-1}. This complex is believed to be $IrBr(CN)Cl(CO)(PMe_3)_2$. The α-chloro ester, $CH_3CHClCO_2C_2H_5$, does not react with *11c*, even when heated in benzene in the presence of AIBN.

The α-halo ether, $CH_3CHClOC_2H_5$, reacts with *11b* and *11c* to give the HCl adduct, $IrHCl_2(CO)L_2$ (L = $PPhMe_2$, PMe_3) (2-9). No attempt was made to identify the fate of the organic residue, so it is not known whether the HCl adduct is formed by elimination from an intermediate alkyl iridium(III) complex, or by reaction with HCl present in the sample of $CH_3CHClOC_2H_5$.



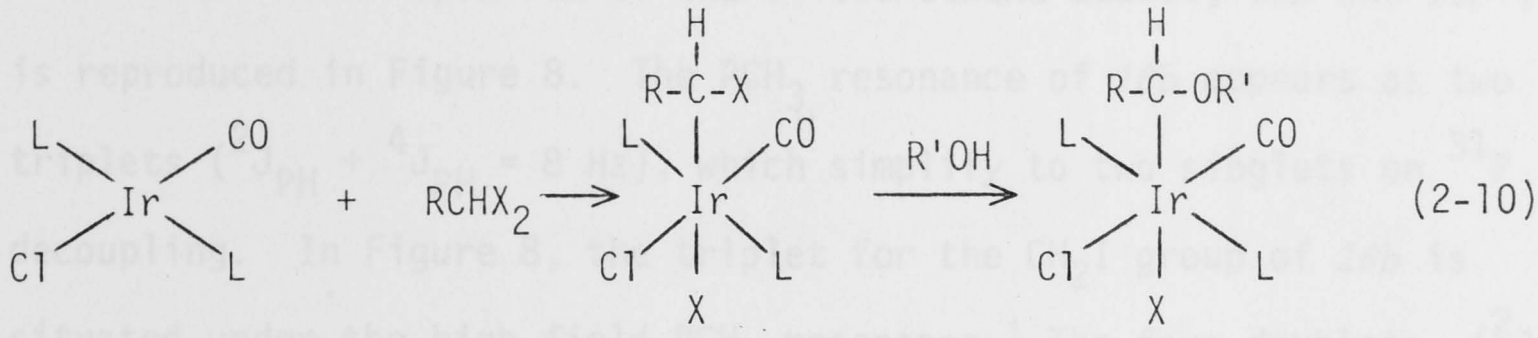
(2-9)

L = $PPhMe_2$, PMe_3

In an attempt to detect possible intermediates formed during oxidative addition the reactions of $C_2H_5CHBrNO_2$ and $CH_3CHBrCO_2C_2H_5$ with *11a-c* in C_6D_6 were monitored by ^1H nmr spectroscopy. However, no intermediates are observed and only resonances attributable to starting materials and products are present throughout the reaction. Intermediates have been reported for some oxidative addition reactions of electronegatively-substituted alkyl halides. For example O-bonded intermediates have been proposed for the addition of $CH_3CHBrCO_2C_2H_5$ to $Pt(PEt_3)_3$[70] and for the addition of $CH_3CHClNO_2$ to $IrCl(CO)(PPhMe_2)_2$[90].

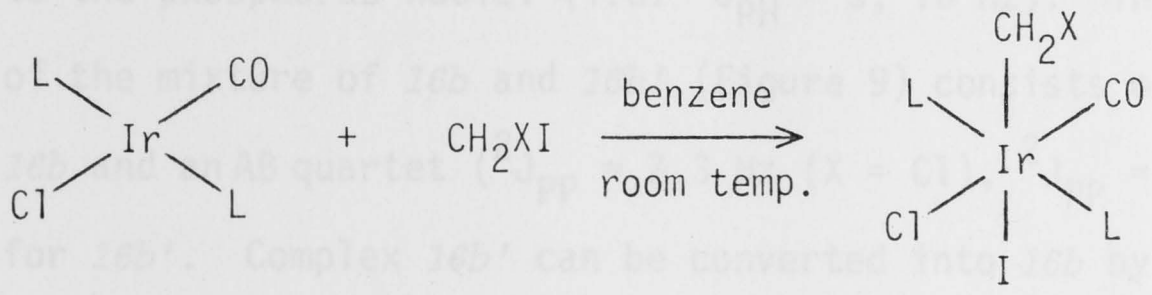
III. Oxidative Addition of 1,1-Dihaloalkanes to $IrCl(CO)L_2$

It would be desirable to be able to prepare *sec*-1-alkoxyalkyl iridium(III) complexes in order to examine the influence of an electron-donating group on the alkyl group rearrangement of *sec*-alkyl iridium(III) complexes. Since *sec*-1-alkoxyalkyl complexes could not be prepared by the direct addition of the appropriate alkyl halide to $IrCl(CO)L_2$, an indirect preparative route, the solvolysis of 1-haloalkyl iridium(III) complexes, was attempted (2-10)[92].



(2-10)

Addition of chloroiodomethane and diiodomethane to *11a-c* was used to assess the feasibility of this route. Reaction with *11a* and *11c* gives the expected alkyl iridium(III) complexes, *16a* and *16c*, in high yield (2-11). The ^1H nmr and ^{31}P nmr data for *16a* and *16c* appear in Tables 20 and 21, respectively.



(2-11)

16a,c

L = (a) PPh_2Me, (c) PMe_3

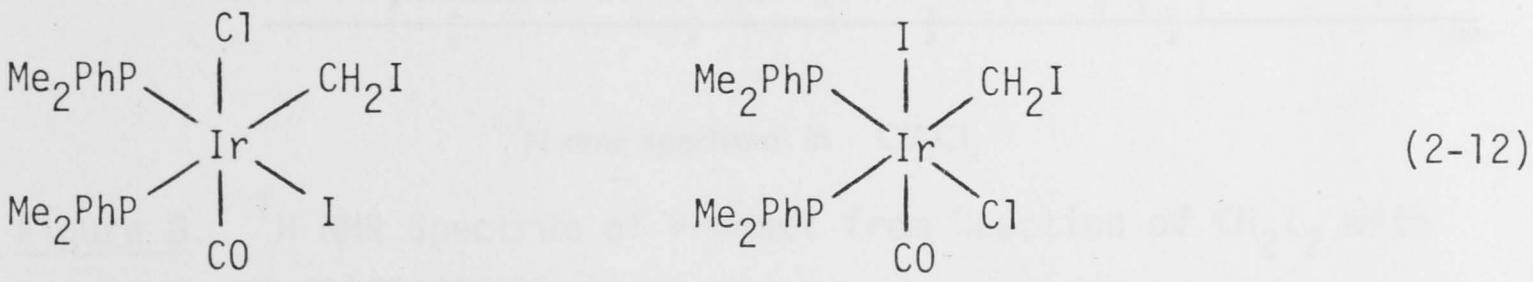
X = Cl, I

Infrared spectra for *16a* and *16c* show one $\nu(CO)$ band in the range 2040-2050 cm^{-1} and one $\nu(IrCl)$ band at ca. 310 cm^{-1} assignable to a Cl trans to CO[47]. In the ^1H nmr spectra the PCH_3 ligand resonance appears as a triplet ($^2J_{PH} + {}^4J_{PH}$ = 8 Hz), as does the CH_2X resonance

($^3J_{PH}$ = 7 Hz), both of which simplify to singlets on ^{31}P decoupling. These data are consistent with the structure shown in (2-11).

Addition of diiodomethane to *11b* gives two, isomeric products, *16b* (69%) and *16b'* (31%), which could not be separated. A solution infrared spectrum of a mixture of *16b* and *16b'* shows only one ν(CO) band at ca. 2045 cm^{-1}, and the far-infrared spectrum shows only one ν(IrCl) band at ca. 310 cm^{-1}. A similar result occurs for chloroiodomethane addition to *11b*.

The ^1H nmr spectrum of the diiodomethane adduct, *16b* and *16b'*, is reproduced in Figure 8. The PCH_3 resonance of *16b* appears as two triplets ($^2J_{PH}$ + $^4J_{PH}$ = 8 Hz), which simplify to two singlets on ^{31}P decoupling. In Figure 8, the triplet for the CH_2I group of *16b* is situated under the high field PCH_3 resonance. The four doublets, ($^2J_{PH}$ + $^4J_{PH}$ = 10, 12 Hz), which simplify to singlets on ^{31}P decoupling, belong to the inequivalent *cis* phosphine ligands of *16b'*. The remaining resonances, two doublets and two triplets, which simplify to two doublets on ^{31}P decoupling, belong to *16b'*, and are consistent with inequivalent methylene protons each being coupled differently to the phosphorus nuclei (i.e. $^3J_{PH}$ = 3, 10 Hz). The ^{31}P nmr spectrum of the mixture of *16b* and *16b'* (Figure 9) consists of a singlet for *16b* and an AB quartet ($^2J_{PP}$ = 7.3 Hz (X = Cl), $^2J_{PP}$ = 10 Hz (X = I)) for *16b'*. Complex *16b'* can be converted into *16b* by the addition of methanol to a dichloromethane solution of the two isomers. Two possible structures of *16b'* (X = I) are shown (2-12).



(2-12)

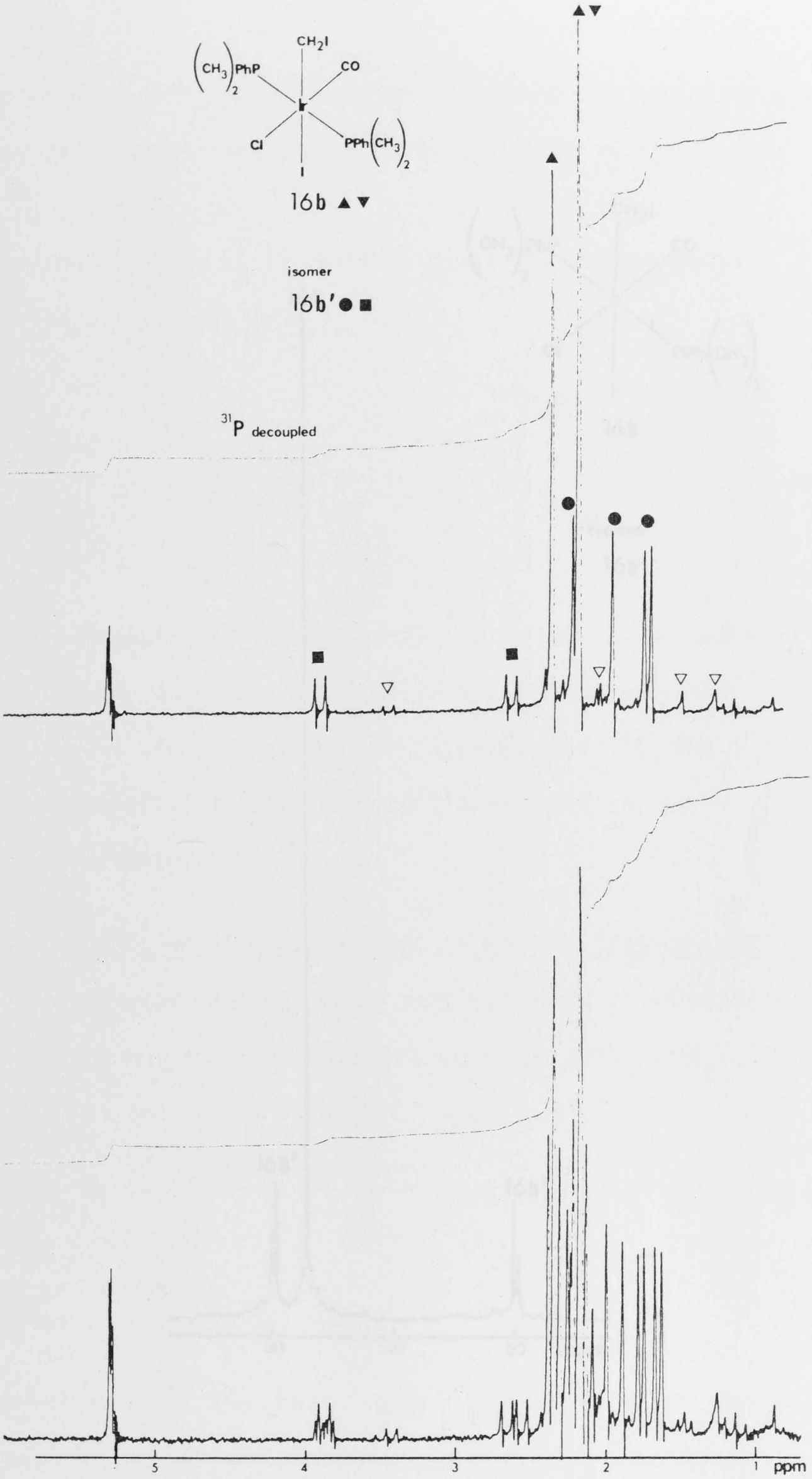
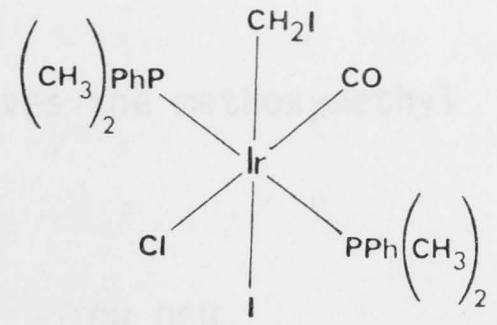


Figure 8. ^1H NMR Spectrum of Product from Reaction of CH_2I_2 with $IrCl(CO)(PPhMe_2)_2$.

▲ PCH_3 of *16b*; ▼ $IrCH_2I$ of *16b*; ● PCH_3 of *16b'*;

■ $IrCH_2I$ of *16b'*; ▽ impurities.

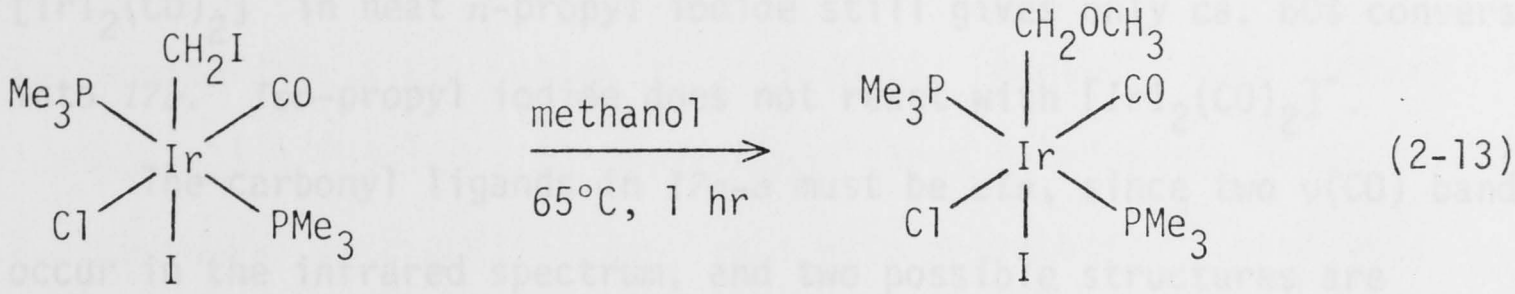


^{31}P nmr spectrum in CH_2Cl_2

Figure 9. $^{31}P\{^1H\}$ NMR Spectrum of Product from Reaction of CH_2I_2 with $IrCl(CO)(PPhMe_2)_2$.

Conversion of *16b'* into *16b* by addition of methanol is reminiscent of the *cis* to *trans* isomerization of phosphine ligands in $IrRCl_2(CO)(PPh_2Me)_2$[78].

Refluxing *16c* (X = I) in methanol gives the methoxymethyl complex, $Ir(CH_2OCH_3)ClI(CO)(PMe_3)_2$ (2-13).



(2-13)

However, reaction of CH_3CHBr_2 with *11c* in benzene or methanol gives the dibromide adduct, $IrBr_2Cl(CO)(PMe_3)_2$, instead of the expected oxidative addition adduct, $Ir(CH(Br)CH_3)BrCl(CO)(PMe_3)_2$. Thus, *sec*-1-alkoxyalkyl iridium(III) complexes could not be prepared by this route.

IV. Oxidative Addition of Alkyl Halides to Anionic Iridium Complexes

In order to examine alkyl group rearrangements of anionic alkyl iridium(III) complexes an attempt was made to prepare $AsPh_4[IrRI_3(CO)_2]$ by the addition of alkyl iodides to $AsPh_4[IrI_2(CO)_2]$ (2-14).

$$[IrI_2(CO)_2]^- + RI \xrightarrow{\text{dichloromethane}} [IrRI_3(CO)_2]^- \quad (2\text{-}14)$$

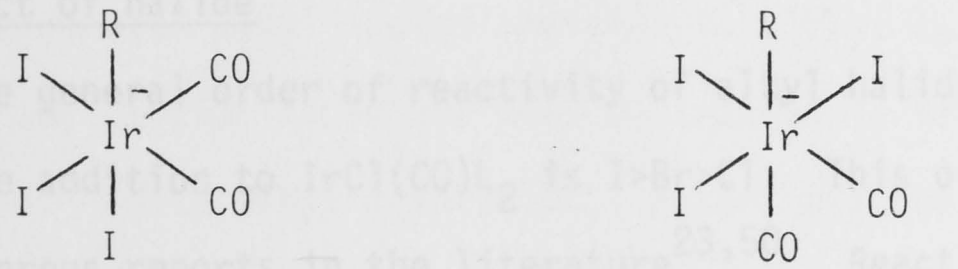
17a-c

R = (a) methyl, (b) ethyl, (c) propyl

The iridium(III) anion, *17a*, which shows two ν(CO) bands at 2045 cm^{-1} and 2100 cm^{-1} in the infrared spectrum, is stable as a solid and in solution. In contrast, *17b* and *17c* are stable in solution only in the presence of an excess of alkyl iodide and will revert to $[IrI_2(CO)_2]^-$ on attempted isolation. Monitoring the addition of alkyl iodide by infrared spectroscopy shows the disappearance of $[IrI_2(CO)_2]^-$(ν(CO) bands at 1968 cm^{-1} and 2050 cm^{-1}) and the appearance of *17a-c* (ν(CO)

bands at ca. 2045 cm^{-1} and at ca. 2095 cm^{-1}). Addition of a ten-fold excess of ethyl iodide to $[IrI_2(CO)_2]^-$ in refluxing dichloromethane gives complete conversion into *17b* in 24 h, however under the same conditions, *n*-propyl iodide gives only 60% conversion into *17c* (even after one week only 60% conversion occurs). Dissolution of $[IrI_2(CO)_2]^-$ in neat *n*-propyl iodide still gives only ca. 60% conversion into *17c*. *Iso*-propyl iodide does not react with $[IrI_2(CO)_2]^-$.

The carbonyl ligands in *17a-c* must be *cis*, since two ν(CO) bands occur in the infrared spectrum, and two possible structures are shown (2-15).



(2-15)

Discussion.

I. Preparation of Alkyl Iridium(III) Complexes

A. Effect of alkyl group

Both primary and secondary alkyl iodides react with $IrCl(CO)L_2$ (L = $PPhMe_2$, PMe_3 but not PPh_2Me) to give the expected product, $IrRClI(CO)L_2$, whereas *tert*-butyl iodide affords only the dihalide adduct $IrClI_2(CO)L_2$. These results can be contrasted to those for the addition of *sec*-alkyl halides to $Pt(PEt_3)_3$, in which equal quantities of $PtI_2(PEt_3)_2$ and $PtHI(PEt_3)_2$ are formed[20]. Alkyl halides with electronegative substituents react more readily with $IrCl(CO)L_2$ than do simple alkyl halides, as shown by the addition of $CH_3CHBrC(O)CH_3$ to $IrCl(CO)(PPh_2Me)_2$. Once again the iridium system can be contrasted to the platinum system where addition of $CH_3CHBrCO_2C_2H_5$ to PtL_3 (L = $PPhMe_2$, PEt_3) gives mainly the dihalide complex $PtBr_2L_2$[57]. Electronegative substituents in the α-position appear to activate alkyl halides

towards oxidative addition more readily than substituents in the β-position. For example, $CH_3CHBrCO_2C_2H_5$ oxidatively adds to $IrCl(CO)(PMe_3)_2$ within 5 min at room temperature whereas $BrCH_2CH_2CO_2C_2H_5$ requires 18 h reflux in benzene in the presence of 5 mole % AIBN. Unfortunately, neither *sec*-1-alkoxyalkyl nor *sec*-1-haloalkyl iridium(III) complexes could be prepared by the addition of the appropriate alkyl halide to $IrCl(CO)L_2$. However, both primary 1-alkoxyalkyl iridium(III) complexes without β-hydrogens[38] and primary 2-alkoxyalkyl iridium(III) complexes with β-hydrogens[92] have been reported.

(B) Effect of halide

The general order of reactivity of alkyl halides towards oxidative addition to $IrCl(CO)L_2$ is I>Br>Cl. This order is consistent with numerous reports in the literature[23,50]. Reaction of *sec*-alkyl bromides with $IrCl(CO)(PMe_3)_2$ in refluxing benzene in the presence of catalytic amounts of AIBN gives a mixture of products. In contrast, a room temperature addition of ethyl and butyl bromide to *11c* occurs under uv irradiation to give the expected product, $IrRBrCl(CO)(PMe_3)_2$ in high yield[23]. The method of uv irradiation is a potentially useful means of enhancing the addition of alkyl halides to $IrCl(CO)L_2$ and should enable a more diverse series of alkyl iridium(III) complexes to be prepared.

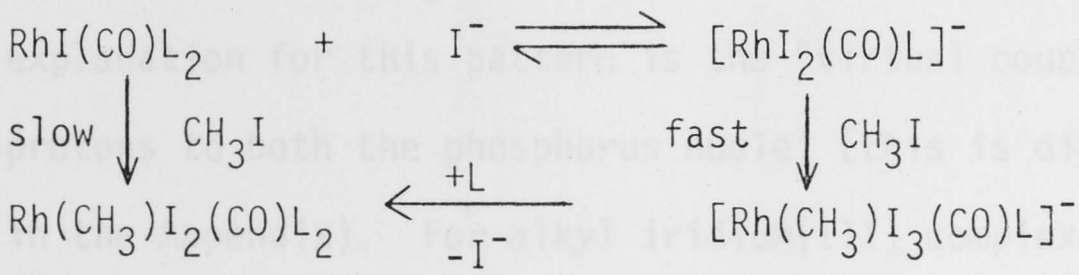
(C) Effect of phosphine ligands

Transition metal complexes containing the smaller, more basic phosphines, such as PMe_3, are expected to be more reactive than those containing larger, less basic phosphines, such as PPh_2Me (see pages 6-8, Chapter One). The reactivity of $IrCl(CO)L_2$ towards oxidative addition follows this trend since $IrCl(CO)(PMe_3)_2$ is the most reactive and $IrCl(CO)(PPh_2Me)_2$ is the least reactive. The

complex, $IrCl(CO)(PEt_3)_2$ reacts with straight-chain primary alkyl iodides but not with *sec*-alkyl or branched-chain *n*-alkyl iodides. Whether this is an electronic or steric effect of the phosphine ligand is not clear. Even though ethyl iodide is unreactive towards $IrCl(CO)(PPh_2Me)_2$ in benzene at room temperature, the expected adduct, $Ir(CH_2CH_3)ClI(CO)(PPh_2Me)_2$, can be obtained by uv irradiation of a benzene solution of the reactants[23].

(D) Anionic alkyl iridium(III) complexes

Oxidative addition of alkyl halides to anionic metal complexes can be faster than to neutral metal complexes (Scheme 18)[93]. This is not the case with alkyl iodide addition to $[IrI_2(CO)_2]^-$, where reaction with *n*-propyl iodide could not even be induced to proceed to completion. These alkyl iridium(III) anions must be relatively unstable since they revert to the iridium(I) anion in the absence of an excess of alkyl iodide. Not all iridium(III) anionic complexes are unstable, since addition of halogen, allyl chloride, acetyl chloride and mercuric halide to $[IrX_2(CO)_2]^-$ (X = Cl, Br) gives stable iridium(III) adducts[51].



Scheme 18. Reaction of CH_3I with $RhI(CO)L_2$ in the Presence of Bu_4NI.

II. NMR Spectra.

In the alkyl chain Ir-C(1)-C(2)-C(3)-C(4) of the complexes, *trans*-$IrRCl_2(CO)(PPh_3)_2$, the chemical shift of the protons on C(3) and C(4) are ca. 0.4 ppm to higher field than expected, an effect attributed to shielding by the aromatic rings of *trans*-triphenyl-

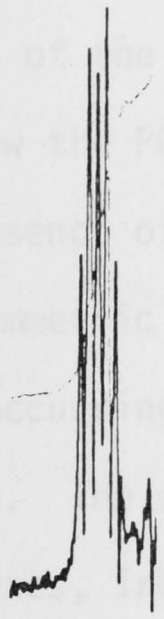
phosphine ligands[75]. A similar upfield shift of protons on C(1)-C(3) occurs for *trans*-$IrRCl_2(CO)(PPh_2Me)_2$, but not for the analogous *cis* isomer[78]. Protons on C(3) and C(4) of the complexes, $IrRClI(CO)L_2$ ($L = PPh_2Me$, $PPhMe_2$), occur ca. 0.65-1.0 ppm to higher field than those of the corresponding PMe_3-containing complexes (Table 22).

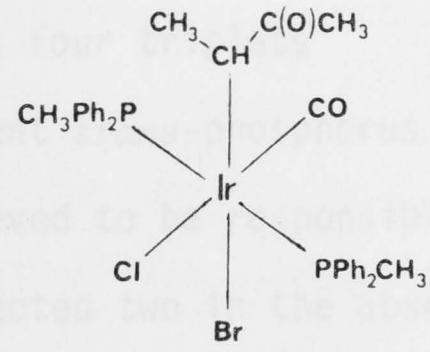
TABLE 22

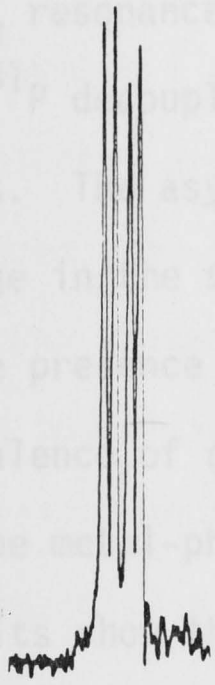
Chemical Shift Difference, ($\Delta\delta$), between Protons on C(3) and (4) of $IrRClI(CO)L_2$ ($L = PMe_3$, $PPhMe_2$).

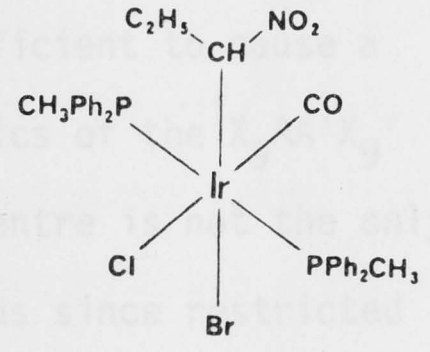
	$\Delta\delta$	
R	C(3)	C(4)
propyl	0.82	
butyl	≈1.0	0.65
sec-butyl	0.64	
iso-butyl	0.75	
$CH_3CH_2CHNO_2$	0.74	

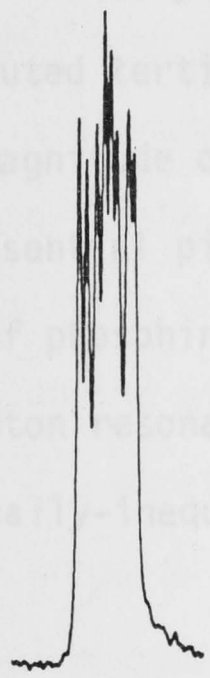
For alkyl iridium(III) complexes with chemically-equivalent phosphorus nuclei in mutually *trans* positions the expected 1:2:1 triplet for the PCH_3 ^1H resonance is observed. The generally accepted explanation for this pattern is the "virtual coupling" of the methyl protons to both the phosphorus nuclei (this is discussed more fully in the Appendix). For alkyl iridium(III) complexes containing a chiral carbon centre the phosphorus nuclei are inequivalent and so the PCH_3 groups form part of an ABX_nY_n spin system. The overall appearance of the PCH_3 resonance in the ^1H nmr spectrum will depend upon the chemical shift differences of the AB nuclei and the XY nuclei, as well as the relative magnitudes of the various coupling constants, J_{AB}, J_{XY}, J_{AX}, J_{AY}, J_{BX}, and J_{BY}. Only small changes seem to be necessary in the relative magnitudes of these values to change dramatically the pattern of the PCH_3 resonance. Figure 10 shows the

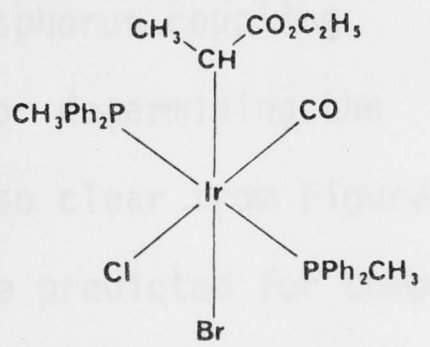












^{1}H nmr PCH_3

Figure 10. PCH_3 Resonance in ^{1}H NMR Spectrum of $IrRBrCl(CO)(PPh_2Me)_2$.

PCH_3 resonances for complexes of the type $IrRClBr(CO)(PPh_2Me)_2$, in which the pattern changes dramatically on changing the alkyl group. The ^1H nmr spectra of the complexes, $Ir(CH_2CHXCH_3)Cl_2(CO)(PPhMe_2)_2$ (X = OH, OCH_3) show the PCH_3 ligand resonance as four triplets because of the presence of chemically-inequivalent *trans*-phosphorus nuclei[92]. The asymmetric carbon centre is believed to be responsible for four signals occurring, rather than the expected two in the absence of a chiral centre. The *trans* phosphine ligands of *sec*-butyl and 2-methylbutyl complexes, $IrRClI(CO)(PMe_3)_2$ must also be inequivalent. However, the PCH_3 resonance appears as a 1:2:1 triplet, which simplifies to a singlet on ^{31}P decoupling, as expected for *trans*-equivalent phosphine ligands. The asymmetry cannot be sufficient to cause a significant change in the spectral characteristics of the $X_9AA'X_9'$ spin system. The presence of a chiral carbon centre is not the only cause of inequivalence of *trans* phosphine ligands since restricted rotation about the metal-phosphorus bond may also produce this effect.[94]

These results show that the proton resonance of the PCH_3 group cannot be used as the only criterion for assigning the stereochemistry of methyl-substituted tertiary phosphine ligands in iridium(III) complexes. The magnitude of the phosphorus-phosphorus coupling constant is an essential piece of information for determining the stereochemistry of phosphine ligands. It is also clear from Figure 10 that the PCH_3 proton resonance pattern cannot be predicted for complexes with *trans* chemically-inequivalent phosphorus nuclei.

Experimental.

General

Reactions involving iridium(I) complexes and tertiary phosphines were performed under nitrogen using standard Schlenk techniques[108].

Benzene and toluene were distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nigrogen; methanol was distilled from magnesium methoxide under nitrogen. Some alkyl iodides were obtained commercially. However, *iso*-butyl, neopentyl, 3-pentyl, 2-octyl, cyclohexyl, 2-methylbutyl and 3-methylbutyl iodides were prepared from the appropriate alcohol and triphenylphosphite-methyliodide[95]. Diiodomethane was prepared from dichloromethane and sodium iodide[96]. Ethyl-2-iodopropionate was prepared via the p-toluenesulphonyl ester from ethyl lactate and sodium iodide[97]. 3-Iodopropionitrile was prepared from 3-bromopropionitrile and sodium iodide in acetone. Alkyl bromides were obtained commercially or prepared by literature procedures. 1-Bromo-1-nitropropane was prepared from 1-nitropropane by treatment with sodium hydroxide and bromine[98]. 3-Bromobutan-2-one was prepared from methylethylketone and bromine[99]. 1-Chloro-1-ethoxy ethane was prepared from diethyl ether and chlorine[100]. All alkyl halides were purified by distillation under nitrogen or vacuum.

Triethylphosphine was obtained commercially, whereas methyldiphenylphosphine[101], dimethylphenylphosphine[101], and trimethylphosphine[102] were prepared by literature procedures. Chloroiridic acid was purchased from Johnson and Matthey Co.

^{1}H nuclear magnetic resonance (nmr) spectra (100 MHz) were recorded on a Varian HA-100 spectrometer at 29°C. Chemical shifts are reported relative to tetramethylsilane and are calculated from the position of solvent absorption. $^{31}P\{^{1}H\}$ nmr spectra (24.28 MHz) were recorded on a Bruker 322S spectrometer at 35°C. Phosphorus chemical

shifts are reported relative to external H_3PO_4 (85%) and are positive to low field.

Infrared spectra (4000-200 cm^{-1}) were recorded as Nujol mulls or dichloromethane solutions using CsI windows of 1mm path length on PE 457 or 225 spectrophotometers and calibrated against polystyrene. Far-infrared spectra (400-100 cm^{-1}) were recorded as polythene discs on an Hitachi FIS 3 spectrophotometer. Microanalyses were carried out in the John Curtin School of Medical Research and in the Research School of Chemistry (Dr. Joyce Fildes and Miss Brenda Stevenson and their associates). Molecular weights were measured at 25°C on ca. 0.02 M solutions in dichloromethane using a Knauer vapour pressure osmometer. Melting points (uncorrected) were measured on a Gallenkamp hot-stage apparatus.

Preparations.

The complexes, $[IrCl(CO)(C_8H_{14})_2]_2$[103], $AsPh_4[IrI_2(CO)_2]$[104], $RhCl(CO)(PPhMe_2)_2$[105], $IrCl(CO)(PPh_2Me)_2$[106], $IrCl(CO)(PPhMe_2)_2$[106], $IrCl(CO)(PMe_3)_2$[107], $IrCl(CO)(PEt_3)_2$[106] and $IrI(CO)(PPhMe_2)_2$[36] were prepared by literature procedures.

(i) Alkylcarbonylchloroiodobis(dimethylphenylphosphine)-iridium(III), $IrRClI(CO)(PPhMe_2)_2$ (*10a-g*)

A solution of $IrCl(CO)(PPhMe_2)_2$ (*11b*) (0.1 g, 0.19 mmol) in benzene (5 mL) was treated with the appropriate alkyl iodide (0.15 mL). The yellow solution became colourless (2-30 min depending on alkyl iodide). Evaporation of volatiles and trituration with hexane gave the product as a white solid (80-90%). Analytical samples were obtained by recrystallization from dichloromethane-hexane. Analytical and spectroscopic data for *10a-g* appear in Tables 4-6. Addition of alkyl iodides to $IrI(CO)(PPhMe_2)_2$ under similar conditions gave

$IrRI_2(CO)(PPhMe_2)_2$. Analytical and spectroscopic data for these complexes also appear in Tables 4-6. Additions of ethyl and *iso*-propyl iodide to $RhCl(CO)(PPhMe_2)_2$ and to $IrCl(CO)(PPh_2Me)_2$ were carried out by an analogous procedure but gave only starting material.

(ii) Benzylbromochlorocarbonylbis(dimethylphenylphosphine)-iridium(III), $Ir(CH_2C_6H_5)BrCl(CO)(PPhMe_2)_2$

A solution of *11b* (0.1 g, 0.19 mmol) in benzene (5 mL) was treated with benzyl bromide (0.15 mL). The yellow solution became colourless over 30 min. Evaporation of volatiles and trituration of the residue with hexane gave the product as a white solid (80%). An analytical sample was obtained by recrystallization from dichloromethane/hexane. Mp 156-57°C; IR (Nujol) 2040 cm^{-1} (CO), 306 cm^{-1} (IrCl), 170 cm^{-1} (IrBr); ^1H nmr (CD_2Cl_2) δ2.08, 2.20 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3), 2.96 (t, $^3J_{PH}$ = 6 Hz, $IrCH_2C_6H_5$), 6.4-7.7 (m, $IrCH_2C_6H_5$); $^{31}P\{^1H\}$ nmr (CH_2Cl_2) δ-30.87 (s).

Anal. Calc. for $C_{24}H_{29}ClIrOP_2$: C, 41.00; H, 4.16; P, 8.82. Found: C, 41.10; H, 4.18; P, 8.71.

(iii) Alkylcarbonylchloroiodobis(trimethylphosphine)iridium(III), $IrRClI(CO)(PMe_3)_2$ (*12a-m*)

A solution of $IrCl(CO)(PMe_3)_2$ (*11c*) (0.1 g, 0.25 mmol) in benzene (5 mL) was treated with the appropriate alkyl iodide (0.5 mL). The yellow solution became colourless (2-60 min, depending on alkyl iodide). Evaporation of volatiles and trituration with hexane gave the product as a white solid (80-95%). Analytical samples were obtained by recrystallization from dichloromethane-hexane. Analytical and spectroscopic data for *12a-m* appear in Tables 7-9.

(iv) Bromocarbonylchloro(2-phenylethyl)bis(trimethylphosphine)-iridium(III)

A solution of *11c* (0.1 g, 0.25 mmol) in benzene (1 mL) was treated with AIBN (5 mg) and $PhCH_2CH_2Br$(125 μL). The yellow solution

was heated at 60°C until it became colourless (ca. 24 h). Evaporation of volatiles and trituration with hexane gave the product as a white solid (0.11 g, 74%), which could be recrystallized from dichloromethane-hexane. Mp 147-50°C: IR (Nujol) 2015 cm^{-1} (CO), 318, 240 cm^{-1} (IrCl); ^{1}H nmr (CD_2Cl_2) δ1.78, 1.84 (t, $^{2}J_{PH} + {}^{4}J_{PH}$ = 8 Hz, PCH_3), 2.04 (m, $IrC\underline{H}_2CH_2Ph$), 2.80 (m, $IrCH_2C\underline{H}_2Ph$); $^{31}P\{^{1}H\}$ nmr (CH_2Cl_2) δ-35.82 (s), -41.25 (s).

Anal. Calcd for $C_{15}H_{27}BrClIrOP_2$: C, 30.38; H, 4.59; P, 10.47. Found: C, 29.87; H, 5.02; P, 9.95.

(v) Carbonylchloroethyliodobis(triethylphosphine)iridium(III)

A solution of $IrCl(CO)(PEt_3)_2$ (0.1 g, 0.20 mmol) in benzene (5 mL) was treated with ethyl iodide (0.15 mL, 1.4 mmol). The yellow solution became colourless after 1 hr. Evaporation of volatiles and trituration with hexane gave the product as a white solid (0.1 g, 77%) which could be recrystallized from dichloromethane-hexane. Mp 96-97°C; IR (Nujol) 2010 cm^{-1} (CO), 305 cm^{-1} (IrCl); $^{1}H\{^{31}P\}$ nmr (CD_2Cl_2) δ1,17 (t, $PCH_2C\underline{H}_3$), 2.20 (m, $PC\underline{H}_2CH_3$), 1.42 (t, J_{HH} = 7 Hz, 3 H, $IrCH_2C\underline{H}_3$), 1.97 (q, J_{HH} = 7 Hz, 2 H, $IrC\underline{H}_2CH_3$); $^{31}P\{^{1}H\}$ (CH_2Cl_2) δ-21.41 (s).

Anal. Calcd for $C_{15}H_{35}ClIIrOP_2$: C, 27.80; H, 5.44; P, 9.57. Found: C, 28.07; H, 5.42; P, 9.85.

The complex $Ir(CH_2CH_2CH_3)ClI(CO)(PEt_3)_2$ was prepared similarly, but could only be obtained as a dark oil: IR (CH_2Cl_2) 2020 cm^{-1} (CO); $^{31}P\{^{1}H\}$ nmr (CH_2Cl_2) δ-21.31 (s).

Addition of *iso*-propyl and neopentyl iodide by an analogous procedure gave only starting material.

(vi) Alkylbromocarbonylchlorobis(methyldiphenylphosphine)-iridium(III), $IrR'BrCl(CO)(PPh_2Me)_2$ (*13a-d*)

A solution of $IrCl(CO)(PPh_2Me)_2$ (*11a*) (0.1 g, 0.15 mmol) in

benzene (5 mL) was treated with the appropriate alkyl bromide (0.15 mL). The yellow solution was stirred until it decolourized (usually 24 h). Evaporation of volatiles and trituration with hexane gave the product as a pale yellow solid (80-95%). Analytical samples were obtained by recrystallization from dichloromethane-hexane. Analytical and spectroscopic data for *13a-d* appear in Tables 10-12.

(vii) Alkylbromocarbonylchlorobis(dimethylphenylphosphine)-iridium(III), $IrR'BrCl(CO)(PPhMe_2)_2$ (*14a-d*)

These complexes were prepared as described in (vi) from *11b* and the appropriate alkyl bromide. The reaction was complete within 1 h. Yields were 80-95%. Analytical samples were obtained by recrystallization from dichloromethane-hexane. Analytical and spectroscopic data for *14a-d* appear in Tables 13-15.

(viii) Alkylcarbonylchlorohalobis(trimethylphosphine)-iridium(III), $IrRClX(CO)(PMe_3)_2$ (X = Br, I) (*15a-g*)

These complexes were prepared as described in (vi) from *11c* and the appropriate alkyl halide. The reaction was over within 10 min. Yields were 80-96%. Analytical samples were obtained by recrystallization from dichloromethane-hexane. Analytical and spectroscopic data for *15a-g* appear in Tables 16-19.

Reaction of $BrCH_2CH_2CO_2Et$ with *11c* was carried out as described in (iv). Addition of $CH_3CHClCO_2C_2H_5$ to *11c* as in (iv) or (vi) gave only starting material.

(ix) Addition of $BrCH_2CH_2CN$ to $IrCl(CO)(PMe_3)_2$

A solution of *11c* (0.1 g, 0.29 mmol) in benzene (5 mL) was treated with $BrCH_2CH_2CN$ (0.15 mL). The yellow solution slowly decolourized over 18 h. Evaporation of volatiles and trituration with hexane gave an off-white solid (0.05 g). IR (Nujol) 2050 cm^{-1} (CO), 2180 cm^{-1} (CN); ^1H nmr (CD_2Cl_2) δ1.76 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3).

(x) Carbonylchloroiodo(iodomethyl)bis(methyldiphenylphosphine)iridium(III)

A solution of *11a* (0.1 g, 0.15 mmol) in benzene (5 mL) was treated with diiodomethane (13μL, 0.15 mmol). The yellow solution immediately became colourless. Evaporation of volatiles and trituration with hexane gave the product as a pale yellow solid (0.11 g, 78%) which could be recrystallized from dichloromethane-methanol. Mp 180-182°C; IR (CH_2Cl_2) 2050 cm^{-1} (CO), (Nujol) 305 cm^{-1} (IrCl).

Anal. Calcd for $C_{28}H_{28}ClI_2IrOP_2$: C, 36.40; H, 3.05; P, 6.70. Found: C, 36.20; H, 3.01; P, 6.63.

The chloroiodomethane adduct, $Ir(CH_2Cl)ClI(CO)(PPh_2Me)_2$, was prepared similarly. Mp 192-94°C; IR (Nujol) 2040 cm^{-1} (CO), 310 cm^{-1} (IrCl).

Anal. Calcd for $C_{28}H_{28}Cl_2IIrOP_2$: C, 40.40; H, 3.39; P, 7.44. Found: C, 40.17; H, 3.37; P, 7.50.

The chloroiodomethane adduct, $Ir(CH_2Cl)ClI(CO)(PMe_3)_2$ was prepared similarly. Mp 197-99°C; IR (CH_2Cl_2) 2045 cm^{-1} (CO), IR (Nujol) 312 cm^{-1} (IrCl).

Anal. Calcd for $C_8H_{20}Cl_2IIrOP_2$: C, 16.45; H, 3.45; P, 10.60. Found: C, 16.50; H, 3.41; P, 10.90.

The chloroiodomethane adduct, $Ir(CH_2Cl)ClI(CO)(PPhMe_2)_2$, was prepared similarly. Mp 178-80°C; IR (CH_2Cl_2) 2045 cm^{-1} (CO), IR (Nujol) 308 cm^{-1} (IrCl).

Anal. Calcd for $C_{18}H_{24}Cl_2IIrOP_2$: C, 30.52; H, 3.41; P, 8.74. Found: C, 30.27; H, 3.36; P, 8.55.

^1H and ^{31}P nmr data for these complexes appear in Tables 20 and 21. Addition of CH_3CHBr_2 to *11c* in benzene gave $IrBr_2Cl(CO)(PMe_3)_2$. IR (Nujol) 2040 cm^{-1} (CO); ^1H nmr (CD_2Cl_2) δ1.66 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3).

(xi) Bromocarbonylchloro(methoxymethyl)bis(trimethylphosphine)-iridium(III)

A solution of $Ir(CH_2I)ClI(CO)(PMe_3)_2$ (0.1 g, 0.15 mmol) in methanol (5 mL) was refluxed for 1 h. Evaporation of volatiles and trituration with hexane gave a yellow solid (0.07 g, 80%). ^1H nmr (CD_2Cl_2) δ2.0 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3), 3.26 (s, 3 H, $IrCH_2OC\underline{H}_3$), 4.42 (t, $^3J_{PH}$ = 5 Hz, 2 H, $IrC\underline{H}_2OCH_3$).

(xii) Addition of 1-chloro-1-ethoxyethane to *11c*

A solution of *11c* (0.1 g, 0.25 mmol) in toluene (5 mL) at 0°C was treated with $CH_3CHClOC_2H_5$ (17 μl, 0.25 mmol). The yellow solution became colourless within 10 min. Evaporation of volatiles and trituration with hexane gave a white solid (0.05 g) identified as carbonyldichlorohydridobis(trimethylphosphine)iridium(III) by comparison with an authentic sample[36]. IR (Nujol) 2190 cm^{-1} (IrH), 2030 cm^{-1} (CO), 310 cm^{-1} (IrCl); ^1H nmr (CD_2Cl_2) δ1.73 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3), -16.8 (t, $^2J_{PH}$ = 12 Hz, IrH).

(xiii) Tetraphenylarsonium dicarbonylmethyltriiodoiridium(III)

A solution of $[IrI_2(CO)_2]^-$ (0.15 g, 0.17 mmol) in dichloromethane (5 mL) was treated with an excess of methyl iodide (0.5 mL) and refluxed for 30 min. Evaporation of volatiles and trituration with ether gave a yellow solid (0.1 g, 57%). IR (CH_2Cl_2) 2045, 2100 cm^{-1} (CO) (lit. IR (CH_3NO_2) 2049, 2102 cm^{-1})[51].

The ethyl iodide adduct, IR (CH_2Cl_2) 2040, 2090 cm^{-1} (CO), and propyl iodide adduct, IR (CH_2Cl_2) 2045, 2095 cm^{-1} (CO), were prepared similarly, but were unstable in the absence of an excess of alkyl iodide.

(xiv) Attempted Addition of *tert*-butyl iodide to *11c*

Addition of $(CH_3)_3CI$ to *11c* in benzene gave $IrClI_2(CO)(PMe_3)_2$. IR(CH_2Cl_2) 2050 cm^{-1} (CO); ^1H nmr (C_6D_6) δ1.54 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3).

TABLE 4

Analytical Data for $IrRXI(CO)(PPhMe_2)_2$

Complex R	M.P. °C	Analyses: found (calculated) % C	H	P	Cl	I	MW(CH_2Cl_2)
X = Cl							
ethyl	168-72	33.43 (33.19)	4.26 (3.96)		4.41 (5.16)	18.42 (18.45)	685 (688)
n-propyl	166-67	34.16 (34.23)	4.28 (4.16)	8.73 (8.82)	4.35 (5.05)	17.14 (18.08)	
iso-propyl	159-61	33.92 (34.23)	4.40 (4.16)	8.55 (8.82)			707 (702)
n-butyl	146-48	35.32 (35.24)	4.49 (4.37)	8.78 (8.66)	4.69 (4.95)	17.50 (17.75)	
iso-butyl	164-66	35.21 (35.24)	4.63 (4.37)	8.27 (8.66)			729 (716)
sec-butyl	108-10	35.79 (35.24)	4.62 (4.37)	8.94 (8.66)			
n-octyl	oil	38.62 (38.89)	5.60 (5.09)	7.80 (8.03)			
X = I							
n-propyl	187-89	30.42 (30.25)	3.69 (3.66)	7.89 (7.82)			
iso-propyl		30.86 (30.25)	3.68 (3.66)				

TABLE 5

Infrared and ^{31}P NMR[a] Data for $IrRXI(CO)(PPhMe_2)_2$

Complex R	$\nu(CO)$ cm^{-1} NUJOL	$\nu(CO)$ cm^{-1} CH_2Cl_2	$\nu(IrCl)$ [b] cm^{-1}	δ [c]
X = Cl				
ethyl	2025	2022	307	- 32.68
n-propyl	2010	2015	301	- 32.13
iso-propyl	2020, 2030	2020	317	- 35.13
n-butyl	2030	2020	303	- 32.68
sec-butyl	2025	2020	303	- 35.13
iso-butyl	2010	2025	302	- 34.18
n-octyl		2020		- 32.47
X = Br				
benzyl	2040	2040	306	- 30.87
X = I				
n-propyl	2030	2030		- 46.15
iso-propyl		2030		- 48.71

a. ^{31}P nmr spectra were measured in CH_2Cl_2 at 35°C. Chemical shifts are referenced to external 85% H_3PO_4 and are positive to low field.

b. Samples measured as polythene discs.

c. Singlets.

TABLE 6

^{1}H NMR Data for $IrRClI(CO)(PPhMe_2)_2$ [a]

R	δ[b] A	δ[b] B	δ[b] C	J_{HH} Hz	δ[b] Phosphine Methyls [d,e]
ethyl	$\overset{A}{CH_2}\overset{B}{CH_3}$ 1.23 (sx, 2 H)[c]	0.80 (t, 3H)		7	2.10 (t), 2.32 (t)
n-propyl	$\overbrace{CH_2CH_2}^{A}\overset{B}{CH_3}$ 1.00 (m, 4 H)	0.14 (t, 3H)		7	2.12 (t), 2.29 (t)
iso-propyl	$(\overset{A}{CH_3})_2\overset{B}{CH}$ 0.82 (d, 6 H)	2.14 (sp, 1 H)		7	2.13 (t), 2.30 (t)
n-butyl	$\overbrace{CH_2CH_2}^{A}\overbrace{CH_2CH_3}^{B}$ 0.86 (m, 4 H)	0.27 (m, 5 H)		7	2.06 (t), 2.22 (t)
sec-butyl	$\overset{A}{CH_3}\overbrace{CH}^{B}\overset{C}{CH_2CH_3}$ 0.71 (d, 3 H)	0.88-1.30 (m)	0.18 (t, 3 H)	7	2.08 (t), 2.26 (t)
iso-butyl	$\overset{A}{CH_2}\overset{B}{CH}\overset{C}{(CH_3)_2}$ 1.39 (d, 2 H)	1.02 (m)	0.25 (d, 6 H)	7	2.12 (t), 2.30 (t)
n-octyl	$\overset{A}{CH_2(CH_2)_6CH_3}$ 0.20-1.20 (m)			7	2.04 (t), 2.22 (t)

a. ^{1}H nmr spectra were measured in CD_2Cl_2 at 29°C with chemical shifts (δ) in parts per million downfield of tetramethylsilane.

Cont.

TABLE 6 Cont.

b. d = doublet, m = multiplet, q = quartet, s = singlet, t = triplet, sp = septet, sx = sextet.

c. $^{3}J_{PH}$ = 7 Hz, coupling of phosphorus nuclei to α-methylene protons.

d. $^{2}J_{PH} + {}^{4}J_{PH} = 8$ Hz.

e. Ph protons appear as multiplets in the region δ7-8.

TABLE 7

Analytical Data for $IrRClI(CO)(PMe_3)_2$

Complex R	M.P. °C	Analyses: found (calculated) % C	H	P	MW(CH_2Cl_2)
ethyl	140-50	19.41 (19.16)	4.21 (4.08)	10.99 (11.00)	558 (564)
n-propyl	122-24	20.71 (20.77)	4.24 (4.33)	10.77 (10.74)	
iso-propyl	128-30	21.11 (20.77)	4.62 (4.33)	10.95 (10.74)	575 (578)
n-butyl	116-18	22.35 (22.31)	4.66 (4.56)	10.30 (10.48)	608 (592)
iso-butyl	132-34	22.44 (22.31)	4.55 (4.56)	10.19 (10.48)	
sec-butyl	112-14	22.82 (22.31)	4.76 (4.56)	10.41 (10.48)	589 (592)
3-pentyl	117-19	24.13 (23.79)	4.82 (4.82)	10.42 (10.23)	598 (606)
n-octyl	67-69	28.06 (27.70)	5.52 (5.44)	9.96 (9.95)	
neopentyl	188-92	23.96 (23.79)	4.84 (4.82)	10.27 (10.23)	
2-methylbutyl	107-09	24.08 (23.79)	4.84 (4.82)	10.51 (10.23)	

TABLE 8

Infrared and ^{31}P NMR [a] Data for $IrRClI(CO)(PMe_3)_2$

Complex R	$\nu(CO)$ cm^{-1} NUJOL	$\nu(CO)$ cm^{-1} CH_2Cl_2	$\nu(IrCl)$ [b] cm^{-1}	δ [c]
ethyl	2020	2020	305	- 40.12
n-propyl	2020	2022	305	- 40.62
iso-propyl	2010, 2030	2030	311	- 41.63
n-butyl	2022	2022	306	- 40.52
sec-butyl	2020	2022	300	- 41.73
iso-butyl	2015	2022	307	- 40.83
3-pentyl	2010	2020	305	- 41.22
neopentyl	2010	2020	303	- 42.22
2-methylbutyl	2018	2025	307	- 40.82
3-methylbutyl		2025		- 41.02
n-octyl		2022	306	- 40.92
2-octyl	2022	2022		- 41.64
cyclohexyl		2020		- 42.93

a. ^{31}P nmr spectra were measured in CH_2Cl_2 at 35°C. Chemical shifts are referenced to external 85% H_3PO_4 and are positive to low field.

b. Samples measured as polythene discs.

c. Singlets.

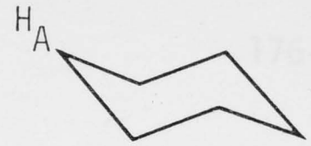
TABLE 9

^{1}H NMR Data for $IrRClI(CO)(PMe_3)_2$[a]

R		δ[b] A	B	C	D	J_{HH} Hz	δ[b] Phosphine Methyls[c]
ethyl	$\overset{A}{CH_2}\overset{B}{CH_3}$	1.6-1.8 (m)	1.42 (t, 3 H)			7	1.82 (t)
n-propyl	$\overset{A}{\overbrace{CH_2CH_2}}\overset{B}{CH_3}$	1.6-1.9 (m)	0.96 (t, 3 H)			7	1.82 (t)
iso-propyl	$\overset{A}{(CH_3)_2}\overset{B}{CH}$	1.37 (d, 6 H)	2.92 (sp, 1 H)			7	1.86 (t)
n-butyl	$\overset{A}{\overbrace{CH_2CH_2CH_2}}\overset{B}{CH_3}$	1.2-1.8 (m)	0.92 (t, 3 H)			6	1.81 (t)
sec-butyl	$\overset{A}{CH_3}\overset{B}{CH}\overset{C}{CH_2}\overset{D}{CH_3}$	1.35 (d, 3 H)	2.67 (m, 1 H)	1.6-1.8 (m)	0.92 (t, 3 H)	7	1.86 (t)
iso-butyl	$\overset{A}{CH_2}\overset{B}{CH}\overset{C}{(CH_3)_2}$	1.8 (m)	1.5-1.9 (m)	1.00 (d, 6 H)		6	1.80 (t)
neopentyl	$\overset{A}{CH_2}C\overset{B}{(CH_3)_3}$	2.15 (t, 2 H)[d]	1.60 (s, 6 H)				1.88 (t)
3-methylbutyl	$\overset{A}{CH_2}\overset{B}{CH_2}\overset{A}{CH}\overset{B}{(CH_3)_2}$	1.3-1.7 (m)	0.82 (d & m, 8 H)			6	1.70 (t)

Cont.

TABLE 9 cont.

R		δ^b A	B	C	D	J_{HH} Hz	δ^b Phosphine Methyls [c]
2-methylbutyl	$\overset{A}{CH_2}\overset{A}{CH}(\overset{B}{CH_3})\overset{A}{CH_2}\overset{C}{CH_3}$	0.9-2.0 (m)	0.96 (d)	0.94 (m)		5	1.80 (t)
n-octyl	$\overbrace{CH_2(CH_2)_6}^{A}\overset{B}{CH_3}$	1.20 (m, 12 H)	0.81 (t, 3 H)			7	1.73 (t)
2-octyl	$\overset{A}{CH_3}\overset{B}{CH}(\overbrace{CH_2)_5}^{C}CH_3$	1.37 (d)	2.7 (m)	0.8 - 1.4 (m)		7	1.86 (t)
3-pentyl	$\overset{A}{CH}(\overset{B}{CH_2}\overset{C}{CH_3})_2$	2.49 (m, 1 H)	1.6-1.8 (m)	0.97 (t, 6 H)		7	1.88 (t)
cyclohexyl		2.80 (m, 1 H)	1.2-2.0 (m)				1.87 (t)

a. ^1H nmr spectra were measured in CD_2Cl_2 at 29°C with chemical shifts (δ) in parts per million downfield of tetramethylsilane.

b. d = doublet, m = multiplet, sp = septet, t = triplet.

c. $^2J_{PH} + {}^4J_{PH} = 8$ Hz.

d. $^3J_{PH} = 7$ Hz, coupling of phosphorus nuclei to α-methylene protons.

TABLE 10

Analytical Data for $IrRBrCl(CO)(PPh_2Me)_2$

Complex R	M.P. °C	Analyses: found (calculated) % C	H	P	Other	MW (CH_2Cl_2)
CH_2CO_2Et (0.5 CH_2Cl_2) [a]	181-84	43.93 (43.66)	4.00 (3.93)	6.83 (7.16)		828 (823)
CH_3CHCO_2Et (1.0 CH_2Cl_2) [a]	156-59	43.52 (42.98)	3.95 (4.04)	6.52 (6.72)		889 (837)
$CH_3C(O)CHCH_3$	111-16	45.83 (46.12)	4.19 (4.12)	7.57 (7.68)		
$EtCHNO_2$	176-78	43.42 (43.72)	3.96 (3.91)	7.27 (7.52)	N 1.76 (1.70)	824 (820)

a. Dichloromethane content estimated from ^1H nmr spectrum.

TABLE 11

Infrared and ^{31}P NMR[a] Data for $IrRBrCl(CO)(PPh_2Me)_2$

R	ν(CO) and (C=O) cm^{-1}		ν(IrCl) [b] cm^{-1}	ν(IrBr) [b] cm^{-1}	δ_A	δ_B	$^2J_{AB}$
	NUJOL	CH_2Cl_2					
$CH_2CO_2C_2H_5$	2063	2050	300	180	- 24.51 [c]		
	1691	1700					
$CH_3CHCO_2C_2H_5$	2030	2050	305	e	- 25.48	- 28.40	408
	1705	1705					
$CH_3C(O)CHCH_3$	2045	2045	305	183	- 25.95 [d]	- 26.25 [d]	
	1640	1675					
$C_2H_5CHNO_2$	2042	2057	304	e	- 25.03	- 31.17	401

a. ^{31}P nmr spectra were measured in CH_2Cl_2 at 35°C. Chemical shifts (δ) are referenced to external 85% H_3PO_4 and are positive to low field.

b. Far-infrared spectra were measured as polythene discs.

c. Singlet.

d. Only central doublet of AB quartet observed.

e. Not recorded.

TABLE 12

^{1}H NMR Data for $IrRBrCl(CO)(PPh_2Me)_2$ [a]

Complex R	δ[b] A	B	C	D	J_{HH} Hz	δ[b] Phosphine Methyls [e]
A B C $CH_2CO_2CH_2CH_3$	2.0 (m)	3.20 (q, 2 H)	0.51 (t, 3 H)		7	2.01 (t) [c]
A B C D $CH_3CHCO_2CH_2CH_3$	0.46 (d, 3 H)	3.13 (q, 2H)	2.94 (m) 3.41 (m)	0.83 (t, 3 H)	7	2.23, 2.32 (m) [d]
A B C $CH_3C(O)CHCH_3$	1.35 (s, 3 H)	3.51 (m)	0.70 (d, 3 H)		7	2.47, 2.50 (m) [d]
A B C $CH_3CH_2CHNO_2$	0.16 (t, 3 H)	1.55 (m)	5.48 (m)		7	2.52, 2.56 (m) [d]

a. ^{1}H nmr spectra were measured in CD_2Cl_2 at 29°C with chemical shifts (δ) in parts per million downfield of tetramethylsilane.

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

c. $^{2}J_{PH} + {}^{4}J_{PH} = 8$ Hz

d. Two singlets on ^{31}P decoupling.

e. Ph protons appear as multiplets in the region δ7-8.

TABLE 13

Analytical Data for $IrRBrCl(CO)(PPhMe_2)_2$

Complex R	M.P. °C	Analyses: found (calculated) % C	H	P	Other
CH_2CO_2Et	116-20	35.89 (36.08)	4.26 (4.18)	8.71 (8.87)	
CH_3CHCO_2Et	110-12	36.60 (37.07)	4.27 (4.38)	8.62 (8.69)	
$CH_3C(O)CHCH_3$	111-16	37.07 (36.93)	4.34 (4.28)	8.98 (9.08)	
$EtCHNO_2$	165-72	34.72 (34.37)	4.10 (3.89)	9.04 (8.87)	N 1.75 (2.10)

TABLE 14

Infrared and ^{31}P NMR[a] Data for $IrRBrCl(CO)(PPhMe_2)_2$

R	ν(CO) and (C=O) cm^{-1} NUJOL	CH_2Cl_2	$\nu(IrCl)^b$ cm^{-1}	$\nu(IrBr)^b$ cm^{-1}	δ_A	δ_B	$^2J_{AB}$ Hz
$CH_2CO_2C_2H_5$	2045 1700	2050 1700	306	183	- 30.71 [c]		
$CH_3CHCO_2C_2H_5$	2050 1695	2040 1700	306	d	- 30.68	- 33.27	401
$CH_3C(O)CHCH_3$		2030 1670	308	176	- 31.07	- 33.45	403
$C_2H_5CHNO_2$	2050	2050	313	189	- 30.56	- 34.09	394

a. ^{31}P nmr spectra were measured in CH_2Cl_2 at 35°C. Chemical shifts (δ) are referenced to external 85% H_3PO_4 and are positive to low field.

b. Far-infrared spectra were measured as polythene discs.

c. Singlet.

d. Not recorded.

TABLE 15

^{1}H NMR Data for IrRBrCl(CO)($PPhMe_2$)$_2$ [a]

Complex R	δ[b] A	B	C	D	J_{HH} Hz	δ[b] Phosphine Methyls [i]
A B C $CH_2CO_2CH_2CH_3$	2.13 (t, 2 H)[c]	3.82 (q, 2 H)	1.08 (t, 3 H)		7	2.07 (t), 2.18 (t)[d]
A B C D $CH_3CHCO_2CH_2CH_3$	0.82 (d, 3 H)	3.10 (m)[e]	3.56 (m)	0.90 (t, 3 H)	7	2.10, 2.14, 2.16, 2.22[f]
A B C $CH_3C(O)CHCH_3$	1.39 (s, 3 H)	3.11 (q, 1 H)	0.76 (d, 3 H)		7	2.10, 2.20[g]
A B C $CH_3CH_2CHNO_2$	0.16 (t, 3 H)	1.60 (m)	4.96 (m)[h]		7	2.11, 2.12, 2.14, 2.24[f]

a. ^{1}H nmr spectra were measured in CD_2Cl_2 at 29°C with chemical shifts (δ) in parts per million downfield of tetramethylsilane.

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

c. $^3J_{PH}$ = 6 Hz, coupling of phosphorus nuclei to α-methylene protons.

d. $^2J_{PH} + {}^4J_{PH}$ = 8 Hz.

Cont.

TABLE 15 Cont.

e. $^{3}J_{PH}$ = 1.5 Hz.

f. Four singlets on ^{31}P coupling.

g. Two singlets on ^{31}P decoupling.

h. ^{31}P decoupled spectrum shows 4 lines as the X-part of an ABX spectrum.

i. Ph protons appear as multiplets in the region δ7-8.

TABLE 16

Analytical Data for $IrRXCl(CO)(PMe_3)_2$

Complex R	M.P. °C	Analyses: found (calculated) % C	H	P	Other
X = Br					
CH_2CO_2Et	116-18	23.18 (22.98)	4.37 (4.38)	10.95 (10.78)	
CH_3CHCO_2Et	116-18	24.71 (24.47)	4.70 (4.62)	10.35 (10.53)	
$CH_3C(O)CHCH_3$	140-42	23.90 (23.65)	4.58 (4.51)	11.18 (11.09)	
$EtCHNO_2$	156-62	21.08 (20.93)	4.11 (3.87)	10.60 (10.80)	N 2.44 (2.41)
$CH_2CH_2CO_2Et$	100-02	24.67 (24.47)	4.54 (4.62)	10.41 (10.53)	MW 580 (589)
X = I					
CH_2CH_2CN	160-63	20.48 (20.40)	3.71 (3.77)	10.70 (10.51)	N 2.33 (2.38)
CH_3CHCO_2Et	141-42	22.92 (22.67)	4.63 (4.28)	9.59 (9.74)	

TABLE 17

Infrared Data for $IrRXCl(CO)(PMe_3)_2$

R	ν(CO) cm^{-1} and ν(C=O) cm^{-1}		ν(IrCl)[a] cm^{-1}	ν(IrBr)[a] cm^{-1}
X = Br	NUJOL	CH_2Cl_2		
CH_2CO_2Et	2030	2045	310	186
	1695	1705		
CH_3CHCO_2Et	2035	2040	312	180
	1685	1700		
$CH_3C(O)CHCH_3$	2020	2025	310	173
	1665	1670		
$EtCHNO_2$	2040	2045	323	b
$CH_2CH_2CO_2Et$	2025	2030	306	177
	1708			
X = I				
CH_2CH_2CN	2030	2030	306	
	2240[c]	2245[c]		
CH_3CHCO_2Et	2020	2040	310	
	1690	1705		

a. Far-infrared spectra were measured as polythene discs.

b. Not recorded.

c. ν(CN)

TABLE 18

^{1}H NMR Data for $IrRXCl(CO)(PMe_3)_2$ [a]

Complex R	A	B	C	D	J_{HH} Hz	Phosphine Methyls
			δ[b]			δ[b]
X = Br						
A B C $CH_2CO_2CH_2CH_3$	2.10 (t) [c]	3.73 (q, 2 H)	1.10 (t, 3 H)		7	1.60 (t) [d]
A B C D $CH_3CHCO_2CH_2CH_3$	1.10 (d, 3 H)	3.06 (m)	3.84 (m)	1.10 (t, 3H)	7	1.62 (d) [e]
A B C $CH_3C(O)CHCH_3$	1.92 (s, 3 H)	3.13 (q, 1 H)	1.16 (d, 3 H)		7	1.58 (t) [e]
A B C $CH_3CH_2CHNO_2$	0.90 (t, 3 H)	2.10 (m)	5.48 (m) [f]		7	1.77, 1.78 [e]
A B C D $CH_2CH_2CO_2CH_2CH_3$	1.90 (m)	2.53 (t, 3 H)	4.07 (q, 3H)	1.20 (t, 3 H)	7	1.74 (t) [d]
X = I						
A B C D $CH_3CHCO_2CH_2CH_3$	1.18 (d)	3.49 (m)	4.08 (m, 2 H)	1.24 (t)	7	1.87, 1.88 [e]
A B CH_2CH_2CN	1.98 (m)	2.63 (t, 2 H)			7	1.86 (t) [d]

Cont.

TABLE 18 Cont.

a. ^{1}H nmr spectra were measured in CD_2Cl_2 at 29°C with chemical shifts (δ) in parts per million downfield of tetramethylsilane.

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

c. $^{3}J_{PH}$ = 6 Hz.

d. $^{2}J_{PH}$ + $^{4}J_{PH}$ = 8 Hz.

e. Two singlets on ^{31}P decoupling.

f. ^{31}P decoupled spectrum shows 4 lines of equal intensity for the X part of an ABX spectrum.

TABLE 19

^{31}P NMR Data for $IrRXCl(CO)(PMe_3)_2$[a]

R	δ_A	δ_B	J_{AB}
X = Br			
CH_2CO_2Et	- 36.62[b]		
CH_3CHCO_2Et	- 35.78	- 39.92	410
$CH_3C(O)CHCH_3$	- 38.71		(1.2 Hz)[c]
$EtCHNO_2$	- 37.91[d]	- 38.31[d]	(9.7 Hz)[c]
$CH_2CH_2CO_2Et$	- 35.70[b]		
X = I			
CH_3CHCO_2Et	- 40.96	- 46.52	406
CH_2CH_2CN	- 42.13[b]		

a. ^{31}P nmr spectra were measured in CH_2Cl_2 at 35°C. Chemical shifts (δ) are referenced to external 85% H_3PO_4 and are positive to low field.

b. Singlets.

c. Separation of central doublet of AB quartet, outer lines not observed.

d Position of one arm of doublet

TABLE 20

^{1}H NMR Data for $Ir(CH_2X)ClI(CO)L_2$ [a]

Complex	δ [b] CH_2X	δ [b] Phosphine Methyls
L = PPh_2Me		
X = Cl	3.59 (t, 7 Hz) [c]	2.61 (t) [d]
= I	2.46 (t, 7 Hz) [c]	2.63 (t) [d]
L = PMe_3		
X = Cl	3.94 (t, 6 Hz) [c]	1.86 (t) [d]
= I	2.80 (t, 7 Hz) [c]	1.86 (t) [d]
L = $PPhMe_2$		
X = Cl	(*16b*) 3.27 (t, 6 Hz) [c]	(*16b*) 2.16 (t), 2.34 (t) [d]
	(*16b'*) 3.74 (t, $^3J_{PH}$ = 8 Hz, $^2J_{HH}$ = 8 Hz), 5.24 (two x t, $^3J_{PH}$ = 3 Hz, $^2J_{HH}$ = 8 Hz)	*(16b')* 1.68 (d), 1.78 (d), 1.90 (d), 2.16 (d)[e]
X = I	(*16b*) 2.16 (t, 7 Hz) [c]	(*16b*) 2.16 (t), 2.24 (t) [d]
	(*16b'*)[g] 2.60 (two x d, $^3J_{PH}$ = 10 Hz, $^2J_{HH}$ = 7 Hz) 3.88 (two x t, $^3J_{PH}$ = 3 Hz, $^2J_{HH}$ = 7 Hz)	(*16b'*) 1.68 (d), 1.72 (d), 1.94 (d), 2.20 (d) [f]

Cont.

TABLE 20 Cont.

a. ^{1}H nmr spectra were measured in CD_2Cl_2 at 29°C with chemical shifts (δ) in parts per million downfield of tetramethylsilane.

b. d = doublet, t = triplet.

c. $^{3}J_{PH}$

d. $^{2}J_{PH} + {}^{4}J_{PH} = 8$ Hz

e. $^{2}J_{PH} + {}^{4}J_{PH} = 10$ Hz

f. $^{2}J_{PH} + {}^{4}J_{PH} = 12$ Hz

g. The methylene protons in this isomer are inequivalent and are coupled differently to the two phosphorus nuclei.

TABLE 21

^{31}P NMR Data for $Ir(CH_2X)ClI(CO)L_2$

	δ^b	
	X = Cl	X = I
L = PPh_2Me	- 26.15	- 27.26
L = PMe_3	- 40.93	- 41.33
L = $PPhMe_2$	(*16b*) - 32.98	(*16b*) - 33.89
	(*16b'*)- 29.61[c], -49.62[c]	(*16b'*) - 31.07[d], - 51.47[d]

a. ^{31}P nmr spectra were measured in CH_2Cl_2 at 35°C. Chemical shifts (δ) are referenced to external 85% H_3PO_4 and are positive to low field.

b. Singlets, unless otherwise stated.

c. Doublets with $^2J_{PP}$ = 7.3 Hz.

d. Doublets with $^2J_{PP}$ = 10 Hz.

APPENDIX I

An Analysis of Spin System $X_nAA'X'_n$

The stereochemistry of methyl-substituted tertiary phosphine ligands may be assigned from the pattern of the proton resonance of the PCH_3 group. Thus, the methyl resonance of two phosphine ligands in mutually *trans* positions is usually a 1:2:1 triplet due to "virtual coupling" with both phosphorus nuclei, whereas two phosphine ligands in mutually *cis* positions give rise to a 1:1 doublet[85]. These two situations are, in fact, limiting cases of the general spin system, $X_nAA'X'_n$ (where A is P and X is H, and n=3 for PPh_2Me, n=6 for $PPhMe_2$ and n=9 for PMe_3), where $J_{XX'}$ is assumed to be 0 and the A and X nuclei are chemically equivalent but magnetically inequivalent. The general appearance of the X portion of this spectrum is outlined in Figure 11[86].

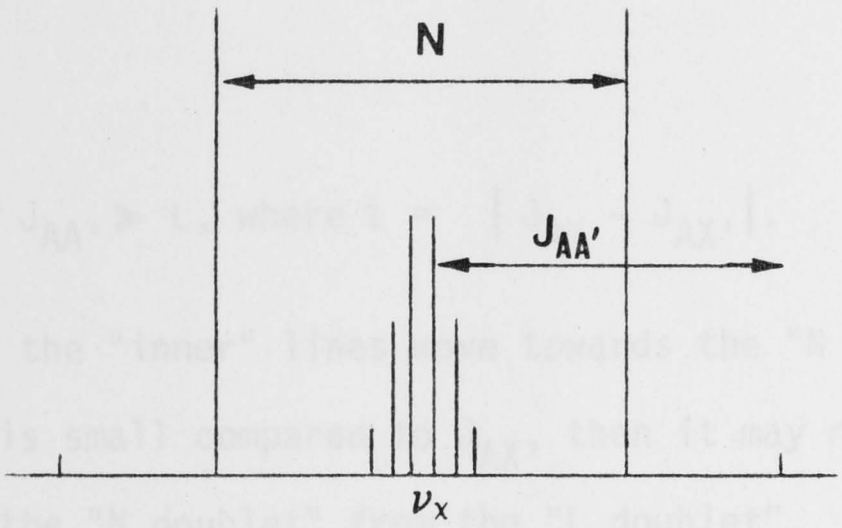


Figure 11. General Appearance of X portion of $X_3AA'X_3'$ Spin System.

Half the intensity resides in the "N doublet", while the remaining half is distributed between the "inner" and "outer" lines centred on ν_X. The intensity of the "outer" lines is much smaller than that of the "inner" lines, and the overall appearance of the spectrum is dependent on $J_{AA'}$ and the two types of couplings $J_{AX} + J_{AX'}$

The "N doublet" in Figure 11 is equal to $J_{AX} + J_{AX'}$ and is the coupling normally reported for PCH_3 ligand resonances (i.e. $^2J_{PH} + {}^4J_{PH}$).

The two limiting cases for the spin system, $X_nAA'X_n'$, can now be seen. If $J_{AA'}$ becomes very large the "outer" lines have negligible intensity and the "inner" lines move closer to ν_X and the whole spectrum has the appearance of a 1:2:1 triplet (Figure 12) as observed for mutually *trans* phosphines.

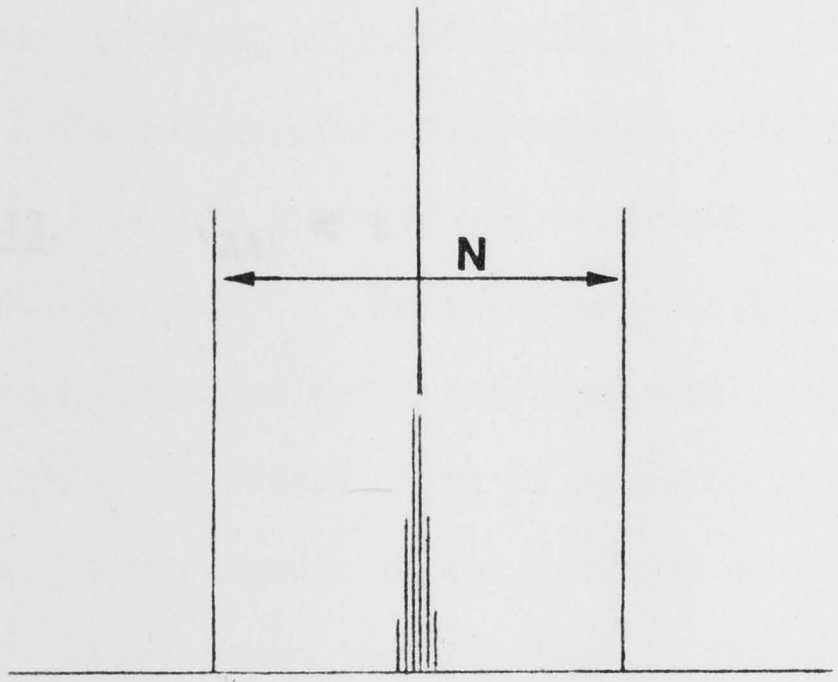


Figure 12. $J_{AA'} \gg L$, where $L = |J_{AX} - J_{AX'}|$.

If $J_{AA'} \rightarrow 0$, the "inner" lines move towards the "N doublet" (Figure 13) and if $J_{AX'}$ is small compared to J_{AX}, then it may not be possible to distinguish the "N doublet" from the "L doublet". In this case only one doublet will be observed, as for *cis*, chemically-equivalent phosphine ligands.

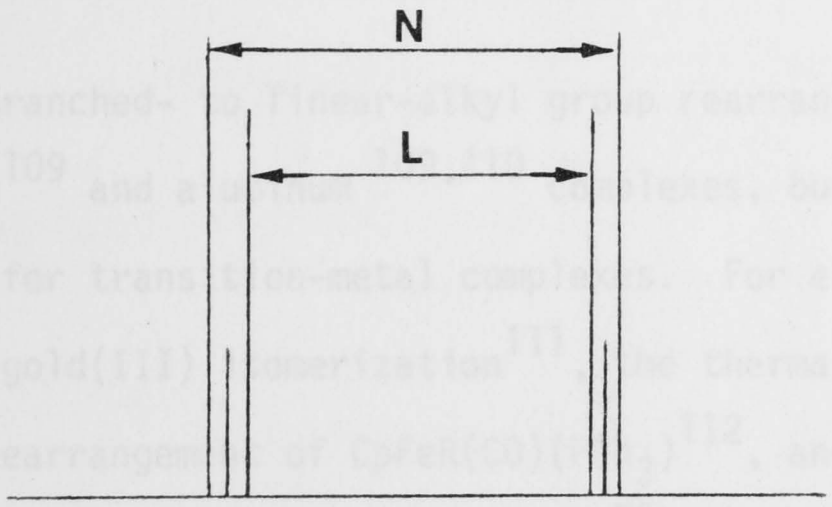
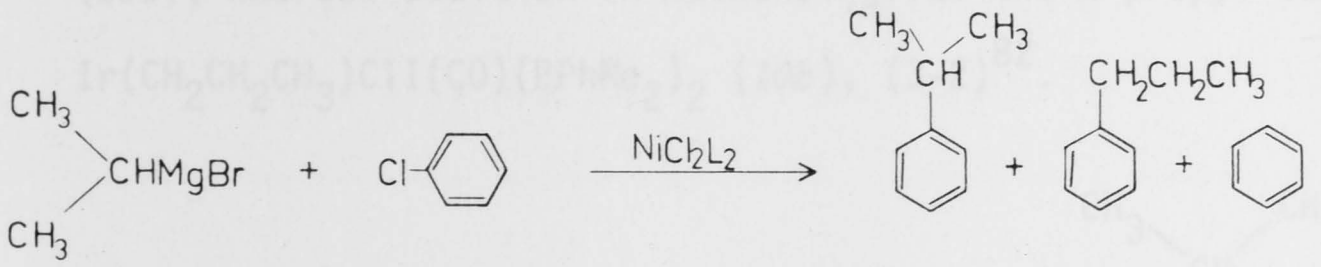


Figure 13. $J_{AA'} \ll L$

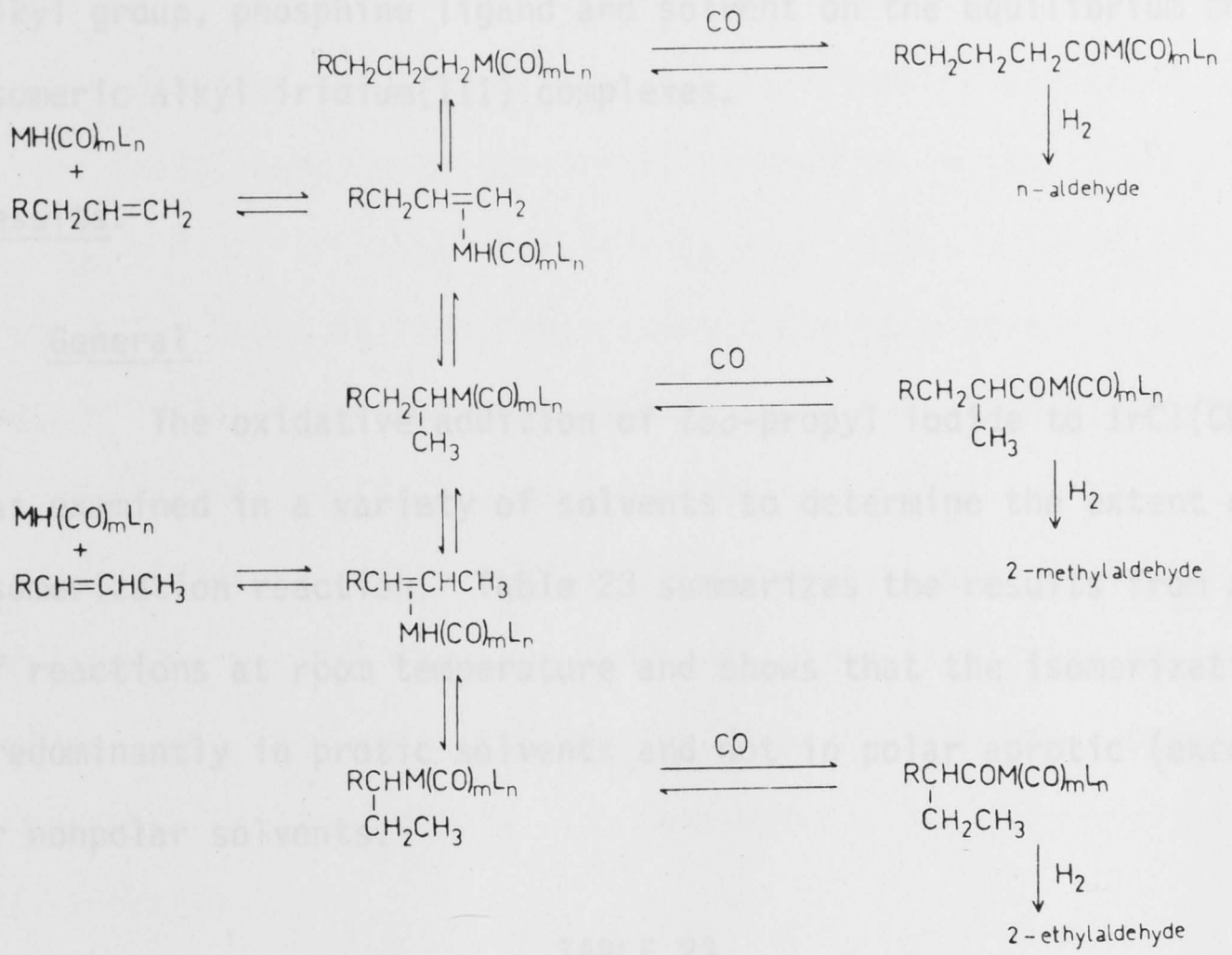
CHAPTER THREE

Alkyl Group Rearrangements of Mono-Alkyl Iridium(III) Complexes

Branched- to linear-alkyl group rearrangements are well known for boron[109] and aluminum [109,110] complexes, but only a few have been reported for transition-metal complexes. For example, the *tert*- to *iso*-butylgold(III) isomerization[111], the thermally-induced *sec*- to *n*-butyl rearrangement of $CpFeR(CO)(PPh_3)$[112], and the *iso*- to *n*-propyl group rearrangement of $[IrRCl_2(CO)_2]_2$[75]. Addition of Cp_2ZrHCl to internal olefins to give, exclusively, *n*-alkylzirconium complexes, Cp_2ZrRCl, probably proceeds via transient *sec*-alkyls, but these have not been detected[113]. There are many instances in which an equilibrium between *sec*- and *n*-alkyl transition-metal intermediates can account for the observed distribution of products, e.g. isomerization of alkyl-Grignard reagents in the presence of an *a*-olefin and $TiCl_4$[114] or $NiCl_2$[115], alkyl group isomerization in the nickel-catalyzed cross-coupling of Grignard reagents and aryl halides (3-1)[116], and isomerization of alkyl and acyl carbonyl complexes of cobalt[117-119] and iron[120] (Scheme 19).

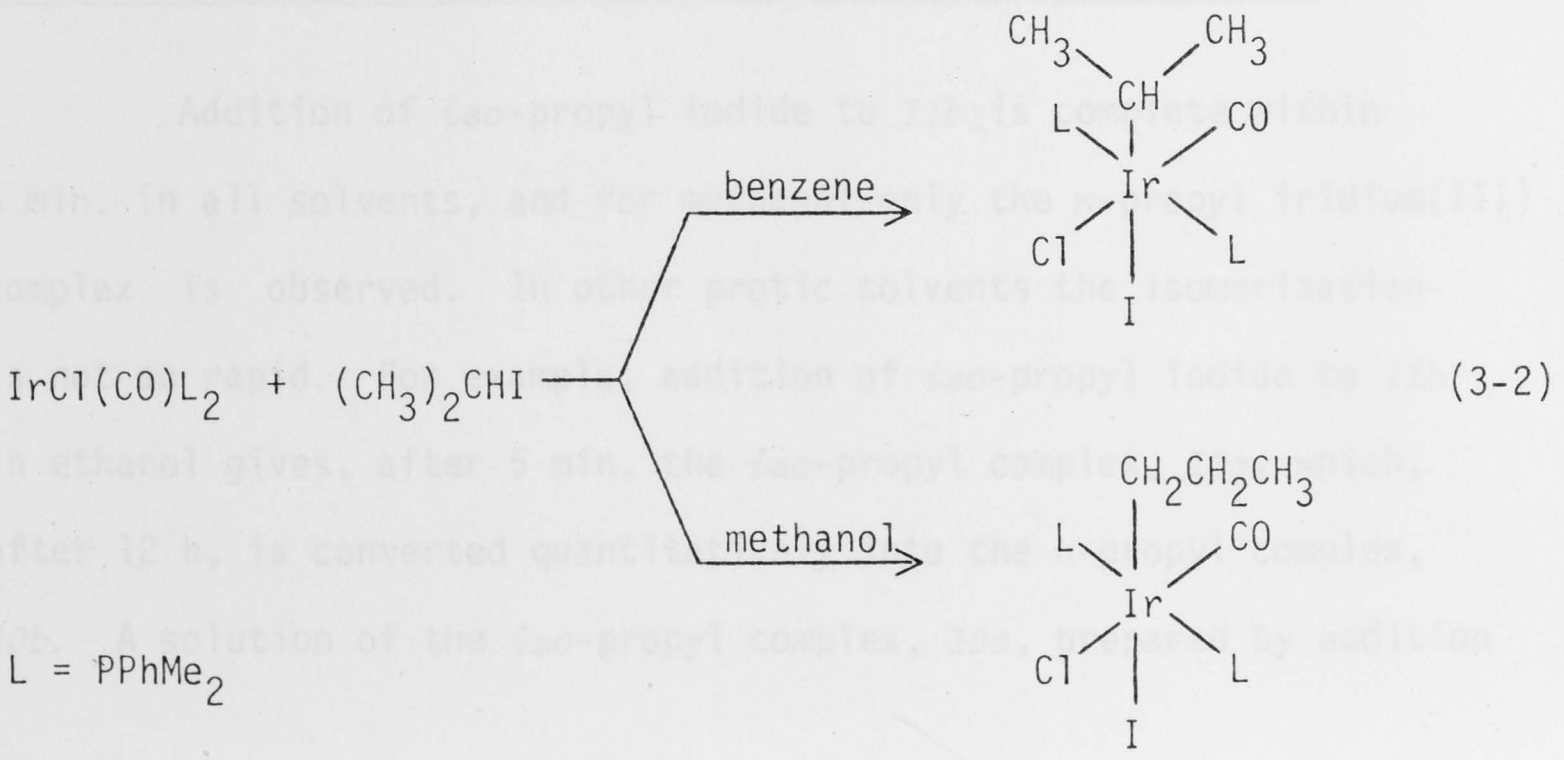


(3-1)



Scheme 19. Isomerization of Alkyl Cobalt Carbonyl Complexes.

Addition of *iso*-propyl iodide to $IrCl(CO)(PPhMe_2)_2$ in benzene gives the *iso*-propyl complex, $Ir(CH(CH_3)_2)ClI(CO)(PPhMe_2)_2$ (*10c*), whereas addition in methanol gives the *n*-propyl complex, $Ir(CH_2CH_2CH_3)ClI(CO)(PPhMe_2)_2$ (*10b*), (3-2)[82].



(3-2)

This Chapter explores the scope of this alkyl group rearrangement and, in particular, examines the effect of changes in alkyl group, phosphine ligand and solvent on the equilibrium between isomeric alkyl iridium(III) complexes.

Results.

I. General

The oxidative addition of *iso*-propyl iodide to $IrCl(CO)(PPhMe_2)_2$ was examined in a variety of solvents to determine the extent of the isomerization reaction. Table 23 summarizes the results from a variety of reactions at room temperature and shows that the isomerization occurs predominantly in protic solvents and not in polar aprotic (except DMSO) or nonpolar solvents.

TABLE 23

Addition of *iso*-Propyl Iodide to *11b* in Various Solvents

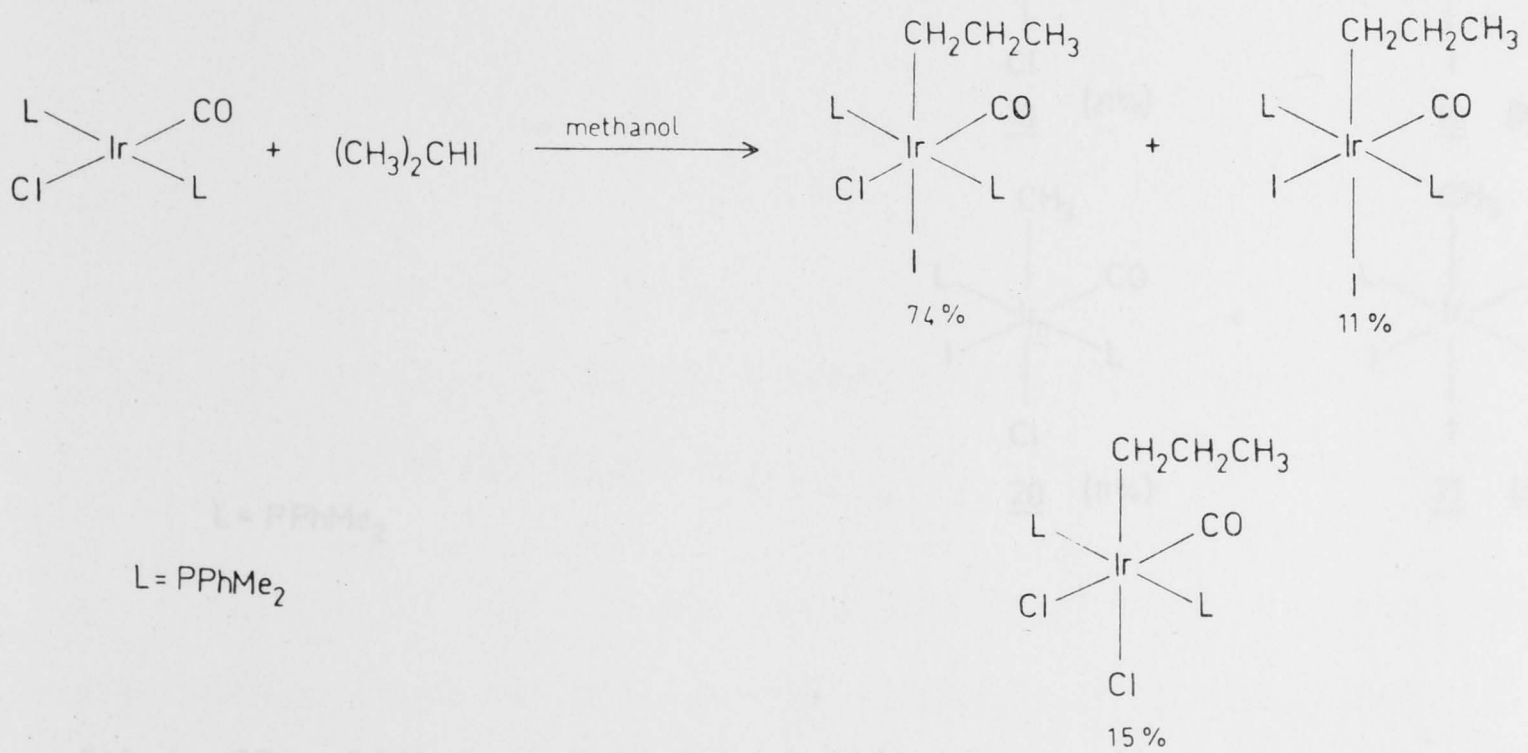
ISOMERIZATION	NO ISOMERIZATION
methanol	benzene
ethanol	dichloromethane
propanol	tetrahydrofuran
propan-2-ol	acetonitrile
dimethylsulphoxide	acetone

Addition of *iso*-propyl iodide to *11b* is complete within 5 min. in all solvents, and for methanol only the *n*-propyl iridium(III) complex is observed. In other protic solvents the isomerization is not so rapid. For example, addition of *iso*-propyl iodide to *11b* in ethanol gives, after 5 min, the *iso*-propyl complex, *10c*, which, after 12 h, is converted quantitatively into the *n*-propyl complex, *10b*. A solution of the *iso*-propyl complex, *10c*, prepared by addition

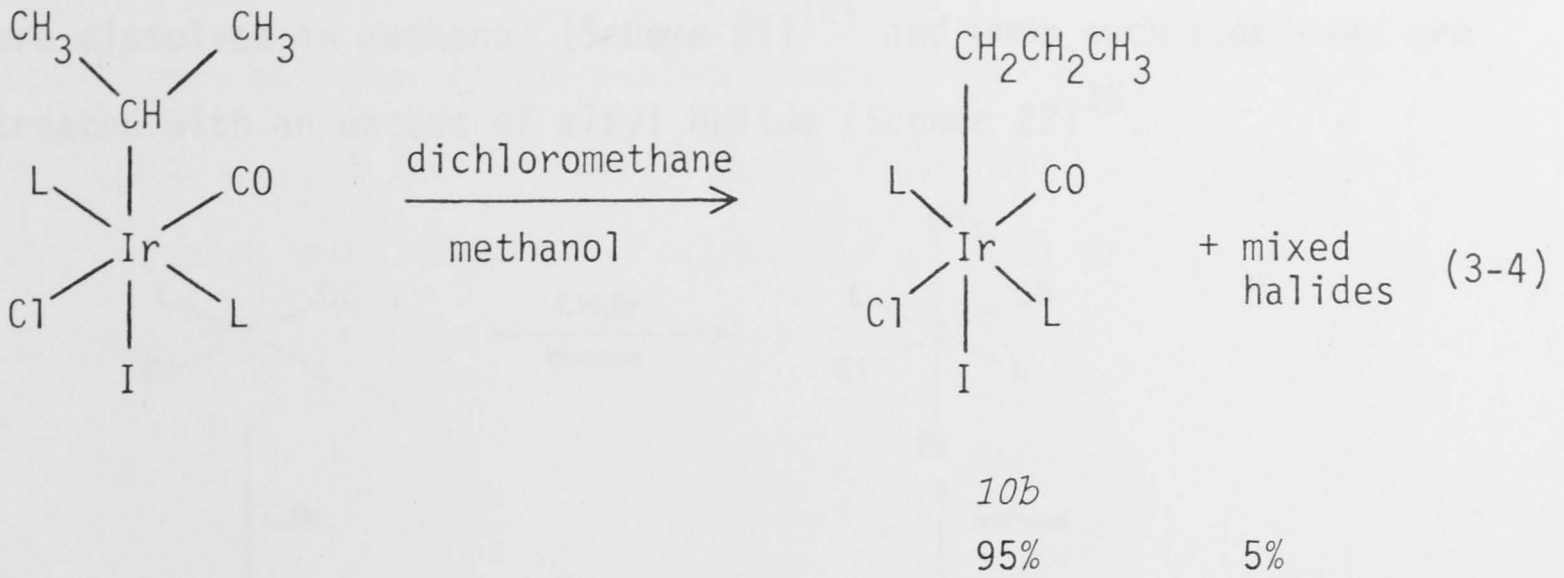
iso-propyl iodide to *11b* in benzene, is indefinitely stable to isomerization at room temperature in dichloromethane, whereas isomerization begins as soon as methanol is added. For example, a freshly prepared solution of *10c* in dichloromethane/methanol (4:1 volume ratio) shows only *iso*-propyl resonances in the ^{1}H nmr, δ0.82 (d, J_{HH} = 7 Hz, IrCH($C\underline{H}_3$)$_2$),2.14 (sp, J_{HH} = 7 Hz, IrC$\underline{H}$(CH_3)$_2$), but after a few hours at room temperature these have disappeared completely and are replaced by resonances due to the *n*-propyl complex, *10b*, δ0.14 (t, J_{HH} = 7 Hz, $CH_2CH_2C\underline{H}_3$), 0.9-1.1 (m, $C\underline{H}_2C\underline{H}_2CH_3$).

Other *sec*-alkyl iridium(III) complexes will also rearrange to the isomeric *n*-alkyl complexes when dissolved in dichloromethane/methanol, e.g. the *sec*-butyl complex, *10e*, and the PMe_3-containing complexes, *12c* (*iso*-propyl), *12e* (*sec*-butyl), *12j* (3-pentyl) and *12l* (2-octyl).

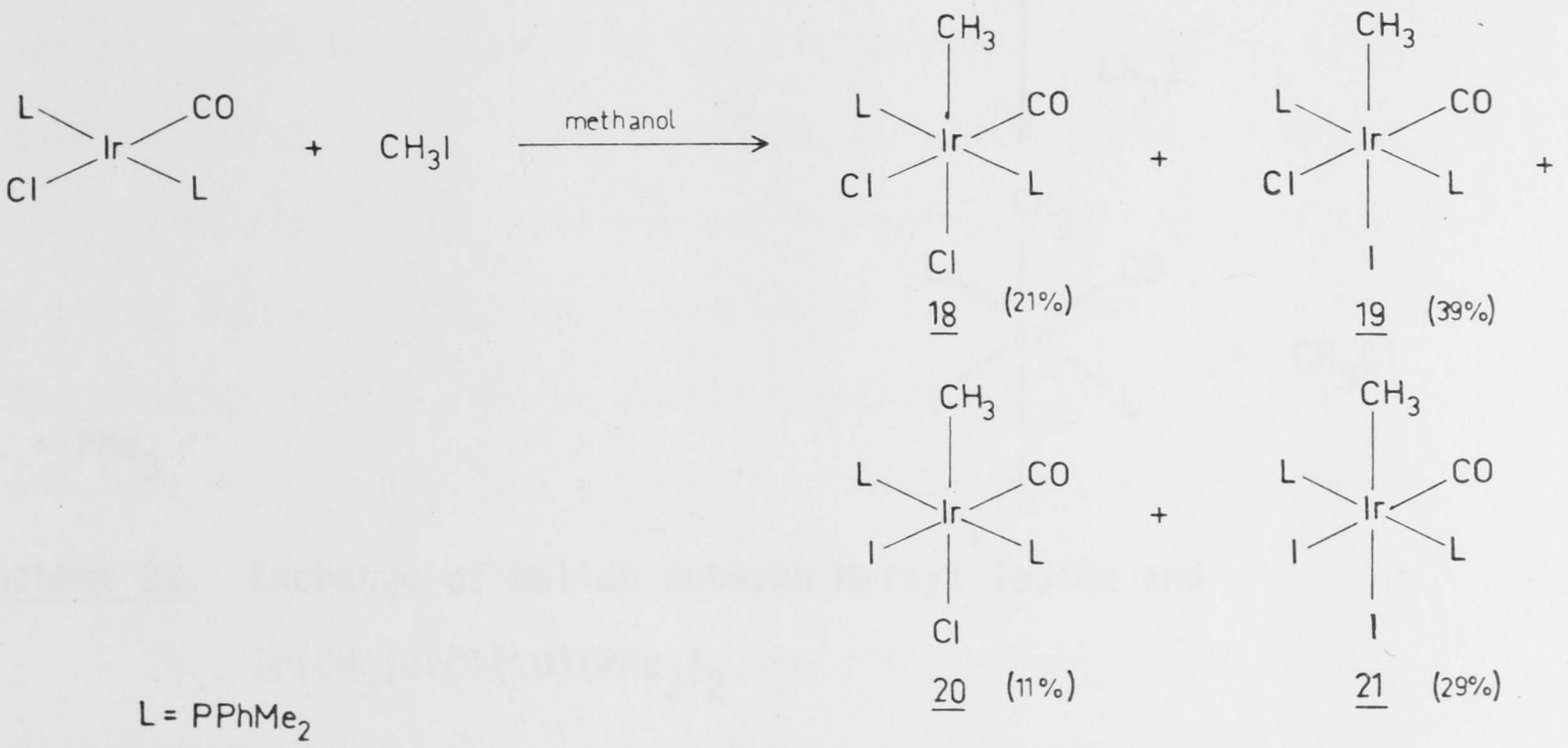
The *iso*- to *n*-propyl group rearrangement of *10c* to *10b* is accompanied by "halide scrambling", which is more extensive for the reaction of *iso*-propyl iodide with *11b* in methanol (3-3) than for the dissolution of the *iso*-propyl complex, *10c*, in dichloromethane/methanol (3-4).



(3-3)

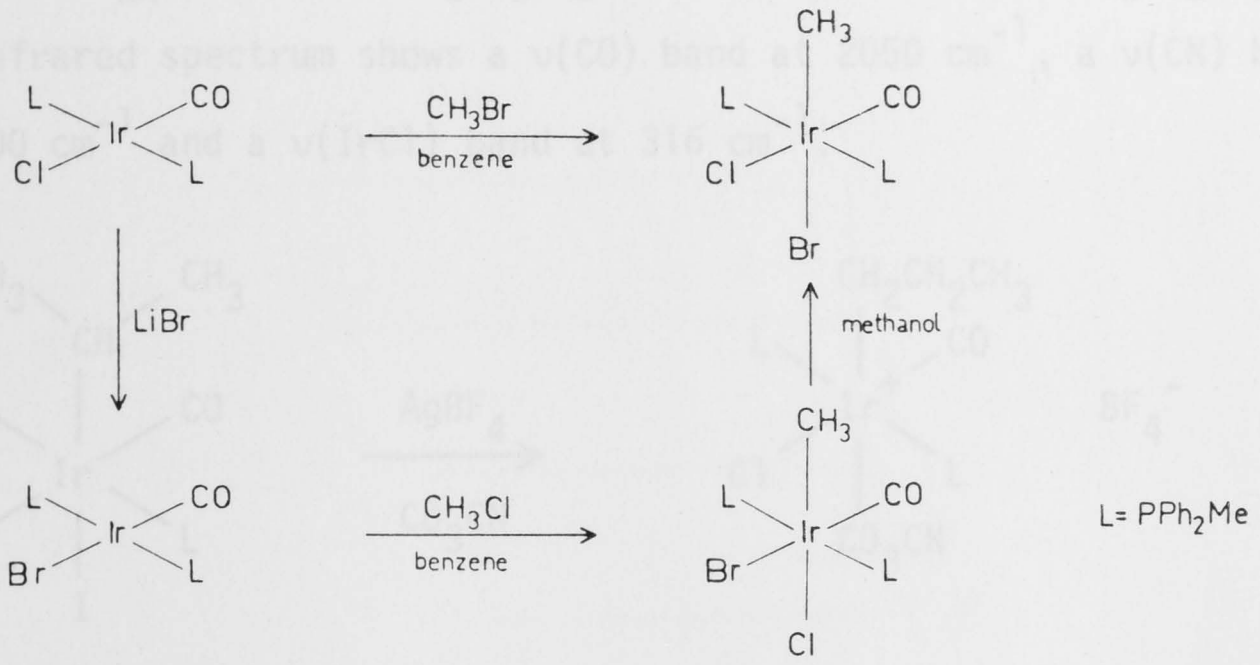


Halide scrambling may occur even when alkyl group rearrangement is not observed. For example, addition of *iso*-propyl iodide to *11b* in acetonitrile gives the *iso*-propyl complex, *10c*, and 10% each of the diiodide and dichloride analogues. Deeming and Shaw[47] report that the addition of methyl iodide to *11b* in methanol gives three products: *19* (40%), *20* (5%), *21* (55%). However, when this reaction is repeated four products are obtained, as shown in Scheme 20.

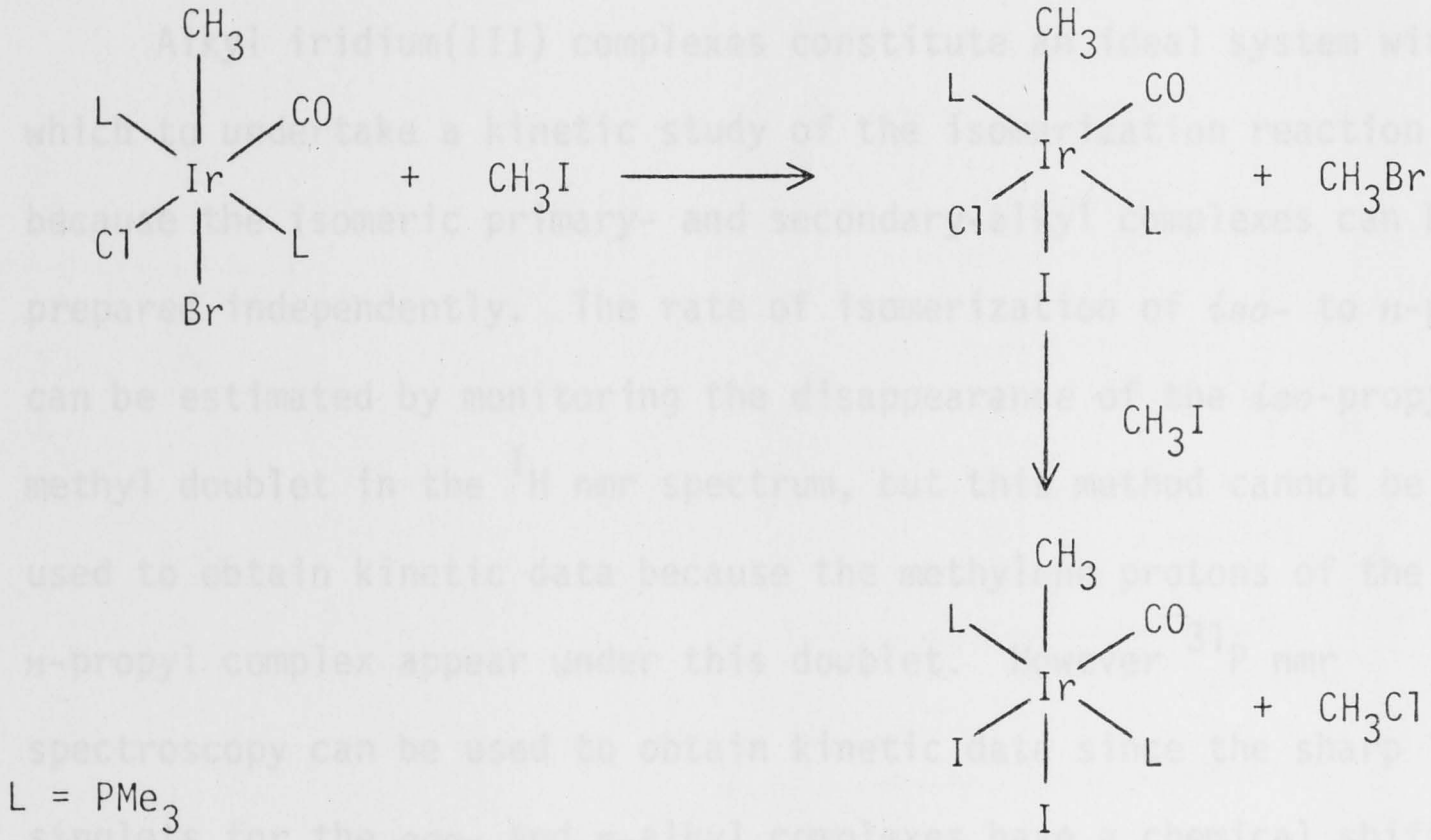


Scheme 20. Addition of CH_3I to $IrCl(CO)(PPhMe_2)_2$ in Methanol.

Halide exchange also occurs when alkyl iridium(III) complexes are dissolved in methanol (Scheme 21)[121] and when such complexes are treated with an excess of alkyl halide (Scheme 22)[35].



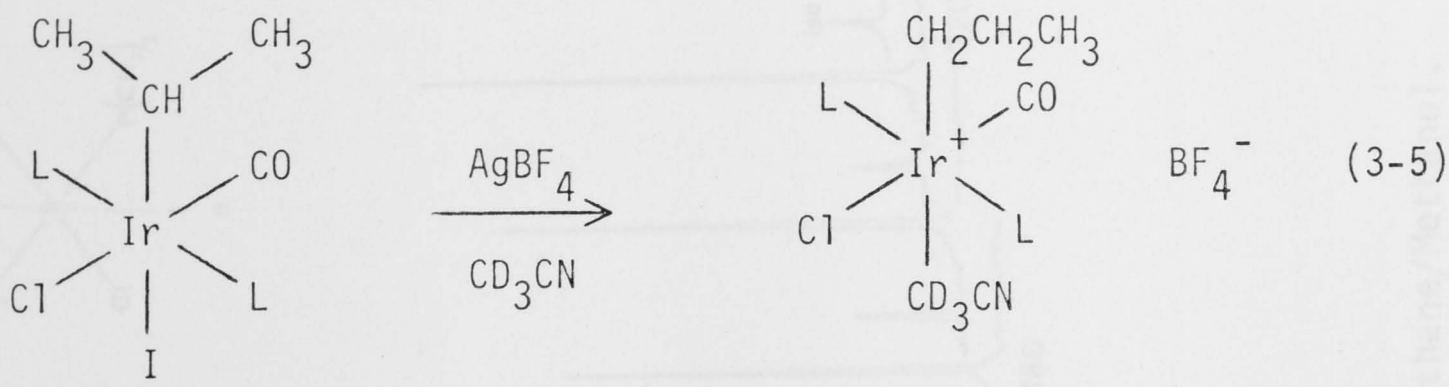
Scheme 21. Exchange of Halide Ligands in $Ir(CH_3)BrCl(CO)(PPh_2Me)_2$.



Scheme 22. Exchange of Halide Between Methyl Iodide and $Ir(CH_3)BrCl(CO)(PMe_3)_2$.

Addition of $AgBF_4$ to the *iso*-propyl complex *10c* in acetonitrile gives the *n*-propyl cationic complex $[Ir(CH_2CH_2CH_3)Cl(CH_3CN)(CO)(PPhMe_2)_2]BF_4$ in which the iodide *trans* to the alkyl group has been

removed and rapid alkyl group rearrangement has taken place (3-5). The ^1H nmr spectrum of the cation shows typical *n*-propyl resonances at δ0.57 (t, J_{HH} = 6 Hz, $IrCH_2\underline{CH_2}\underline{CH_3}$) and 0.76-1.18 (m, $Ir\underline{CH_2}\underline{CH_2}CH_3$). The infrared spectrum shows a ν(CO) band at 2050 cm^{-1}, a ν(CN) band at 2300 cm^{-1} and a ν(IrCl) band at 316 cm^{-1}.



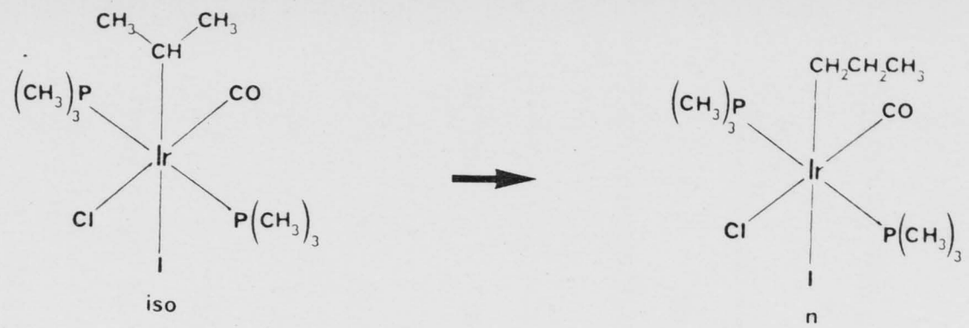
(3-5)

L = $PPhMe_2$

II. Kinetic Results

Alkyl iridium(III) complexes constitute an ideal system with which to undertake a kinetic study of the isomerization reaction because the isomeric primary- and secondary-alkyl complexes can be prepared independently. The rate of isomerization of *iso*- to *n*-propyl can be estimated by monitoring the disappearance of the *iso*-propyl methyl doublet in the ^1H nmr spectrum, but this method cannot be used to obtain kinetic data because the methylene protons of the *n*-propyl complex appear under this doublet. However ^{31}P nmr spectroscopy can be used to obtain kinetic data since the sharp singlets for the *sec*- and *n*-alkyl complexes have a chemical shift difference of ca. 1-3 ppm (see Experimental, page 68, Chapter Two).

The ^{31}P nmr spectra of the *iso*-propyl complex, *12c*, in dichloromethane/methanol (4:1 volume ratio) are reproduced in Figure 14 and show the gradual disappearance of the resonance of the *iso*-propyl complex *12c* and concomitant growth of the resonance of the *n*-propyl complex, *12b*. A plot of ln(a/a-x), where a is the initial



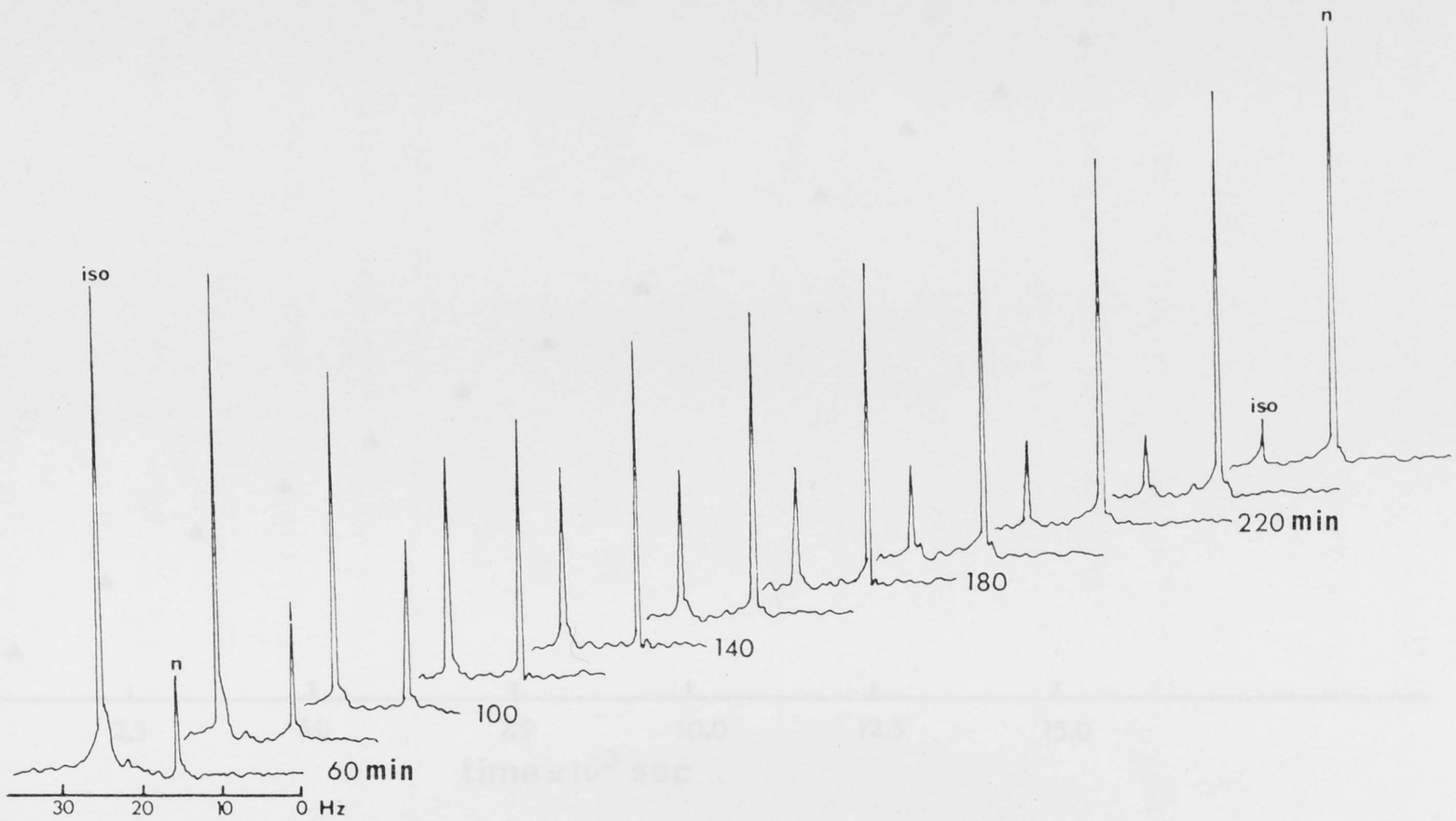


Figure 14. $^{31}P\{^{1}H\}$ NMR Spectra of $Ir(CH(CH_3)_2)ClI(CO)(PMe_3)_2$ in Dichloromethane/Methanol.

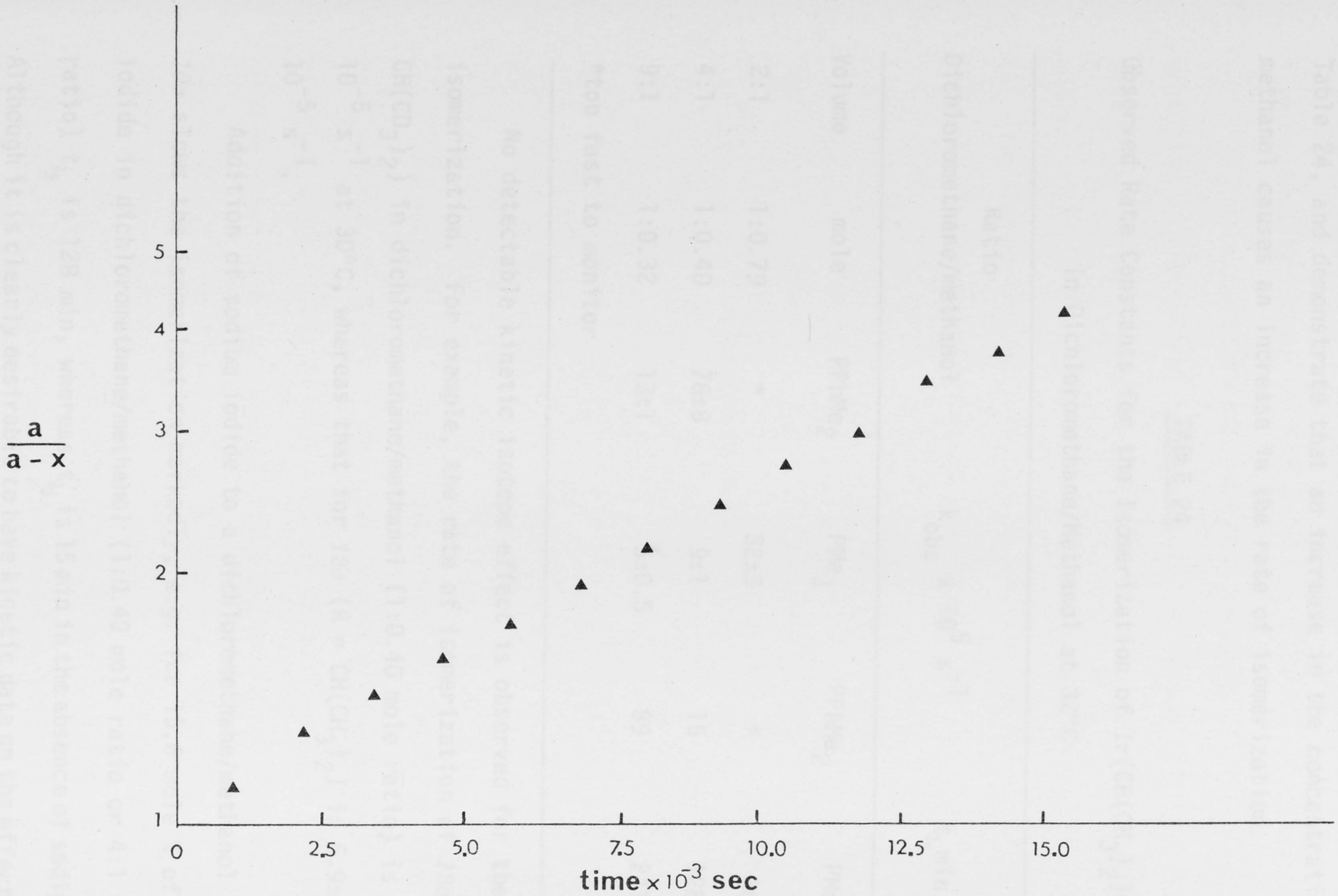


Figure 15. Plot of ln (a/a-x) vs time for $Ir(CH(CH_3)_2)ClI(CO)(PMe_3)_2$ in Dichloromethane/Methanol (4:1 Volume Ratio).

concentration of *sec*-alkyl and x is the concentration of *n*-alkyl at time t, versus time is shown in Figure 15.

The observed rate constants (k_{obs}) for the isomerization of $Ir(CH(CH_3)_2)ClI(CO)(PPhMe_2)_2$ in dichloromethane/methanol appear in Table 24, and demonstrate that an increase in the concentration of methanol causes an increase in the rate of isomerization.

TABLE 24

Observed Rate Constants for the Isomerization of $Ir(CH(CH_3)_2)ClI(CO)L_2$ in Dichloromethane/Methanol at 32°C

Ratio Dichloromethane/methanol		$k_{obs} \times 10^5\ s^{-1}$		$t_{1/2}$ min	
Volume	mole	$PPhMe_2$	PMe_3	$PPhMe_2$	PMe_3
2:1	1:0.79	*	32±3	*	36
4:1	1:0.40	78±8	9±1	15	128
9:1	1:0.32	13±1	5±0.5	89	231

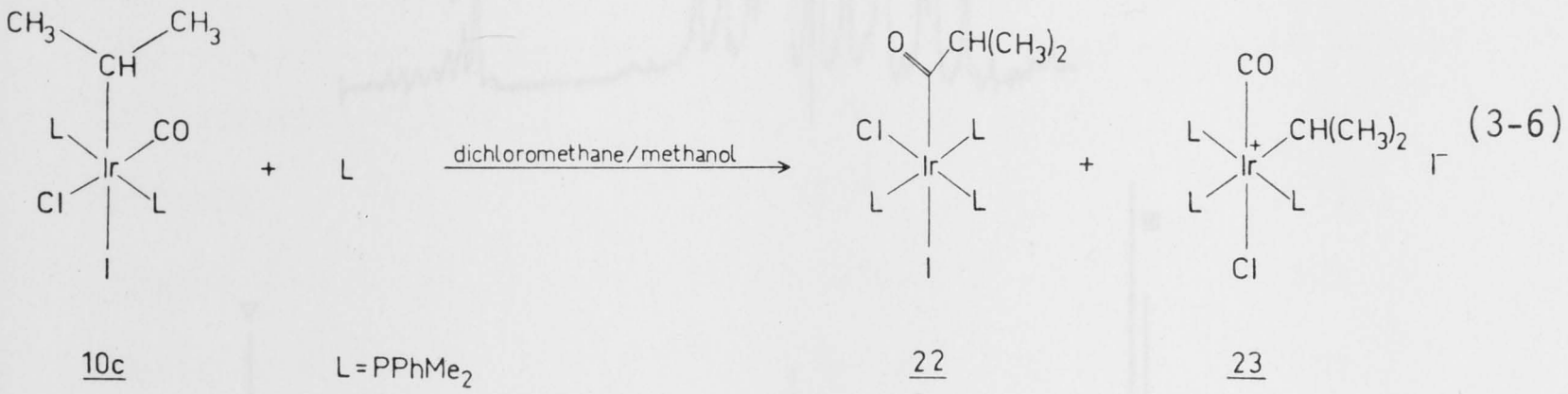
*too fast to monitor

No detectable kinetic isotope effect is observed for the isomerization. For example, the rate of isomerization of *12c'* (R = $CH(CD_3)_2$) in dichloromethane/methanol (1:0.40 mole ratio) is 6.9±0.5 x $10^{-5}\ s^{-1}$ at 30°C, whereas that for *12c* (R = $CH(CH_3)_2$) is 6.9±0.5 x $10^{-5}\ s^{-1}$.

Addition of sodium iodide to a dichloromethane/methanol solution of *10c* slows the isomerization markedly, e.g. for 15.6 mole % of sodium iodide in dichloromethane/methanol (1:0.40 mole ratio or 4:1 volume ratio) $t_{1/2}$ is 128 min, whereas $t_{1/2}$ is 15 min in the absence of sodium iodide. Although it is clearly desirable to have kinetic data on the effect of added iodide on the rate of isomerization, experimental difficulties were

encountered in that the solubility of sodium iodide in dichloromethane/methanol (4:1 volume ratio) is low. Various techniques could be used to increase the amount of iodide in solution, such as the use of crown ethers or $Bu_4N^+I^-$, and these techniques are under further investigation.

An unsuccessful attempt was made to study the effect of added phosphine on the rate of isomerization. Although there is no observable reaction of $PPhMe_2$ with *10c* in benzene, addition of one equivalent of $PPhMe_2$ to *10c* in dichloromethane/methanol (4:1 volume ratio) gives mostly the acyl complex *22*, and two other minor products (3-6), one of which is probably *23*.



(3-6)

10c L = $PPhMe_2$ 22 23

The solid state infrared spectrum of this mixture shows an acyl band, ν(C=O), at 1600 cm^{-1}, whereas in dichloromethane a terminal carbonyl band, ν(CO), at 2030 cm^{-1} and an acyl band ν(C=O), at 1600 cm^{-1} are observed, the acyl band predominating. In the ^1H nmr spectrum of the mixture (Figure 16) the PCH_3 resonances of complex *22* occur as two triplets ($^2J_{PH} + {}^4J_{PH}$ = 8 Hz) and one doublet ($^2J_{PH} + {}^4J_{PH}$ = 10 Hz) at δ2.02, 2.06 and 1.59, respectively. The resonances for the *iso*-propyl group occur at δ0.50 (d, J_{HH} = 7 Hz, $CH(C\underline{H}_3)_2$) and at δ3.45 (m, $C\underline{H}(CH_3)_2$). A complex analogous to *22* has been prepared by the addition of 2-methylpropanoyl chloride to

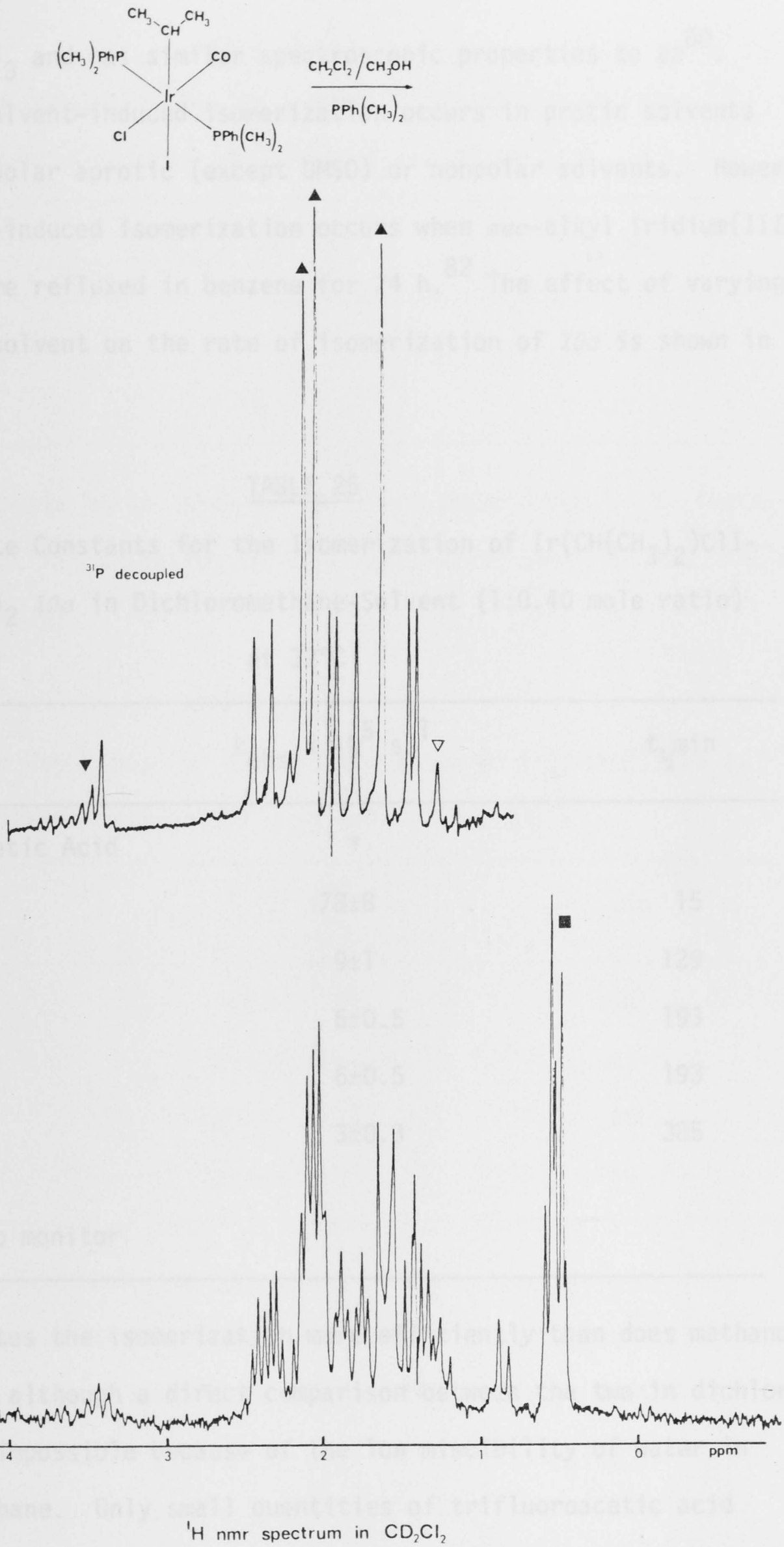


Figure 16. ^1H NMR Spectra of Product from Reaction of $PPhMe_2$ with $Ir(CH(CH_3)_2)ClI(CO)(PPhMe_2)_2$.
▲ PCH_3 of *22*; ▼ $C\underline{H}(CH_3)_2$ of *22*; ■ $CH(C\underline{H}_3)_2$ of *22*; ▽ impurities.

$IrCl(PPhMe_2)_3$ and has similar spectroscopic properties to *22*[80].

The solvent-induced isomerization occurs in protic solvents but not in polar aprotic (except DMSO) or nonpolar solvents. However, a thermally-induced isomerization occurs when *sec*-alkyl iridium(III) complexes are refluxed in benzene for 24 h.[82] The effect of varying the protic solvent on the rate of isomerization of *10c* is shown in Table 25.

TABLE 25

Observed Rate Constants for the Isomerization of $Ir(CH(CH_3)_2)ClI(CO)(PPhMe_2)_2$ *10c* in Dichloromethane-Solvent (1:0.40 mole ratio) at 32°C

Solvent	$k_{obs} \times 10^5\ s^{-1}$	$t_{\frac{1}{2}}$ min
Trifluoroacetic Acid	*	
Methanol	78±8	15
Ethanol	9±1	129
Acetic Acid	6±0.5	193
Propanol	6±0.5	193
Propan-2-ol	3±0.3	385

*Too fast to monitor

Water promotes the isomerization more efficiently than does methanol (Table 26), although a direct comparison between the two in dichloromethane is impossible because of the low miscibility of water in dichloromethane. Only small quantities of trifluoroacetic acid (10 µl in 2 mL of dichloromethane) are required for isomerization to be observed.

TABLE 26

Observed Rate Constants for the Isomerization of *10c* in Tetrahydrofuran-Solvent (1:0.40 mole ratio) at 32°C

Solvent	$k_{obs} \times 10^5\ s^{-1}$	$t_{1/2}$ min
Water	7±1	165
Methanol	<0.3	

An increase in the size of the alkyl group leads to an increase in the rate of isomerization up to a limit after which it has little effect (Table 27).

TABLE 27

Observed Rate Constants for the Isomerization of $IrRClI(CO)(PMe_3)_2$ in Dichloromethane-Methanol (1:0.40 mole ratio) at 32°C

R	$k_{obs} \times 10^5\ s^{-1}$	$t_{1/2}$ min
iso-propyl	9±1	128
sec-butyl	14±2	83
3-pentyl	25±2	46
2-octyl	25±2	46

Isomerization of the *iso*-propyl complex *10c*, in which a chloride is *trans* to the carbonyl ligand, is faster than that of the analogous *iso*-propyl complex in which iodide is *trans* to the carbonyl ligand (Table 28).

TABLE 28

Observed Rate Constants for the Isomerization of $Ir(CH(CH_3)_2)$-$XI(CO)(PPhMe_2)_2$ in Dichloromethane/Methanol (1:0.40 mole ratio) at 32°C

X	$k_{obs} \times 10^5\ s^{-1}$	$t_{\frac{1}{2}}$ min
Cl	13±1	89
I	5±0.5	231

III. Deuterium Labelling

Dissolution of the deuterated ethyl complex, $Ir(CD_2CH_3)ClI(CO)$-$(PPhMe_2)_2$ (*24*), in dichloromethane/methanol (1:1 volume ratio) at room temperature does not cause any scrambling of the deuterium label. However, when *24* is heated in dichloromethane/methanol at 80°C for a few hours, substantial scrambling of the deuterium label does occur (Figure 17). Addition of trifluoroacetic acid (TFA) to a dichloromethane solution of complex *24* at room temperature causes a rapid scrambling of the deuterium label (Figure 17). Since deuterium is not incorporated into the ethyl group of $Ir(CH_2CH_3)ClI$-$(CO)(PPhMe_2)_2$ upon addition of CF_3COOD, TFA cannot be inducing deuterium scrambling in *24* by protonation. Deuterium scrambling in *24* is much slower than isomerization of the *iso*-propyl complex, *10c*, to the *n*-propyl analogue. Addition of $AgPF_6$ to a CD_3CN solution of *24* gives no scrambling of the deuterium label until after 16 h, compared to immediate isomerization of the *iso*-propyl complex, *10c*, under the same conditions.

To determine whether the alkyl group rearrangement could proceed through tertiary-carbon intermediates, the deuterated *iso*-butyl complex, $Ir(CD_2CH(CH_3)_2)ClI(CO)(PMe_3)_2$ (*25*), was prepared. Scrambling

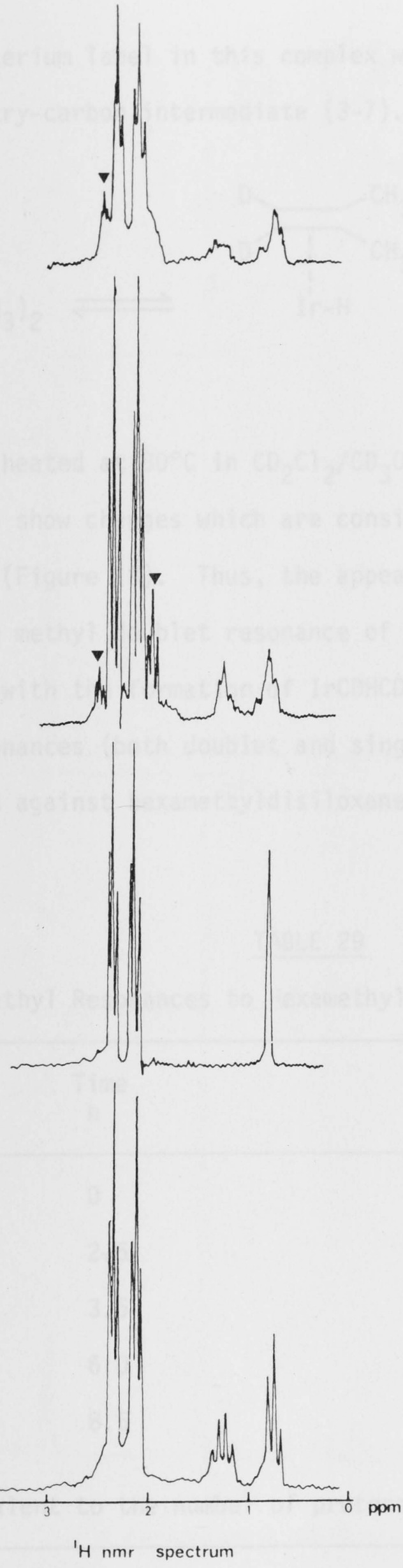
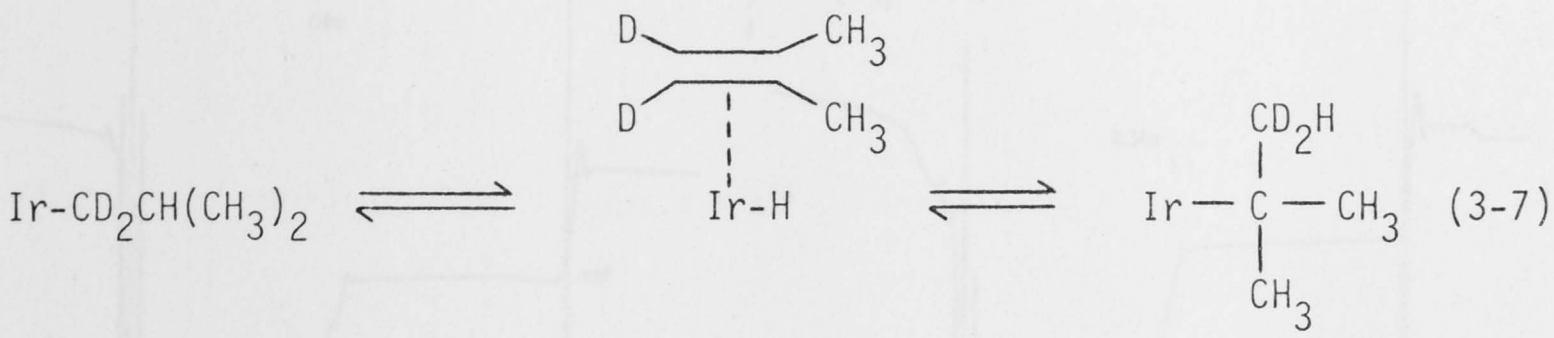


Figure 17. ^1H NMR Spectra Showing Deuterium Scrambling of $Ir(CD_2CH_3)ClI(CO)(PPhMe_2)_2$.

▼ unidentified side products.

of the deuterium label in this complex would imply the formation of a tertiary-carbon intermediate (3-7).



(3-7)

When *25* is heated at 80°C in CD_2Cl_2/CD_3OD (1:1 volume ratio) the ^1H nmr spectra show changes which are consistent with deuterium scrambling (Figure 18). Thus, the appearance of a broad singlet between the methyl doublet resonance of the *iso*-butyl group is consistent with the formation of $IrCDHCD(CH_3)_2$. The integral of the methyl resonances (both doublet and singlet) decreases with time (integrated against hexamethyldisiloxane standard) as seen in Table 29.

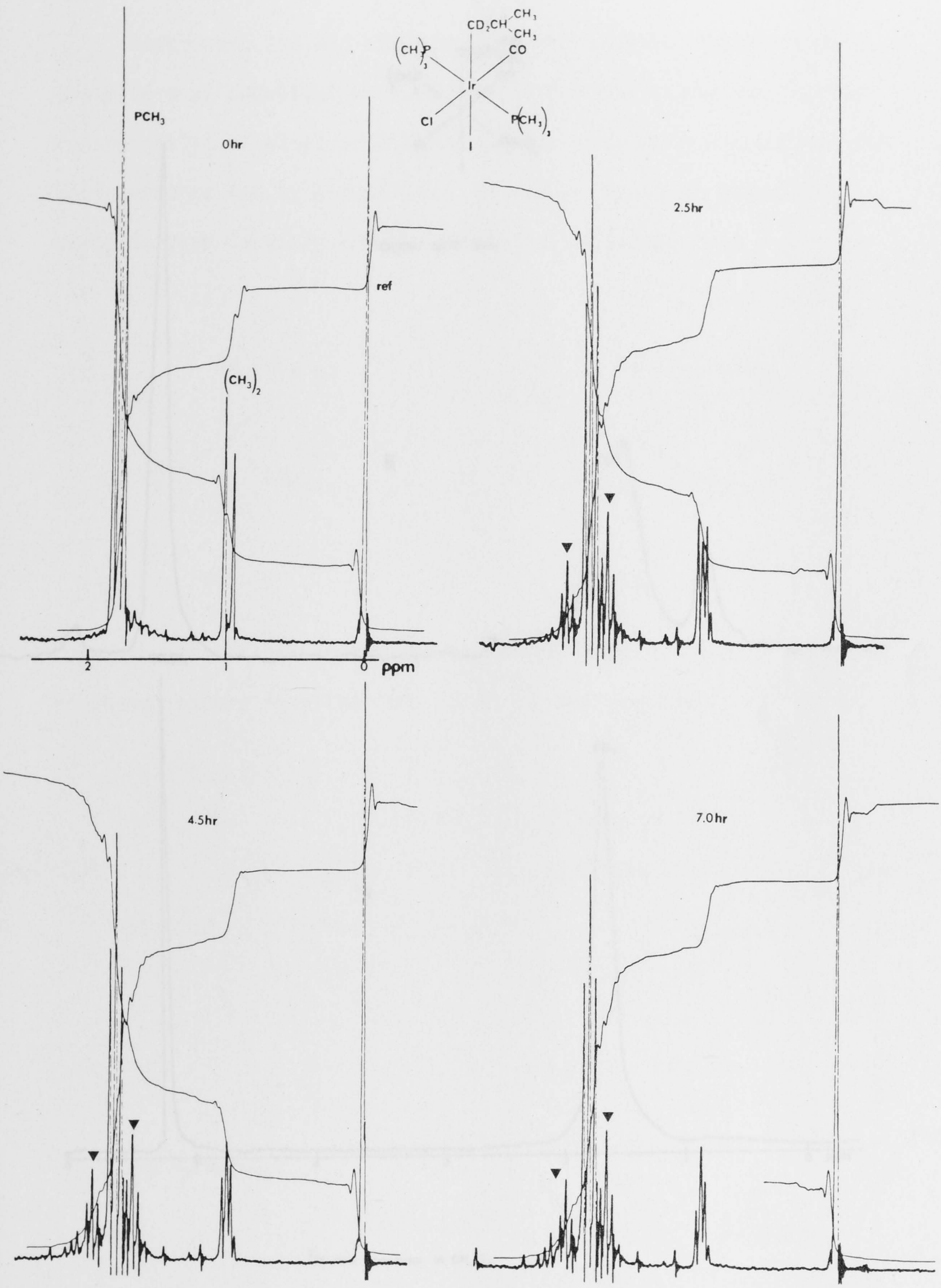
TABLE 29

Ratio of Methyl Resonances to Hexamethyldisiloxane Standard in *25*

Time h	Ratio*
0	1.18
2.5	1.10
3.5	1.04
6.0	1.00
8.5	0.96

*not equivalent to the number of protons

In addition, the ^2H nmr spectrum of a sample of *25*, which has been heated at 80°C in methanol for 24 h, shows that the deuterium label has scrambled throughout the alkyl chain (Figure 19).



^{1}H nmr spectrum in $CD_2Cl_2 : CD_3OD$ (1 : 1)
80°C

Figure 18. ^{1}H NMR Spectra Showing Deuterium Scrambling of $Ir(CD_2CH(CH_3)_2)ClI(CO)(PMe_3)_2$.
▼ unidentified side products, ref = hexamethyldisiloxane.

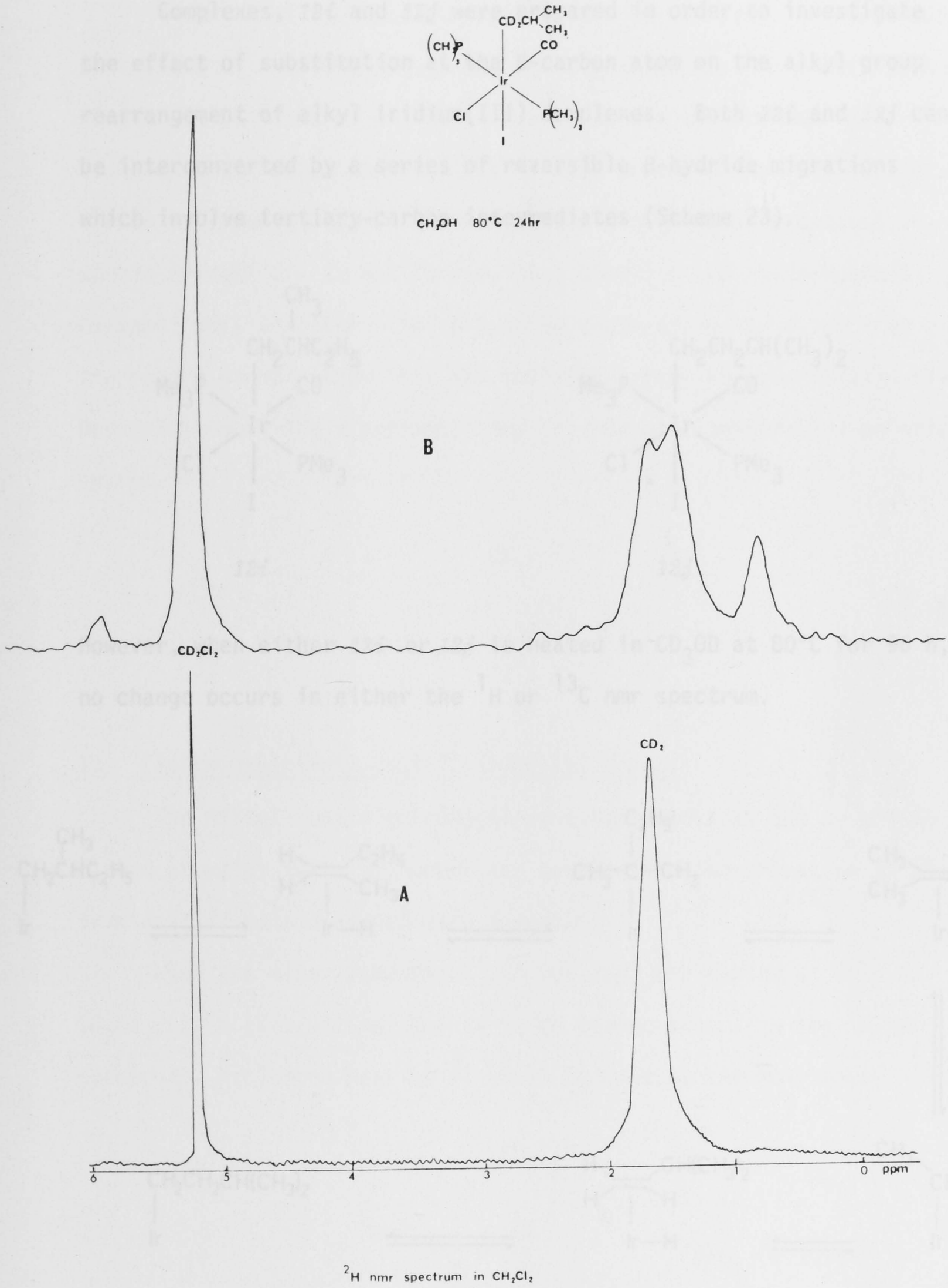
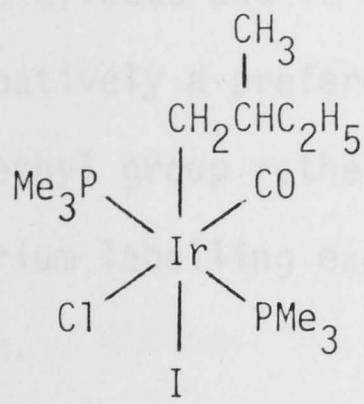
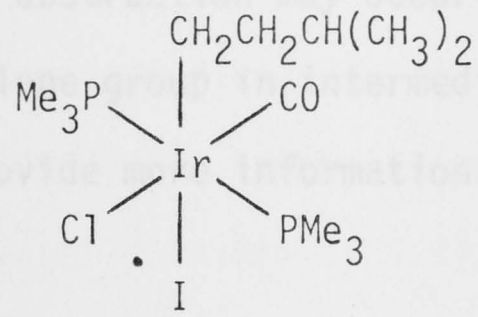


Figure 19. ^2H NMR Spectra Showing Deuterium Scrambling of $Ir(CD_2CH(CH_3)_2)ClI(CO)(PMe_3)_2$.
A Spectrum of freshly prepared sample of *25*.
B Spectrum of *25* after being heated in methanol for 24 h at 80°C.

Complexes, *12i* and *12j* were prepared in order to investigate the effect of substitution at the β-carbon atom on the alkyl group rearrangement of alkyl iridium(III) complexes. Both *12i* and *12j* can be interconverted by a series of reversible β-hydride migrations which involve tertiary-carbon intermediates (Scheme 23).

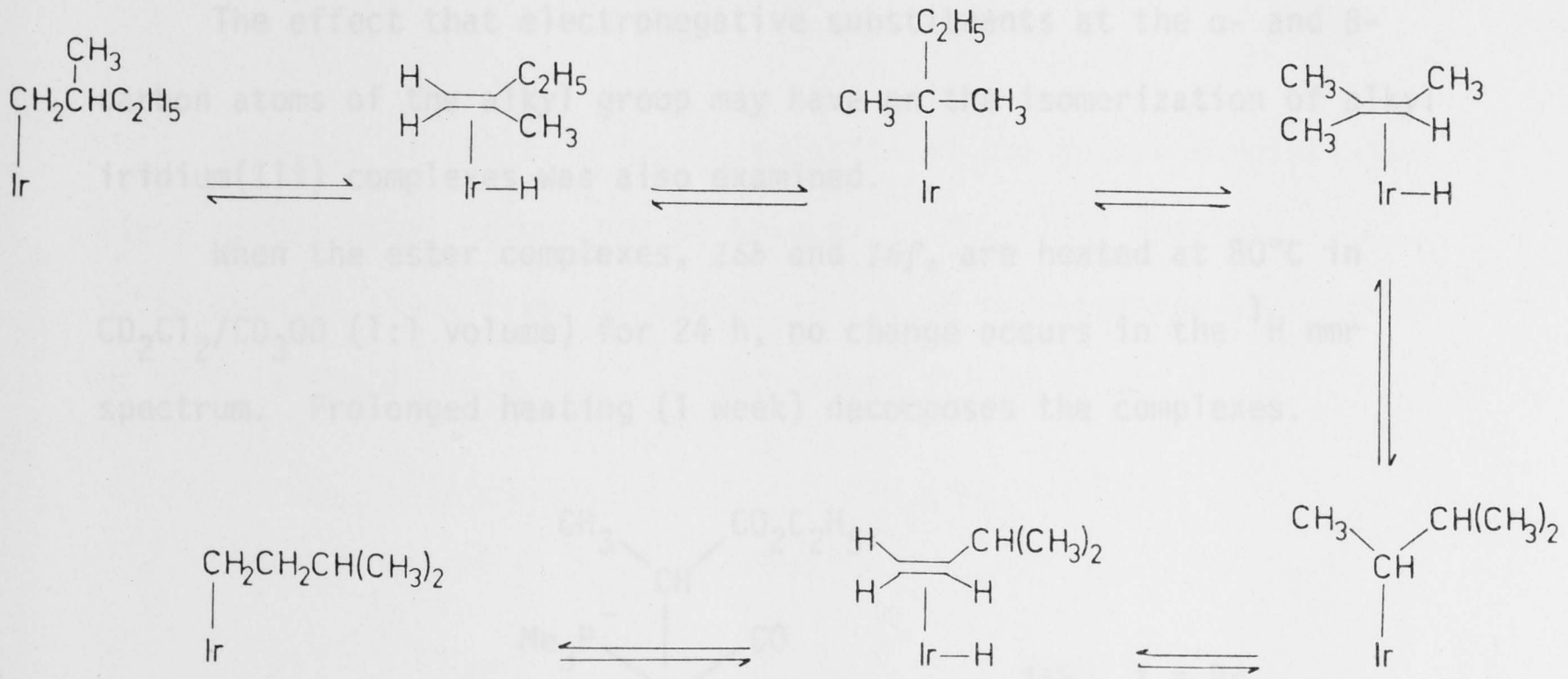


12i



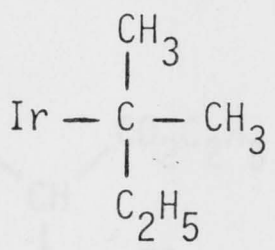
12j

However, when either *12i* or *12j* is heated in CD_3OD at 80°C for 96 h, no change occurs in either the ^1H or ^{13}C nmr spectrum.



Scheme 23. Interconversion of Complexes *12i* and *12j* by β-Hydride Migration.

A number of alternative explanations may be proposed for these observations. For example, β-hydride migration may not occur in these complexes, but this is unlikely in view of the results for the deuterated *iso*-butyl complex. It is also possible that the tertiary carbon intermediate (3-8) is energetically unfavourable because of steric effects and is not formed, thus blocking the rearrangement. Alternatively a preferential β-hydride abstraction may occur from the methyl group rather than the methylene group in intermediate (3-8). Deuterium labelling experiments may provide more information on this system.

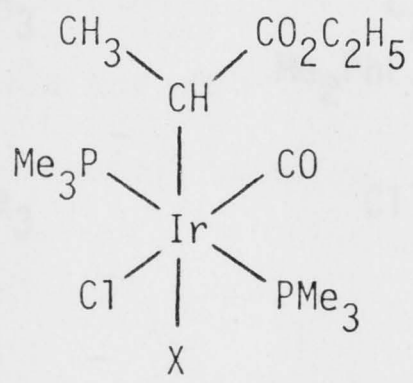


(3-8)

IV. Electronegatively Substituted Alkyl Groups

The effect that electronegative substituents at the α- and β-carbon atoms of the alkyl group may have on the isomerization of alkyl iridium(III) complexes was also examined.

When the ester complexes, *15b* and *15f*, are heated at 80°C in CD_2Cl_2/CD_3OD (1:1 volume) for 24 h, no change occurs in the ^1H nmr spectrum. Prolonged heating (1 week) decomposes the complexes.

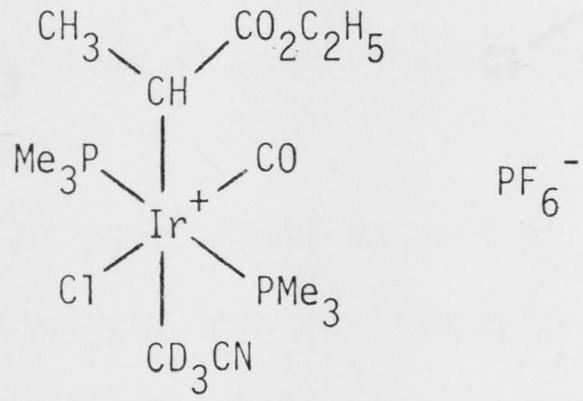


15b, X = Br

15f, X = I

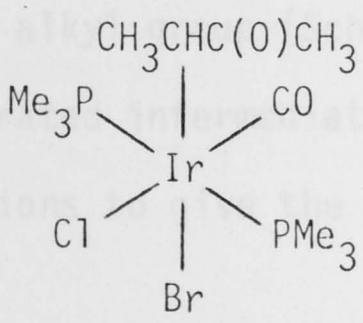
Whereas TFA causes a rapid isomerization of the *iso*-propyl complex *10c*, addition of TFA to a CD_2Cl_2 solution of either *15b* or *15f* causes no change in the ^1H nmr spectra over 24 h.

Addition of $AgPF_6$ to a CD_3CN solution of either *15b* or *15f* gives the cationic complex, *26*, which also fails to isomerize. The ^1H nmr spectrum of a CD_3CN solution of *26* shows only resonances due to the *sec*-alkyl complex even after 24 h at room temperature. This result contrasts with that for unsubstituted alkyl iridium(III) complexes, such as *10c*, which immediately isomerize on addition of $AgPF_6$. After 96 h the CD_3CN solution of *26* shows ^1H resonances attributed to ethyl acrylate and an unknown iridium(III) species. The resonances due to ethyl acrylate increase in intensity between 24 and 96 h, whereas those due to *26* decrease in intensity during this time.

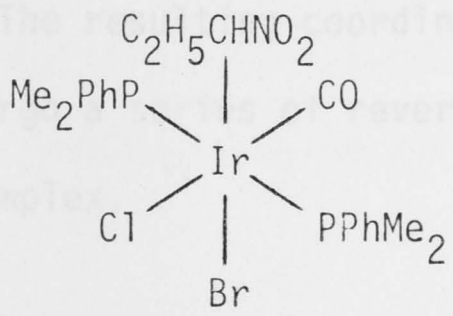


26

Addition of TFA to a CD_2Cl_2 solution of the ketone complex, *15c*, gives methyl ethyl ketone and an unknown iridium(III) species. The nitro complex, *14d*, shows no change in its ^1H nmr spectrum when heated at 80°C in CD_2Cl_2/CD_3OD (1:1 volume ratio) for 24 h.

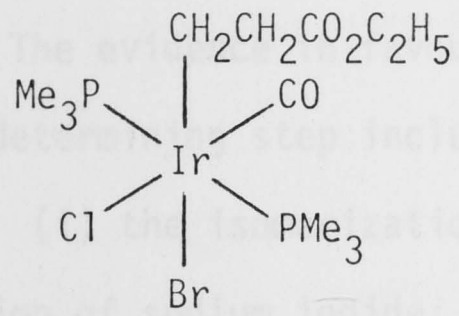


15c

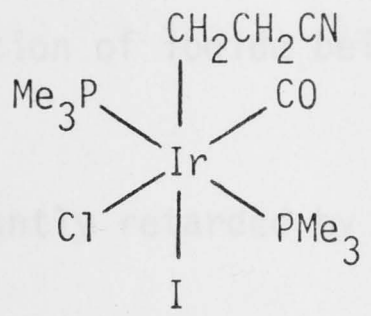


14d

It is possible that the electronic effect of an electronegative substituent on the α-carbon atom might be stabilizing the *sec*-alkyl complex relative to the isomeric *n*-alkyl complex. Thus, primary-alkyl complexes such as *15e* and *15g* with electronegative substituents in the β-position might isomerize to the corresponding *sec*-alkyl complex substituted in the *α*-position. However, under a wide variety of conditions, e.g. heating at 80°C in CD_2Cl_2/CD_3OD for 24 h, the addition of TFA or the abstraction of halide with $AgPF_6$, the ^1H nmr spectra of complexes *15e* and *15g* show no change.



15e

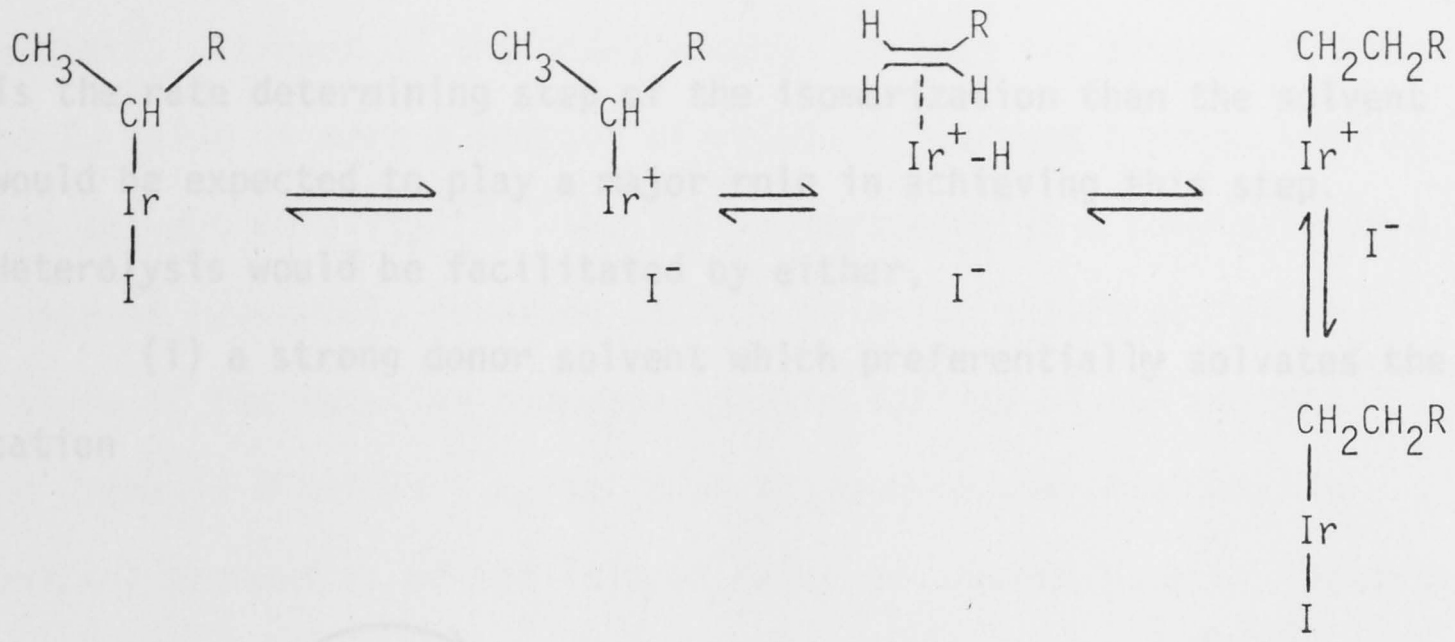


15g

Discussion.

Mechanism of Alkyl Group Rearrangement

On the basis of observations reported in the Results section the alkyl group rearrangements of *sec*-alkyl iridium(III) complexes are postulated to occur by the rate determining loss of iodide *trans* to the alkyl group (Scheme 24). The resulting coordinatively unsaturated intermediate can undergo a series of reversible β-hydride migrations to give the *n*-alkyl complex.



Scheme 24. Mechanism for Isomerization of *sec*-Alkyl Iridium(III) Complexes.

The evidence in favour of dissociation of iodide being the rate determining step includes:

(i) the isomerization is significantly retarded by the addition of sodium iodide;

(ii) the effect of varying the solvent on the rate of isomerization correlates with the relative anion solvating ability of the solvent and suggests that the role of the solvent is to promote the dissociation of halide;

(iii) removal of iodide by the additon of $AgPF_6$ causes immediate isomerization of complexes such as *10c*.

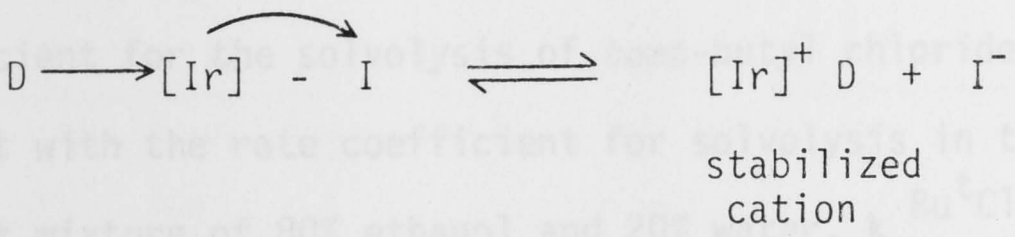
The absence of a detectable kinetic isotope effect for the isomerization suggests that β-hydride migration is not the rate determining step. A kinetic isotope effect of between 2.0 and 2.8 would be expected if β-hydride migration were the rate determining step[139].

Solvent Influence on Alkyl Group Rearrangement

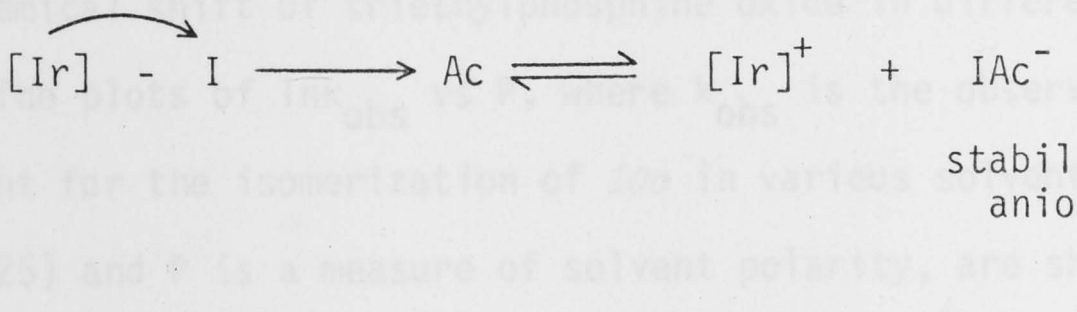
The effect of solvent in influencing the rate of a reaction or the position of equilibrium between various species can often be rationalized on the basis of either the electrophilicity or acceptor properties of the solvent and the nucleophilicity or donor properties of the solvent. If heterolysis of the iridium-iodide bond

is the rate determining step of the isomerization then the solvent would be expected to play a major role in achieving this step. Heterolysis would be facilitated by either,

(i) a strong donor solvent which preferentially solvates the cation



or (ii) a strong acceptor solvent which preferentially solvates the anion.

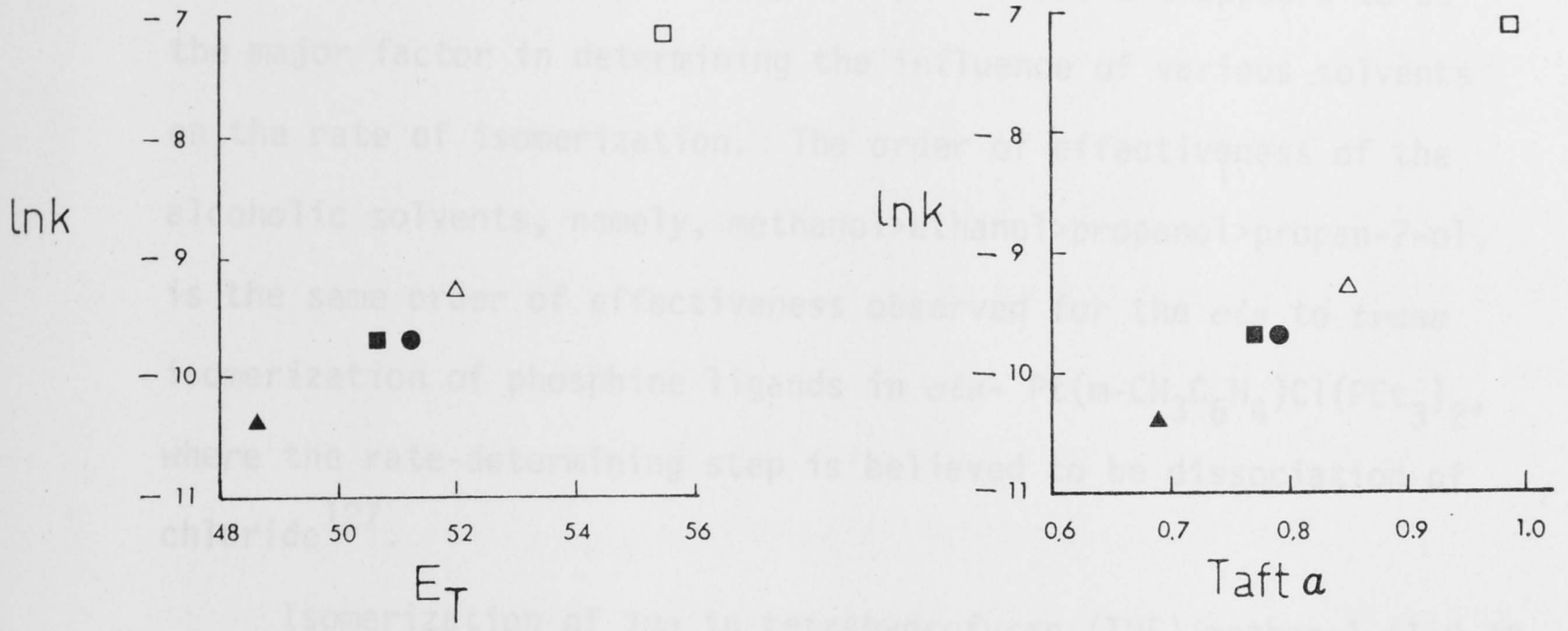


The isomerization of *sec*-alkyl iridium(III) complexes via reversible β-hydride migration should proceed more rapidly for case (ii), where a vacant coordination site is maintained, rather than for case (i), where the solvent will tend to occupy the vacant site created by iodide dissociation.

Several scales of solvent acceptor and solvent donor properties have been proposed[122,123]. For example, the Dimroth-Reichardt E_T parameter is a measure of solvent polarity based on the transition energy for the longest wavelength solvatochromic absorption band of various pyridinium-N-phenoxide betaine dyes[123]. The absorption maxima changes with solvent polarity because the relative solvent interactions are different for the ground state, an ion pair, and the first excited state, which is a radical pair. Solvents interact more readily with the negatively charged oxygen than with the coordinatively

saturated nitrogen of the betaine dyes, so that for protic solvents the E_T value is more a measure of relative hydrogen bonding ability than solvent polarity[124]. The Taft α-parameter is a composite of a number of previously reported solvent polarity scales and gives a measure of the relative hydrogen bonding ability of the solvent[125]. The Grunwald-Winstein Y value is an attempt to characterize the ionizing properties of the solvent based on a comparison of the rate coefficient for the solvolysis of *tert*-butyl chloride, k^{Bu^tCl}, in one solvent with the rate coefficient for solvolysis in the reference solvent mixture of 80% ethanol and 20% water, $k_o^{Bu^tCl}$, so that $Y = \log(k^{Bu^tCl}/k_o^{Bu^tCl})$[122,126]. A further empirical parameter for solvent electrophilicity is the acceptor number, which is based on the ^{31}P nmr chemical shift of triethylphosphine oxide in different solvents[122].

The plots of $\ln k_{obs}$ vs P, where k_{obs} is the observed rate constant for the isomerization of *10c* in various solvents (taken from Table 25) and P is a measure of solvent polarity, are shown in Figure 20. The correlation coefficients for these plots are shown in Table 30. A good correlation exists between the rate of isomerization in various solvents and both the Dimroth-Reichardt E_T parameter[123] and the Taft α parameter[125] for the solvents. Only a fair correlation exists between the rate of isomerization in various solvents and the acceptor number[122] or Grunwald-Winstein Y value[126] of the particular solvents. No correlation is observed between the rate of isomerization in various solvents and the dielectric constant or donor number[122] (a measure of solvent nucleophilicity) of the particular solvents.



▲ *iso*-propanol; ■ propanol; ● acetic acid; △ ethanol; □ methanol.

Figure 20. Plots of lnk_{obs} Versus P, Showing the Degree of Correlation Between k_{obs} and the Polarity of the Solvent.

TABLE 30

Correlation of the Rate Constants from Table 25 with some Empirical Parameters of Solvent Polarity

Parameter	Correlation Coefficient
Acceptor Number[122]	0.866
Grunwald-Winstein's Y[126]	0.884
Dimroth-Reichardt's E_T[123]	0.980
Taft α[125]	0.973

Therefore, electrophilic solvation of the displaced iodide ion through hydrogen bonding by the protic solvent appears to be the major factor in determining the influence of various solvents on the rate of isomerization. The order of effectiveness of the alcoholic solvents, namely, methanol>ethanol>propanol>propan-2-ol, is the same order of effectiveness observed for the *cis* to *trans* isomerization of phosphine ligands in *cis*- $Pt(m\text{-}CH_3C_6H_4)Cl(PEt_3)_2$, where the rate-determining step is believed to be dissociation of chloride[127].

Isomerization of *10c* in tetrahydrofuran (THF)/methanol (1:0.40 mole ratio) is much slower than in dichloromethane/methanol (1:0.40 mole ratio) (Tables 25 and 26). This may be explained by the coordination of THF to the five-coordinate iridium(III) cation (produced by iodide dissociation) which would reduce the extent of reversible β-hydridge migration. Alternatively, THF, being a good donor solvent[122], might reduce the hydrogen-bonding ability of the protic cosolvent and so lower its anion-solvating ability (Figure 21).

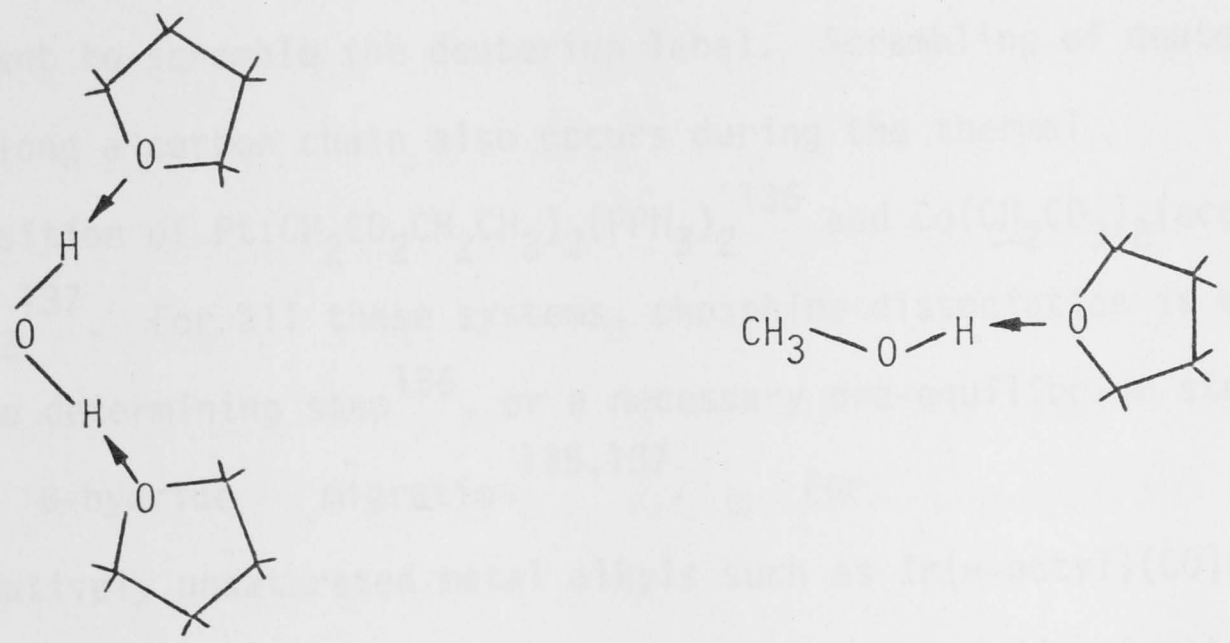


Figure 21. Ability of Donor Solvent to Decrease Acceptor Properties of Cosolvent.

General Discussion of Alkyl Group Rearrangement

The series of equilibria outlined in Scheme 24 clearly favours the *n*-alkyl iridium(III) complex relative to the *sec*-alkyl complex, but it is not known whether all the steps shown are reversible. Dissociation of iodide ion and reversible β-hydride migration still occur for the *n*-alkyl complexes, as shown by the scrambling experiments with $Ir(CD_2CH_3)ClI(CO)(PPhMe_2)_2$ (*24*). The rate of both these reactions is probably different for *n*- and *sec*-alkyl complexes and the scrambling experiments with *24* seem to indicate that β-hydride migration is slower in *n*-alkyl complexes than in *sec*-alkyl complexes. The thermal decomposition temperatures of various primary- and secondary-alkyl metal complexes also support this assumption[134].

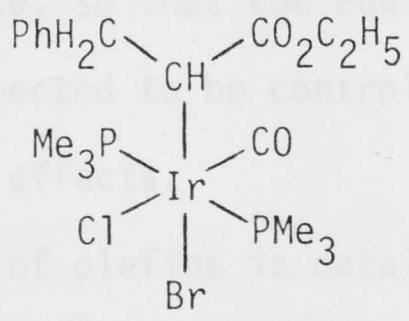
Alkyl group isomerization and scrambling of deuterium labels have also been observed during the thermal decomposition of $CpFeR(CO)(PPh_3)$ (*27*) to $CpFeH(CO)(PPh_3)$ and olefin[112,135]. Thus, the *sec*-butyl complex, *27a* (R = $CH(CH_3)C_2H_5$), is converted into the *n*-butyl isomer by being heated in xylene at 63°C for 4 h. The decomposition of *27b* (R = CD_2CH_3) for only 0.1 of a half life is sufficient to scramble the deuterium label. Scrambling of deuterium atoms along a carbon chain also occurs during the thermal decomposition of $Pt(CH_2CD_2CH_2CH_3)_2(PPh_3)_2$[136] and $Co(CH_2CD_3)_2(acac)$-$PPhMe_2)_2$[137]. For all these systems, phosphine dissociation is either the rate determining step[136], or a necessary pre-equilibrium step before β-hydride migration[135,137]. For coordinatively unsaturated metal alkyls such as Ir(*n*-octyl)$(CO)(PPh_3)_2$, dissociation of phosphine is not important and β-hydride migration is the rate-determining step[138,139].

The results presented in this Chapter suggest that ionic intermediates may provide a low-energy pathway for the formation of

coordinatively unsaturated species in which β-hydride migration takes place readily from *sec*-alkyl iridium(III) complexes.

Scrambling of the deuterium label in the *iso*-butyl iridium(III) complex, *25*, shows that tertiary-carbon intermediates are accessible to the iridium system. Similarly, when the deuterated *iso*-butyl iron complex, *27c* (R = $CD_2CH(CH_3)_2$), is heated at 65°C in xylene for 2.5 h, the deuterium label is scrambled throughout the alkyl chain[112]. However, tertiary-carbon intermediates can block alkyl group isomerization as shown by the addition of internal olefins to Cp_2ZrHCl[140] and by the thermal decomposition of isomeric-acyl manganese complexes[141]. The iridium complexes, *12i* and *12j*, do not interconvert when heated in methanol. In contrast, the iron complexes, *27d* and *27e* (R = (d) $CH_2CH(CH_3)C_2H_5$, (e) $CH_2CH_2CH(CH_3)_2$) do interconvert when heated at 64°C in xylene for 4 h to give an equilibrium mixture of the two isomers (*27e*:*27d* is 5.7:1)[112].

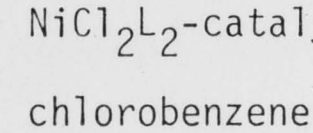
Sec-alkyl iridium(III) complexes with electronegative substituents on the α- or β-carbon atoms do not interconvert. However β-hydride migration does occur in these complexes, since addition of $AgPF_6$ to the 1-carboethoxy complex, *15b* gives ethyl acrylate (this work) and addition of $AgPF_6$ to *28* gives ethyl cinnamate[69]. Thus, it appears that β-hydride migration is irreversible in these complexes. In contrast, the *n*-alkyl iron complex, *27f* (R = CH_2CH_2CN), will isomerize to the *sec*-alkyl iron complex, *27g* (R = $CH(CH_3)CN$), showing that the iron system is strongly influenced by electronic as well as steric effects[145].



28

Formation of *n*-alkyl iridium(III) complexes from their *sec*-alkyl isomers is probably favoured on steric grounds, although this does not prevent the isolation of stable *sec*-alkyl iridium(III) complexes. Rate data suggest that steric effects are important, since the rate of isomerization increases with the size of the phosphine ligand. For example, the isomerization of $PPhMe_2$-containing complexes is fater than that of PMe_3-containing complexes. Furthermore, the rate of isomerization increases with the size of the alkyl group, e.g. $(C_2H_5)_2CH > C_2H_5CHCH_3 > (CH_3)_2CH$. However, the diiodo complex, $Ir(CH(CH_3)_2)I_2(CO)(PPhMe_2)_2$, isomerizes more slowly than does *10c* (Table 28), which is the opposite order to that expected on steric grounds. Steric effects are also believed to be important in the formation of *n*-alkyl iridium(III) complexes from the addition of *a*-branched acyl halides to $IrClL_3$ (L = PPh_3[75], PPh_2Me[78]).

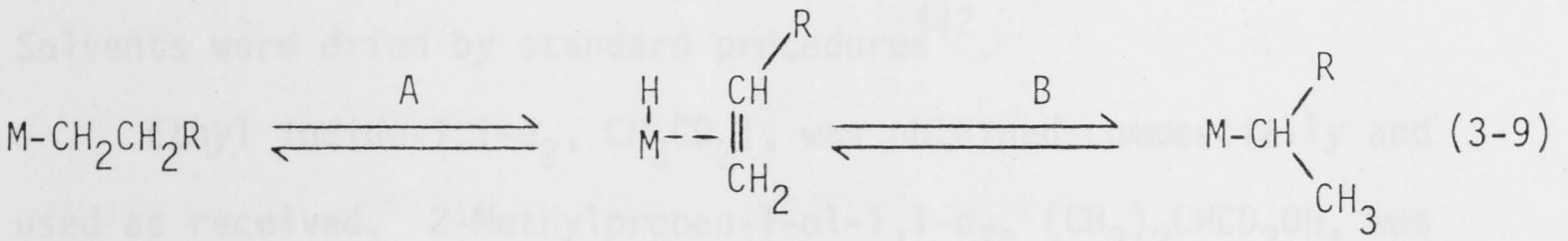
Although steric effects appear to be dominant in determining the distribution of isomeric alkyl iridium(III) complexes, this is not true for all alkyl metal systems. For example, the relative proportions of *iso*-propylbenzene and *n*-propylbenzene, formed from the $NiCl_2L_2$-catalyzed cross-coupling of *iso*-propylmagnesium bromide and chlorobenzene (3-1), are dependent on the phosphine ligand (L)[116].



The electronic influence of L is believed to be dominant in determining this proportion, since for L = dmpe, the major product is *n*-propylbenzene, whereas for L = dppe, *iso*-propylbenzene is the major product. The exact nature of the catalytic species in this reaction is unknown, but it is unlikely to be six-coordinate and is probably four-coordinate, so that the equilibrium between *n*- and *sec*-alkyls might be expected to be controlled more by electronic effects than by steric effects.

Hydroformylation of olefins is catalyzed by a number of transition metal complexes[7], the most important being $CoH(CO)_3L$

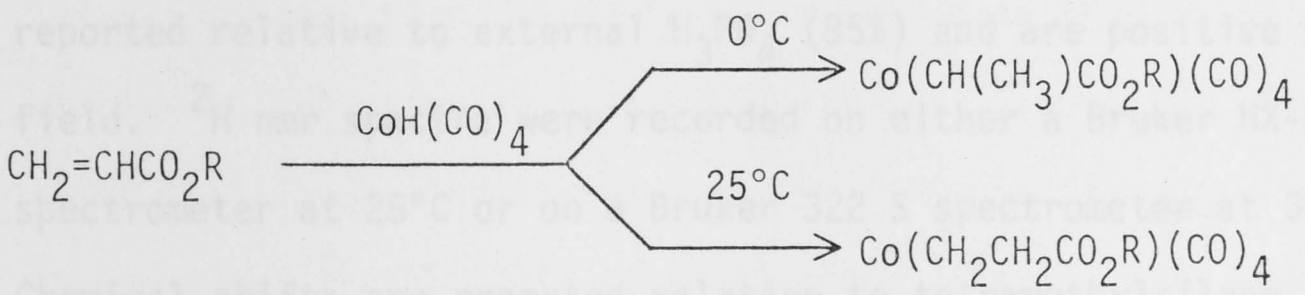
(L = CO or PR_3)[128,129] and $RhH(CO)(PPh_3)_3$[130]. The distribution of isomeric aldehydes will depend upon the direction of addition of metal-hydride to coordinated olefin and upon the extent of interconversion between the resulting isomeric metal alkyls (3-9)[7].



(3-9)

The high linear:branched chain aldehyde ratios obtained by use of phosphine-modified catalysts may be attributed to the steric effect of ancillary ligands in favouring type A* addition of hydride to olefin and in destabilizing the branched alkyl group with respect to β-hydride migration[131]. The results presented in this Chapter suggest that steric effects are important in favouring the *n*-alkyl complexes relative to the *sec*-alkyl complexes.

For electronegatively-substituted olefins (e.g. acrylates, methacrylates and crotonates) electronic effects determine the product isomer distribution at low temperature, whereas steric effects are more important at high temperatures (3-10)[132,133].



(3-10)

In contrast to the above, addition of electronegatively-substituted olefins to $FeH(CO)_4^-$ gives, at all temperatures, the branched chain alkyl complex with the substituent in the α-position, showing that, for this anionic metal complex, electronic effects are more important than steric effects[120].

*Use of the terms Markownikoff and anti-Markownikoff additions has been avoided because of the discrepancy over the polarization of metal-hydride and metal-carbon bonds in different complexes[170].

Experimental.

General

Reactions involving iridium(I) complexes and tertiary phosphines were performed under nitrogen using standard Schlenk techniques. Solvents were dried by standard procedures[142].

Ethyl iodide-1,1-d_2, CH_3CD_2I, was obtained commercially and used as received. 2-Methylpropan-1-ol-1,1-d_2, $(CH_3)_2CHCD_2OH$, was prepared from 2-methylpropanoic acid and $LiAlD_4$[143], and was converted into 1-iodo-2-methyl propane-1,1-d_2, $(CH_3)_2CHCD_2I$, by use of HI[144]. Propan-2-ol-1,1,1,3,3,3-d_6. $(CD_3)_2CHOH$, was prepared from acetone-d_6 and $LiAlH_4$[143], and was converted into 2-iodopropane-1,1,1,3,3,3-d_6, $(CD_3)_2CHI$, by use of HI[144]. Deuterated trifluoroacetic acid, CF_3COOD, was prepared by addition of D_2O to trifluoroacetic anhydride.

^1H nmr spectra (100 M Hz) were recorded on a Varian HA-100 spectrometer at 29°C. Chemical shifts are reported relative to tetramethylsilane and are calculated from the position of solvent absorption. $^{31}P\{^1H\}$ nmr spectra (24.28 M Hz) were recorded on a Bruker 322 S spectrometer at 35°C. Phosphorus chemical shifts are reported relative to external H_3PO_4 (85%) and are positive to low field. ^2H nmr spectra were recorded on either a Bruker HX-270 spectrometer at 25°C or on a Bruker 322 S spectrometer at 35°C. Chemical shifts are reported relative to tetramethylsilane and are calculated from the position of solvent absorption. Infrared spectra (4000-200 cm^{-1}) were recorded as Nujol mulls or dichloromethane solutions by use of CsI windows on PE 457 or 225 spectrophotometers and calibrated against polystyrene. Far-infrared spectra (400-100 cm^{-1}) were recorded as polythene discs on an Hitachi FIS 3 spectrophotometer.

Kinetic Data

The rate of disappearance of the *sec*-alkyl iridium(III) complex

in the $^{31}P\{^{1}H\}$ nmr spectrum (500 Hz bandwidth) at 35°C was used to obtain kinetic data. In order to detect any possible difference in the contributions of T_1 and NOE effects to the intensity of the ^{31}P resonances of the isomeric alkyl complexes, a 50:50 mixture of *10b* and *10c* was subjected to a (180°-τ-90°) pulse sequence. No significant difference was observed in the intensities of the ^{31}P resonances of the two isomers. Reactions were performed in 10 mm nmr tubes with 0.12-0.16 M solutions of *sec*-alkyl iridium(III) complex in 1.5 mL of solvent. Solvent mixtures were prepared in volumetric flasks before each reaction. Since the iridium(III) complexes were air-stable no precautions were taken to exclude air.

Spectral data were accumulated for 10 min.followed by a 10 min delay. This sequence was repeated until the resonance of the *sec*-alkyl complex had disappeared. Time intervals were taken from the mid-point of each accumulation period. The sum of peak heights of the resonances of the *sec*- and *n*-alkyl complexes was proportional to the initial concentration of the *sec*-alkyl complex. Plots of ln (a/a-x) against time, where (a-x) is the concentration of *sec*-alkyl complex at a particular time, were linear, (Figure 15), for at least three half lives, indicating that the isomerization was first order in *sec*-alkyl iridium(III) complex. Repetition of some reactions and calculation of the standard deviations of the rate constants gave values of 10% or less.

Preparations

The preparation of alkyl iridium(III) complexes has been presented in Chapter Two. The deuterated complexes, $Ir(CD_2CH_3)ClI(CO)-(PPhMe_2)_2$, $Ir(CD_2CH(CH_3)_2)ClI(CO)(PMe_3)_2$ and $Ir(CH(CD_3)_2)ClI(CO)(PMe_3)_2$ were prepared by addition of the appropriate alkyl iodide to the

iridium(I) precursor (as described in Chapter Two).

(i) Reaction of methyl iodide with $IrCl(CO)(PPhMe_2)_2$ *(11b)*.

A solution of *11b* (0.1 g, 0.19 mmol) in methanol (5 mL) was treated with methyl iodide (0.15 mL). The yellow solution rapidly became colourless. Evaporation of volatiles and trituration with hexane gave a white solid (0.1 g). ^1H and ^{31}P nmr revealed the presence of four complexes: *18* (21%), *19* (39%), *20* (11%), *21* (29%).

An independent synthesis of each complex confirmed the assignments:-

(a) A solution of *11b* (0.1 g, 0.19 mmol) in benzene (5 mL) was treated with methyl iodide (0.15 mL) to give *19*. ^1H nmr (CD_2Cl_2) δ0.52 (t, $^3J_{PH}$ = 5 Hz, $IrC\underline{H}_3$); ^{31}P nmr (CH_2Cl_2) δ-32.27 (s).

(b) A solution of *11b* (0.1 g, 0.19 mmol) in benzene (5 mL) was cooled to -78°C and methyl chloride (ca. 2 mL) was condensed into the tube. After 4 days at room temperature *18* was obtained. ^1H nmr (CD_2Cl_2) δ0.42 (t, $^3J_{PH}$ = 5 Hz, $IrC\underline{H}_3$); ^{31}P nmr (CH_2Cl_2) δ-25.74 (s).

(c) A solution of $IrI(CO)(PPhMe_2)_2$ (0.1 g, 0.16 mmol) in benzene (5 mL) was treated with methyl iodide (0.15 mL) to give *21*. ^1H nmr (CD_2Cl_2) δ0.85 (t, $^3J_{PH}$ = 5 Hz, $IrC\underline{H}_3$); ^{31}P nmr (CH_2Cl_2) δ-47.86 (s).

(d) A solution of $IrI(CO)(PPhMe_2)_2$ (0.1 g, 0.16 mmol) in benzene (5 mL) was treated with methyl chloride (ca. 2 mL) in a sealed tube. After 4 days at room temperature *20* was obtained. ^1H nmr (CD_2Cl_2) δ0.70 (t, $^3J_{PH}$ = 5 Hz, $IrC\underline{H}_3$); ^{31}P nmr (CH_2Cl_2) δ-39.11 (s).

(ii) Reaction of *iso*-propyl iodide with *11b*.

A solution of *11b* (0.1 g, 0.19 mmol) in methanol (5 mL) was treated with *iso*-propyl iodide (0.15 mL). The yellow solution rapidly became colourless. Evaporation of volatiles and trituration with hexane gave a white solid (0.1 g). ^{31}P nmr (CH_2Cl_2) showed the presence of three complexes, namely *10b* (74%) δ-32.68 (s); $(IrCH_2CH_2CH_3)Cl_2(CO)(PPhMe_2)_2$ (15%) δ-25.34 (s); and $Ir(CH_2CH_2CH_3)I_2(CO)$-

$(PPhMe_2)_2$ (11%) δ-46.46 (s). The diiodo and dichloro complexes were identified by comparison of their ^{31}P nmr resonances with those of the methyl halide adducts in (i) above.

Reaction of *iso*-propyl iodide with *11b* in acetonitrile was carried out in an analogous manner.

(iii) Acetonitrilecarbonylchloropropylbis(dimethylphenylphosphine)iridium(III) tetrafluoroborate, $[Ir(CH_2CH_2CH_3)Cl(CH_3CN)(CO)(PPhMe_2)_2]BF_4$.

A solution of *10c* (0.1 g, 0.14 mmol) in acetonitrile (1.0 mL) was placed in a Schlenk tube wrapped in aluminium foil and treated with silver tetrafluoroborate (0.03 g, 0.16 mmol). A yellow precipitate immediately formed and the mixture was stirred for 0.5 h. Solvent was removed under vacuum and the residue was extracted with three 5 mL portions of dichloromethane which were filtered through celite and evaporated to dryness. The resulting pale yellow solid was recrystallized from dichloromethane/hexane to give a white solid (0.08 g, 80%). IR (Nujol) 2030, 2040 cm^{-1} (CO), 2285 cm^{-1} (CN), 316 cm^{-1} (IrCl); IR (CH_2Cl_2) 2050 cm^{-1} (CO), 2300 cm^{-1} (CN); ^1H nmr (CD_2Cl_2) δ1.95, 1.98 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3), 0.57 (t, J_{HH} = 6 Hz, $IrCH_2CH_2CH_3$), 0.76-1.18 (m, $IrCH_2CH_2CH_3$). ^{31}P nmr (CH_2Cl_2) δ-26.54 (s).

Anal. Calcd. for $C_{22}H_{32}BClF_4IrNOP_2$: C, 37.59; H, 4.59; N, 1.99; P, 8.82. Found: C, 37.56; H, 4.73; N, 1.81; P, 9.00.

(iv) Chloroiodo(2-methylpropanoyl)tris(dimethylphenylphosphine)iridium(III), $Ir(C(O)CH(CH_3)_2)ClI(PPhMe_2)_3$.

A solution of *10c* (0.1 g, 0.14 mmol) in dichloromethane (0.6 mL) and methanol (0.2 mL) was treated with $PPhMe_2$ (0.019 g, 0.14 mmol) and stirred for 0.5 h. Solvent was then removed under vacuum and the residue was triturated with hexane to give an off-white solid (0.08 g). IR (Nujol) 1600 cm^{-1} (C=O); IR(CH_2Cl_2) 2030 cm^{-1} (CO),

1600 cm^{-1} (C=O); ^1H nmr (CD_2Cl_2) showed presence of three species (Figure 16) the major being *22*, δ2.02, 2.06 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, $PC\underline{H}_3$) 1.59 (d, $^2J_{PH} + {}^4J_{PH}$ = 10 Hz, $PC\underline{H}_3$), 0.50 (d, J_{HH} = 7 Hz, $IrC(O)CH(C\underline{H}_3)_2$), 3.45 (m, $IrC(O)C\underline{H}(CH_3)_2$).

(v) Attempted isomerization of substituted alkyl iridium(III) complexes.

(a) A solution of the appropriate alkyl iridium(III) complex (*15b-g*) in CD_2Cl_2 (0.3 mL) and CD_3OD (0.3 mL) was sealed under vacuum in a 5 mm nmr tube and heated at 80°C. No change occurred in the ^1H nmr spectrum over 24 h.

(b) A solution of the appropriate alkyl iridium(III) complex (*15b-g*) in CD_2Cl_2 (0.5 mL) was treated with trifluoroacetic acid (0.05 mL). No change occurred in the ^1H nmr spectrum over 24 h. Addition of 0.2 mL trifluoroacetic acid caused broadening of the ^1H nmr spectrum. For complex *15c*, methyl ethyl ketone was identified in the ^1H nmr spectrum δ1.0 (t, J_{HH} = 7 Hz, $C\underline{H}_3CH_2C(O)CH_3$), 2.1 (s, $CH_3CH_2C(O)C\underline{H}_3$), 2.5 (q, J_{HH} = 7 Hz, $CH_3C\underline{H}_2C(O)CH_3$). Identity confirmed by comparison with ^1H nmr spectrum of authentic sample.

(c) A solution of the appropriate alkyl iridium(III) complex (*15b-g*) in CD_3CN (1.0 mL) was treated with one equivalent of silver hexafluorophosphate. A yellow precipitate of AgI formed and the mixture was stirred for 0.5 h. The supernatant was filtered through celite into a 5 mm nmr tube and the ^1H nmr of the iridium(III) cation was monitored over 24 h. No change occurred over this interval. Over four days the cation derived from *15b* decomposed slowly to give an unknown iridium species, δ1.97 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, $PC\underline{H}_3$) and ethyl acrylate δ4.1 (q, J_{HH}=7 Hz, $CH_2{=}CHCO_2C\underline{H}_2CH_3$), 5.7-6.3 (m, $CH_2{=}C\underline{H}CO_2CH_2CH_3$). Identity confirmed by comparison with ^1H nmr spectrum of authentic sample.

(vi) ^{2}H Scrambling experiments.

(a) A solution of the appropriate alkyl iridium(III) complex (*24* or *25*) in CD_2Cl_2 (0.3 mL) and CD_3OD (0.3 mL) was filtered through celite into a 5 mm nmr tube which was fitted with a pressure seal. The solution was heated at 80°C and the reaction was monitored by ^{1}H nmr spectroscopy.

(b) A solution of the appropriate alkyl iridium(III) complex (*24* or *25*) in methanol (2 mL) was heated at 80°C for 24 h in a sealed tube. The solvent was removed and the resulting residue was taken up in CH_2Cl_2 and the ^{2}H nmr spectrum was recorded.

CHAPTER FOUR

Preparation and Alkyl Group Rearrangements of Dialkyl Iridium(III) Complexes

Introduction.

Low-valent metal alkyl complexes have been postulated as intermediates in many transition metal catalysed organic reactions[3,146]. An understanding of the properties of these types of complexes may allow more selective organic syntheses to be designed.

Alkyl iridium(I) and rhodium(I) complexes have not been extensively studied in this regard because of several low energy decomposition pathways[138,147]. For example, the *n*-octyl complex, $Ir(CH_2(CH_2)_6CH_3)(CO)(PPh_3)_2$ undergoes decomposition at 0°C in ether to give octane, octene and an unidentified iridium species (Scheme 25)[138].

$$IrCl(CO)(PPh_3)_2 + n\text{-octyl-lithium} \xrightarrow[\text{ether}]{0^\circ C} Ir(n\text{-octyl})(CO)(PPh_3)_2 \downarrow$$

$$\text{octane} + \text{octene} + [Ir]$$

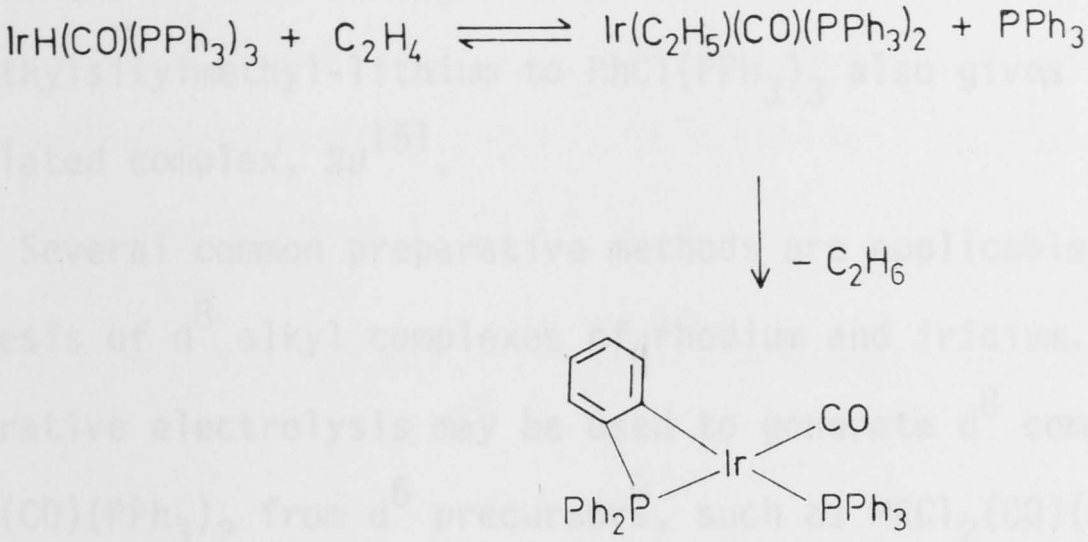
[Ir] = iridium residue

Scheme 25. Thermal Decomposition of $Ir(n\text{-octyl})(CO)(PPh_3)_2$.

Secondary-alkyl rhodium(I) complexes readily udergo β-hydride elimination to give a metal-hydride and olefin (4-1)[148].

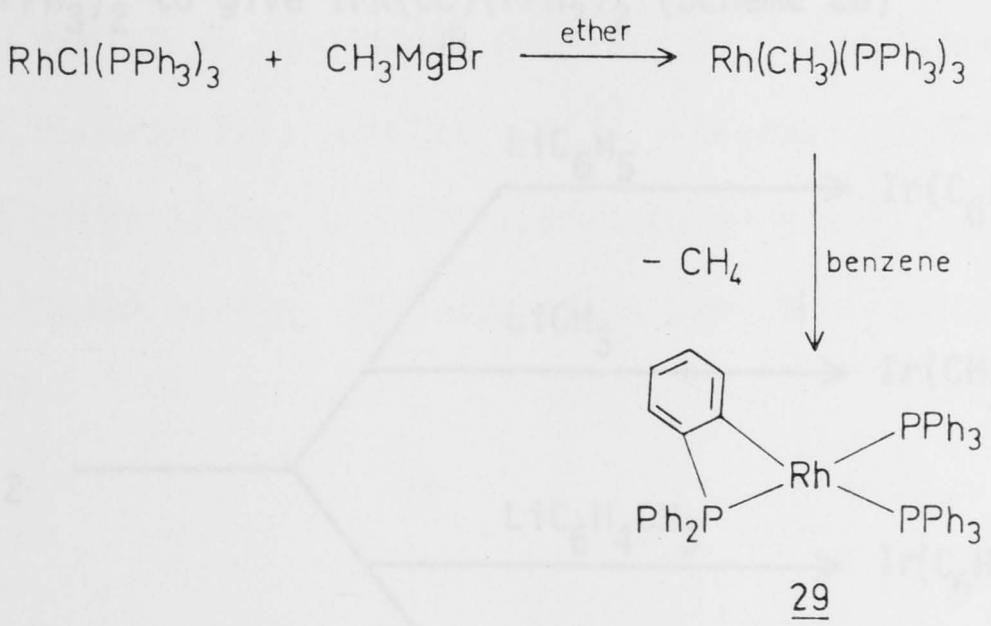
$$RhCl(PPh_3)_3 + [(CH_3)_2CH]_3Al \longrightarrow RhH(PPh_3)_3 + \text{propylene} \qquad (4\text{-}1)$$

Addition of ethylene to $IrH(CO)(PPh_3)_3$ gives an unstable ethyl iridium(I) complex, which can undergo intramolecular rearrangement to give ethane and a cyclometallated iridium(1) complex (Scheme 26)[147].



Scheme 26. Reaction of Ethylene with $IrH(CO)(PPh_3)_3$.

Formation of such cyclometallated complexes is a common pathway for the decomposition of alkyl rhodium(I) and iridium(I) complexes with phenyl-substituted phosphine ligands. Thus, $RhCl(PPh_3)_3$ reacts with methylmagnesium bromide in ether to give $Rh(CH_3)(PPh_3)_3$, which on dissolution in benzene evolves methane to give *29* (Scheme 27)[149].



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Scheme 27. Reaction of Methylmagnesium Bromide with $RhCl(PPh_3)_3$.

Similarly, addition of methyl-lithium to $IrCl(PPh_3)_3$ in ether at -78°C gives $Ir(CH_3)(PPh_3)_3$ which, at room temperature, loses methane to give the iridium analogue of *29*[150]. Addition of neopentyl- or trimethylsilylmethyl-lithium to $RhCl(PPh_3)_3$ also gives the cyclometallated complex, *29*[151].

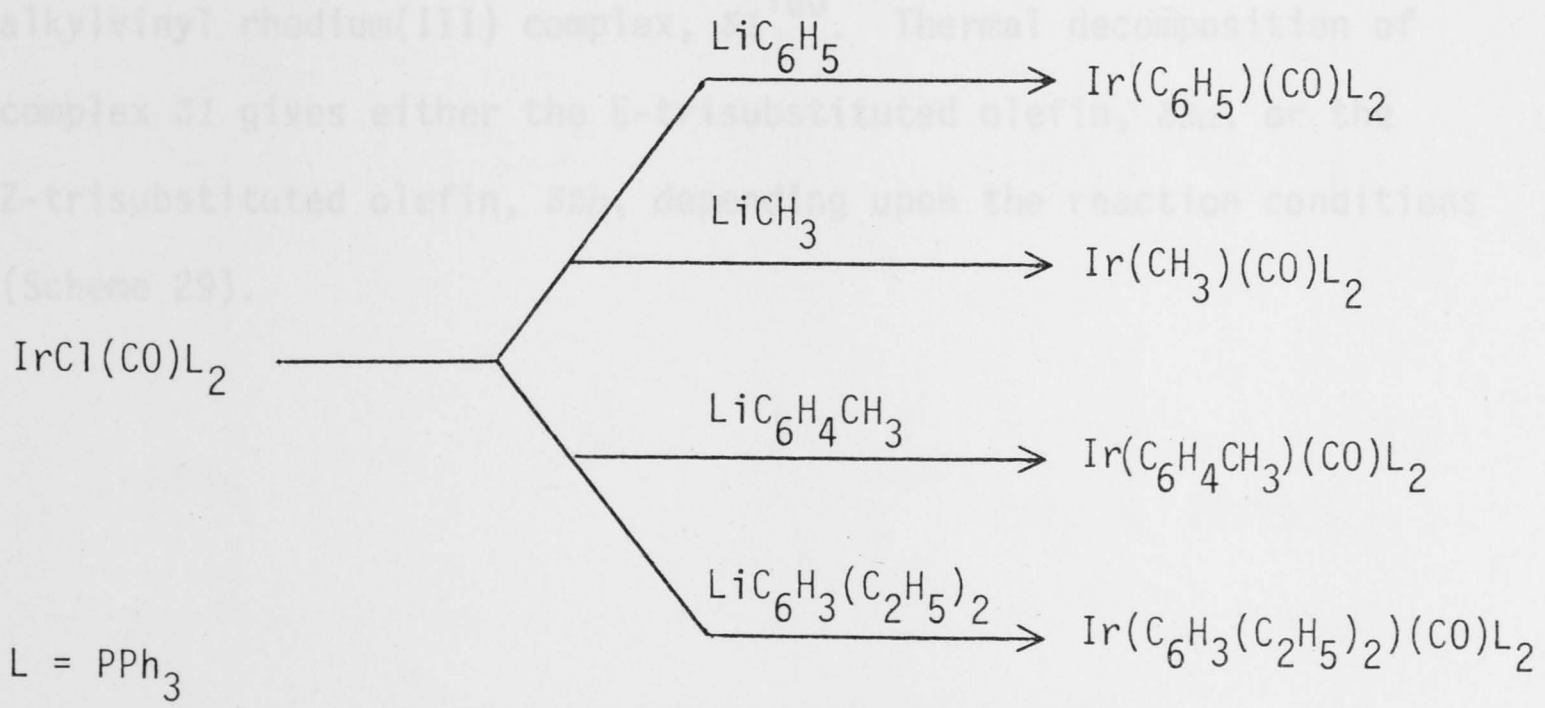
Several common preparative methods are applicable to the synthesis of d^8 alkyl complexes of rhodium and iridium. For example, preparative electrolysis may be used to generate d^8 complexes, such as $MR(CO)(PPh_3)_2$ from d^6 precursors, such as $MRCl_2(CO)(PPh_3)_2$ (4-2)[152]. This procedure is particularly useful for generating low-valent metal alkyls in solution (at low temperature if necessary) without the presence of other species.

$$MRCl_2(CO)(PPh_3)_2 \xrightarrow[\text{reduction}]{\text{electrochemical}} MR(CO)(PPh_3)_2 \qquad (4\text{-}2)$$

M = Rh, R = C_6H_5, p-$CH_3C_6H_4$, p-ClC_6H_4, p-$CH_3OC_6H_4$, CH_3

M = Ir, R = CH_3, C_6H_5

Alternatively, alkyl- or aryl-lithium reagents can react with $IrCl(CO)(PPh_3)_2$ to give $IrR(CO)(PPh_3)_2$ (Scheme 28)[153-156].



Scheme 28. Reaction of Alkyl- or Aryl-Lithium Reagents with $IrCl(CO)(PPh_3)_2$.

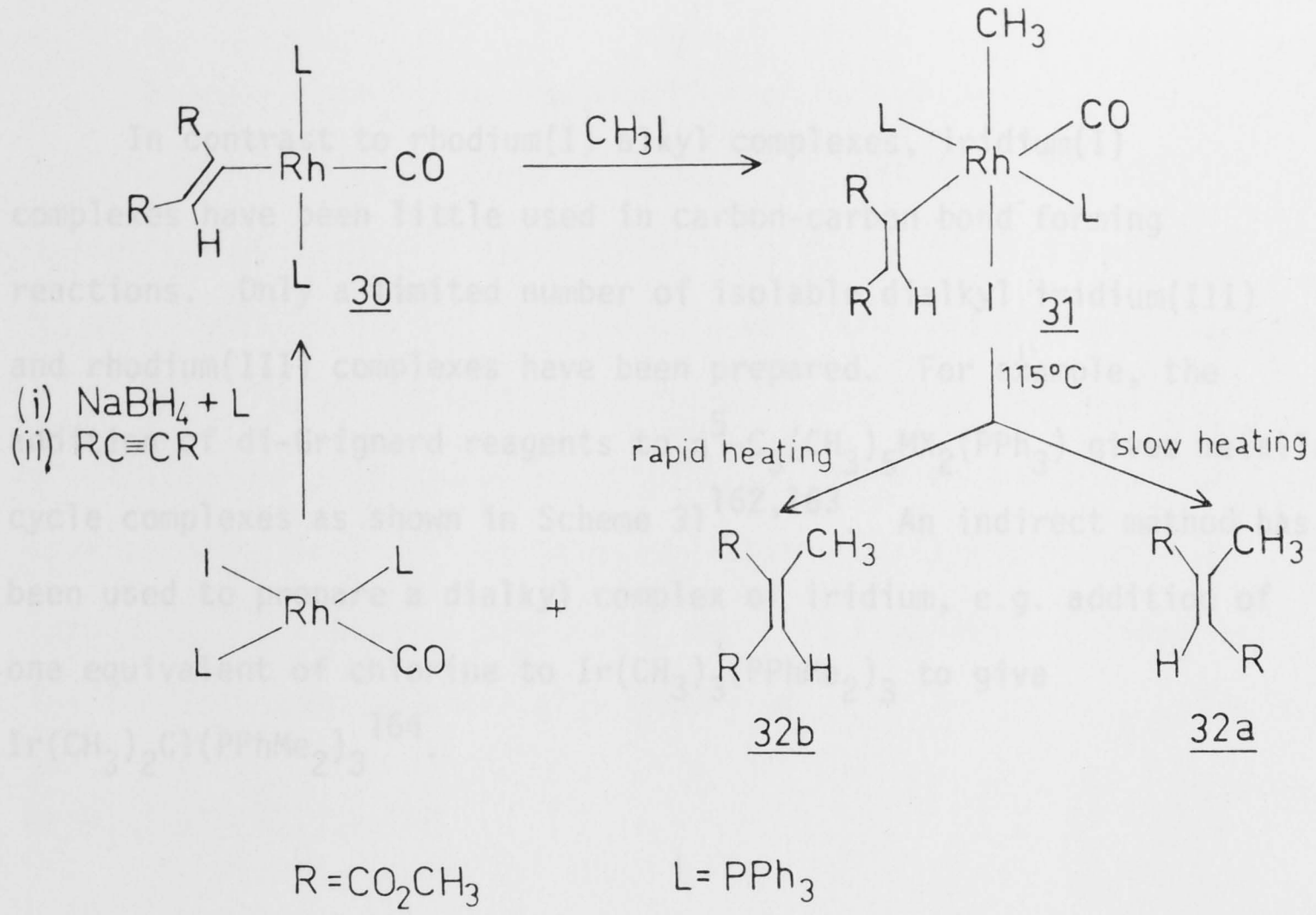
In most of these syntheses the *trans* stereochemistry of the starting material is retained. However, complexes in which the aryl group has ortho substituents generally give mixtures of *cis* and *trans* isomers (e.g. R = 2,6-$(CH_3)_2C_6H_3$ and 2-$(C_2H_5)C_6H_4$). Replacement of the triphenylphosphine ligands with smaller, more basic phosphines gives the *trans* product (4-3)[155].

$$cis\text{-}Ir(2,4,6\text{-}(CH_3)_3C_6H_2)(CO)(PPh_3)_2 \xrightarrow{2L} trans\text{-}Ir(2,4,6\text{-}(CH_3)_3C_6H_2)(CO)L_2 \quad (4\text{-}3)$$

L = PPh_2Me, $PPhMe_2$, PEt_3, PMe_3.

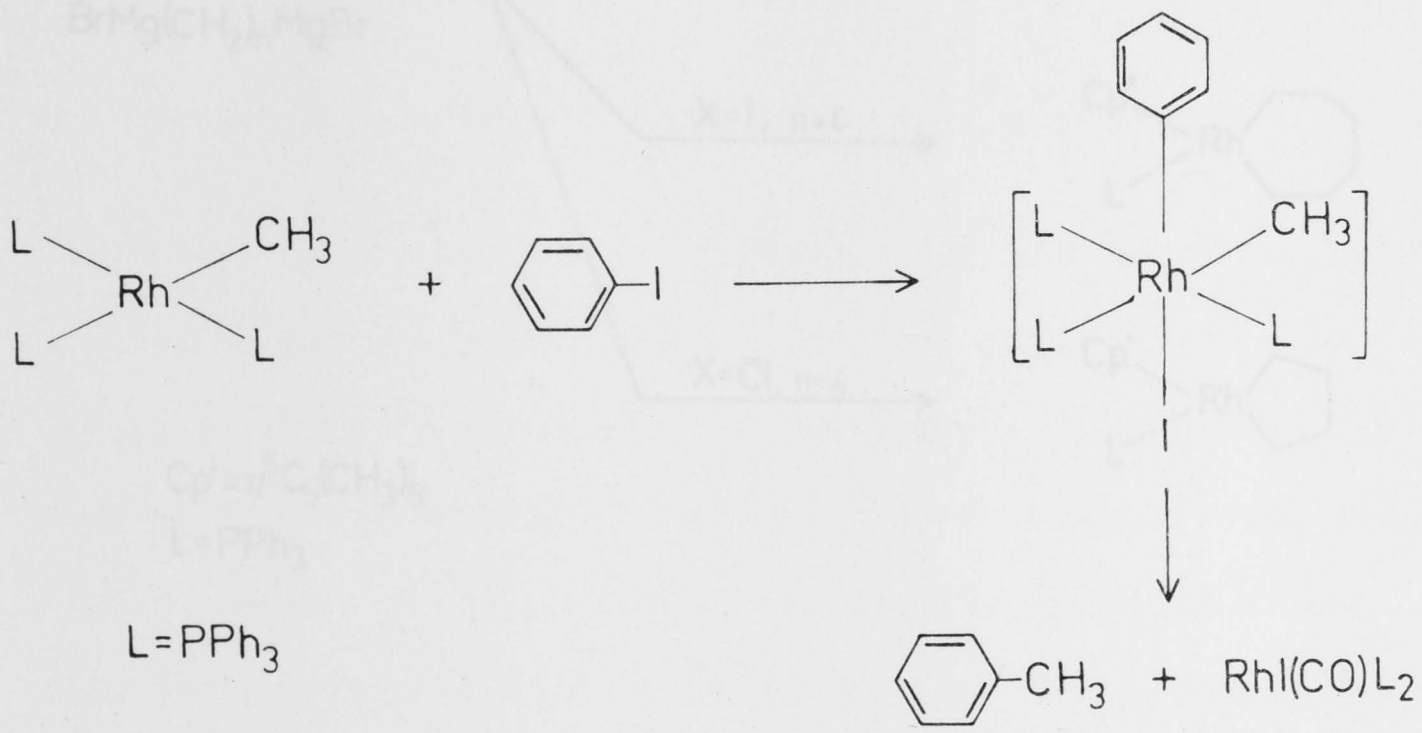
Addition of methyl-lithium to $IrCl(PMe_3)_4$ gives $Ir(CH_3)(PMe_3)_4$ which, in contrast to $Ir(CH_3)(PPh_3)_3$, does not undergo cyclometallation[157]. Similarly, addition of methyl-lithium to $RhCl(PMe_3)_4$ gives $Rh(CH_3)(PMe_3)_3$ which is also stable to cyclometallation[158].

Organorhodium(I) complexes can be used in a number of carbon-carbon bond forming reactions. Thus, addition of acid chlorides to alkylrhodium(I) complexes generated *in situ* by addition of alkyllithium to $RhCl(CO)(PPh_3)_2$ gives unsymmetrical ketones in good yield[159]. Another potentially useful reaction is that between methyl iodide and the vinyl rhodium(I) complex, *30*, to give an isolable alkylvinyl rhodium(III) complex, *31*[160]. Thermal decomposition of complex *31* gives either the E-trisubstituted olefin, *32a*, or the Z-trisubstituted olefin, *32b*, depending upon the reaction conditions (Scheme 29).



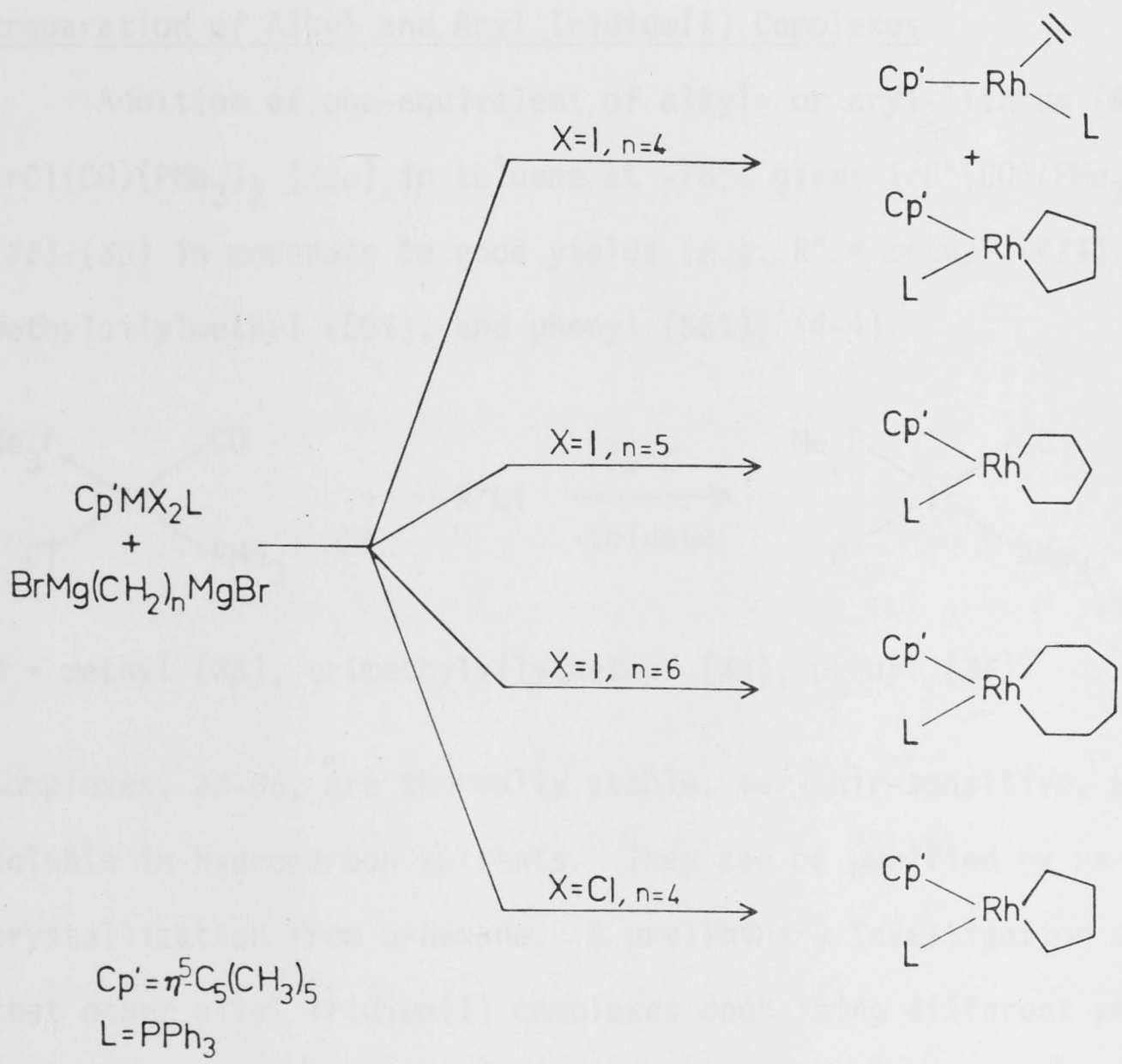
Scheme 29. Preparation and Decomposition of Alkylvinyl-Rhodium(III) Complexes.

Despite the ease with which $Rh(CH_3)(PPh_3)_3$ can undergo cyclometallation it can be used in carbon-carbon bond forming reactions as shown by Scheme 30[161].



Scheme 30. Reaction of Iodobenzene with $Rh(CH_3)(PPh_3)_3$.

In contrast to rhodium(I) alkyl complexes, iridium(I) complexes have been little used in carbon-carbon bond forming reactions. Only a limited number of isolable dialkyl iridium(III) and rhodium(III) complexes have been prepared. For example, the addition of di-Grignard reagents to η^5-$C_5(CH_3)_5MX_2(PPh_3)$ gives metallacycle complexes as shown in Scheme 31[162,163]. An indirect method has been used to prepare a dialkyl complex of iridium, e.g. addition of one equivalent of chlorine to $Ir(CH_3)_3(PPhMe_2)_3$ to give $Ir(CH_3)_2Cl(PPhMe_2)_3$[164].



Scheme 31. Reaction of Di-Grignard Reagents with η^5-$C_5(CH_3)_5MX_2(PPh_3)$.

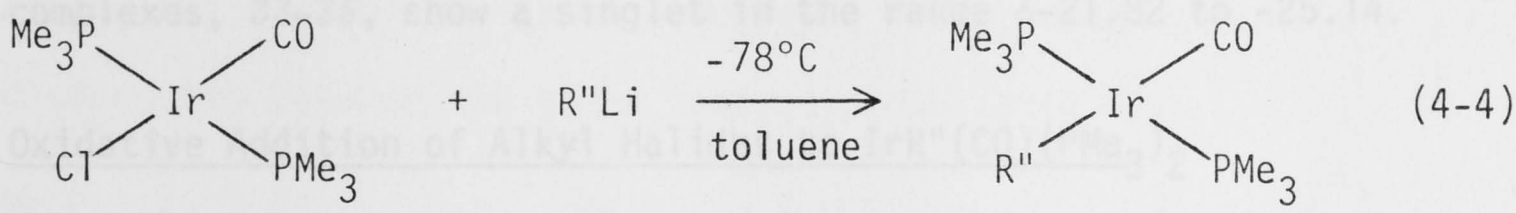
However, apart from the addition of methyl iodide to $Ir(C_6F_5)(CO)(PPh_3)_2$ to give $Ir(CH_3)(C_6F_5)I(CO)(PPh_3)_2$[165], the oxidative addition of alkyl halides to alkyl iridium(I) complexes to give isolable dialkyl iridium(III) complexes has not been reported.

This Chapter explores this prospect and describes the preparation of some new alkyl iridium(I) complexes and their reactions with various alkyl halides to give isolable dialkyl iridium(III) complexes. The general properties and some reactions of these iridium(III) complexes are also described.

Results and Discussion.

Preparation of Alkyl and Aryl Iridium(I) Complexes

Addition of one-equivalent of alkyl- or aryl-lithium (R"Li) to $IrCl(CO)(PMe_3)_2$ (*11c*) in toluene at -78°C gives $IrR"(CO)(PMe_3)_2$ (*33*)-(*35*) in moderate to good yields (e.g. R" = methyl (47%), trimethylsilylmethyl (58%), and phenyl (86%)) (4-4).



(4-4)

R = methyl (*33*), trimethylsilylmethyl (*34*), phenyl (*35*).

Complexes, *33*-*35*, are thermally stable, very air-sensitive, and are soluble in hydrocarbon solvents. They can be purified by recrystallization from *n*-hexane. A preliminary investigation showed that other alkyl iridium(I) complexes containing different phosphine ligands could also be prepared. For example, addition of trimethylsilylmethyl-lithium to $IrCl(CO)L_2$ (L = PPh_3, $PPhMe_2$) gives the expected product, $Ir(CH_2Si(CH_3)_3)(CO)L_2$.

For the preparation of the methyl complex, *33*, only one-equivalent of methyl-lithium should be added to *11c*. Reaction of two-equivalents of methyl-lithium with *11c* gives none of the desired product, *33*, and a brown, hexane-insoluble residue is obtained after evaporation of solvent. Dissolution of this residue in benzene causes rapid decomposition. The residue probably contains an anionic iridium(I) complex which might be stabilized by the addition of a Lewis base. However, this has not been investigated.

Infra-red spectra of complexes, *33-35*, show a ν(CO) band in the range 1935-1940 cm^{-1}, which is about 20 cm^{-1} lower than that observed for *11c*, suggesting that the electron density on the metal atom of these organoiridium(I) complexes is higher than on the metal atom of *11c*[154]. The ^{1}H nmr spectra of *33-35* show a triplet ($^{2}J_{PH} + {}^{4}J_{PH}$ = 8 Hz) for the PCH_3 ligand resonance. For complex, *33*, the methyl protons appear as a triplet (δ0.50, $^{3}J_{PH}$ = 10 Hz) as do the methylene protons of complex *34* (δ0.44, $^{3}J_{PH}$ = 14 Hz). The $^{31}P\{^{1}H\}$ nmr spectra of complexes, *33-35*, show a singlet in the range δ-21.82 to -25.14.

Oxidative Addition of Alkyl Halides to $IrR''(CO)(PMe_3)_2$

Alkyl halides react with complexes *33-35*, to give dialkyl iridium(III) products, $IrRR''X(CO)(PMe_3)_2$, in good yield. To obtain reproducible results, the organoiridium(I) complexes must be re-crystallized twice from hexane, and the alkyl halides distilled once under nitrogen and then vacuum distilled from phosphorus pentoxide at ambient temperature. If this last procedure is not repeated before each reaction substantial quanitites of side products, possibly a mixture of $IrR''X_2(CO)(PMe_3)_2$ and $IrX_3(CO)(PMe_3)_2$, are obtained.

(i) $Ir(CH_3)(CO)(PMe_3)_2$

The methyl complex, *33*, reacts with alkyl iodides or alkyl

bromides, but not alkyl chlorides, at ambient temperature to give dialkyl iridium(III) complexes in 60-70% yield (4-5). These complexes are air-stable as solids and in solution.

$$Ir(CH_3)(CO)(PMe_3)_2 \quad + \quad RX \xrightarrow[\text{benzene}]{25°C} Ir(CH_3)RX(CO)(PMe_3)_2 \qquad (4\text{-}5)$$

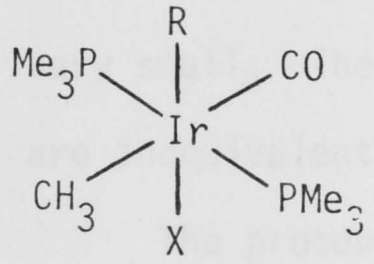
36a-j

X = Br; R = (a) propyl, (b) *iso*-propyl, (c) butyl, (d) *sec*-butyl, (e) pentyl, (f) 2-pentyl.

X = I; R = (g) propyl, (h) *iso*-propyl, (i) butyl, (j) *sec*-butyl.

Analytical and spectroscopic data for complexes, *36a-j*, appear in Tables 31-33.

The PCH_3 ligand resonance for complexes, *36a-c* and *36e-i* appears as a triplet ($^2J_{PH} + {}^4J_{PH}$ = 8 Hz) in the ^1H nmr (Table 33). The $^{31}P\{^1H\}$nmr spectra (Table 32) show a singlet resonance for each of these complexes. These data are consistent with *trans* chemically-equivalent phosphine ligands. However, the nmr data do not distinguish between the three isomers shown in (4-6).



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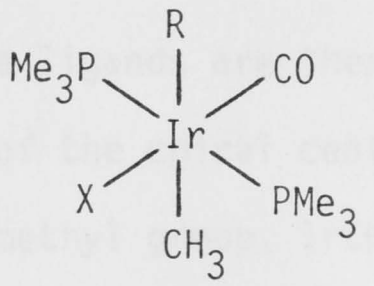
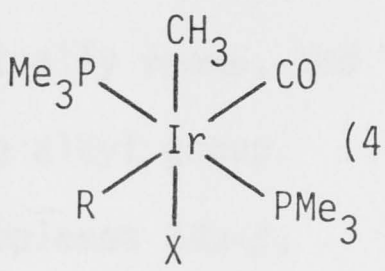


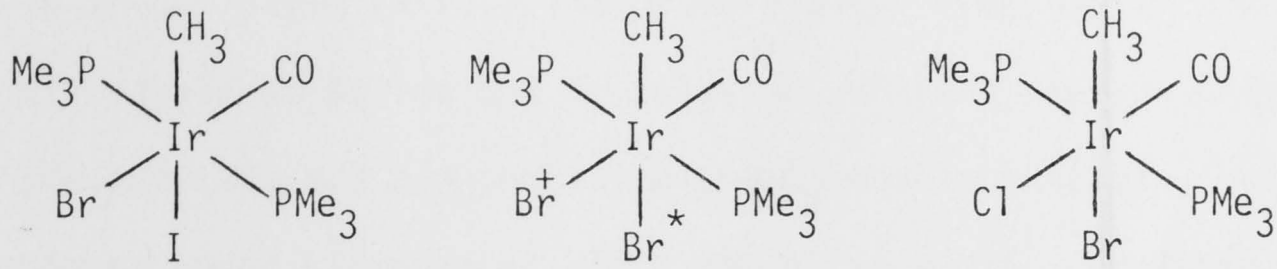
36'



36" (4-6)

Far-infrared data for some model compounds, in which the ν(IrBr) can be readily identified, show that for a bromide *trans* to a carbonyl, ν(IrBr) occurs ca. 192 cm^{-1}, whereas for a bromide *trans* to an alkyl, ν(IrBr) occurs ca. 168 cm^{-1} (Figure 22). This trend is similar to that observed for ν(IrCl)[49]. For complexes, *36a-f*, the far-infrared spectra show ν(IrBr) in the range 154-167 cm^{-1}, which is consistent

with bromide *trans* to an alkyl. These data exclude isomer *36'*, but cannot distinguished between isomers, *36* and *36"*. However, alkyl halides generally react with iridium(I) complexes in a *trans* manner[19] so that isomer, *36*, is more likely than *36"*.



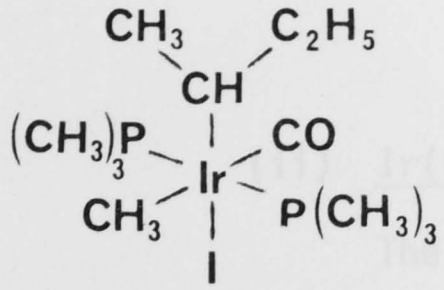
ν(IrBr) = 192 cm^{-1} $\nu(IrBr)^{*}$ = 168 cm^{-1} ν(IrBr) = 168 cm^{-1}

$\nu(IrBr)^{+}$ = 192 cm^{-1} ν(IrCl) = 300 cm^{-1}

Figure 22. Position of ν(IrBr) in Alkyl Iridium(III) Bromides.

In the ^{1}H nmr spectra of the *sec*-butyl complexes, *36d* and *36j* (Table 33), the PCH_3 resonance appears as a five line multiplet which collapses to two singlets on ^{31}P decoupling (Figure 23). This is consistent with chemically-inequivalent phosphorus nuclei. The $^{31}P\{^{1}H\}$ nmr spectrum of each complex shows only a singlet suggesting that the chemical shift difference between the phosphorus nuclei is very small. The phosphine ligands are therefore mutually *trans*, and are inequivalent because of the chiral centre of the alkyl group.

The protons of the methyl group, $IrCH_3$, in complexes *36a-j*, appear as a triplet ($^{3}J_{PH}$ = 8-9 Hz) in the ^{1}H nmr. The chemical shift of this methyl group is sensitive to the nature of the other alkyl group (R). Thus, for the *sec*-alkyl complexes, *36b*, *36d*, and *36f*, the $IrCH_3$ resonance occurs at δ0.60, whereas for the *n*-alkyl complexes, *36a*, *36c*, and *36e*, it occurs at δ0.40. Furthermore, the ^{31}P chemical shifts of the *sec*-alkyl complexes are ca. 1 ppm to higher field than those of the *n*-alkyl complexes.



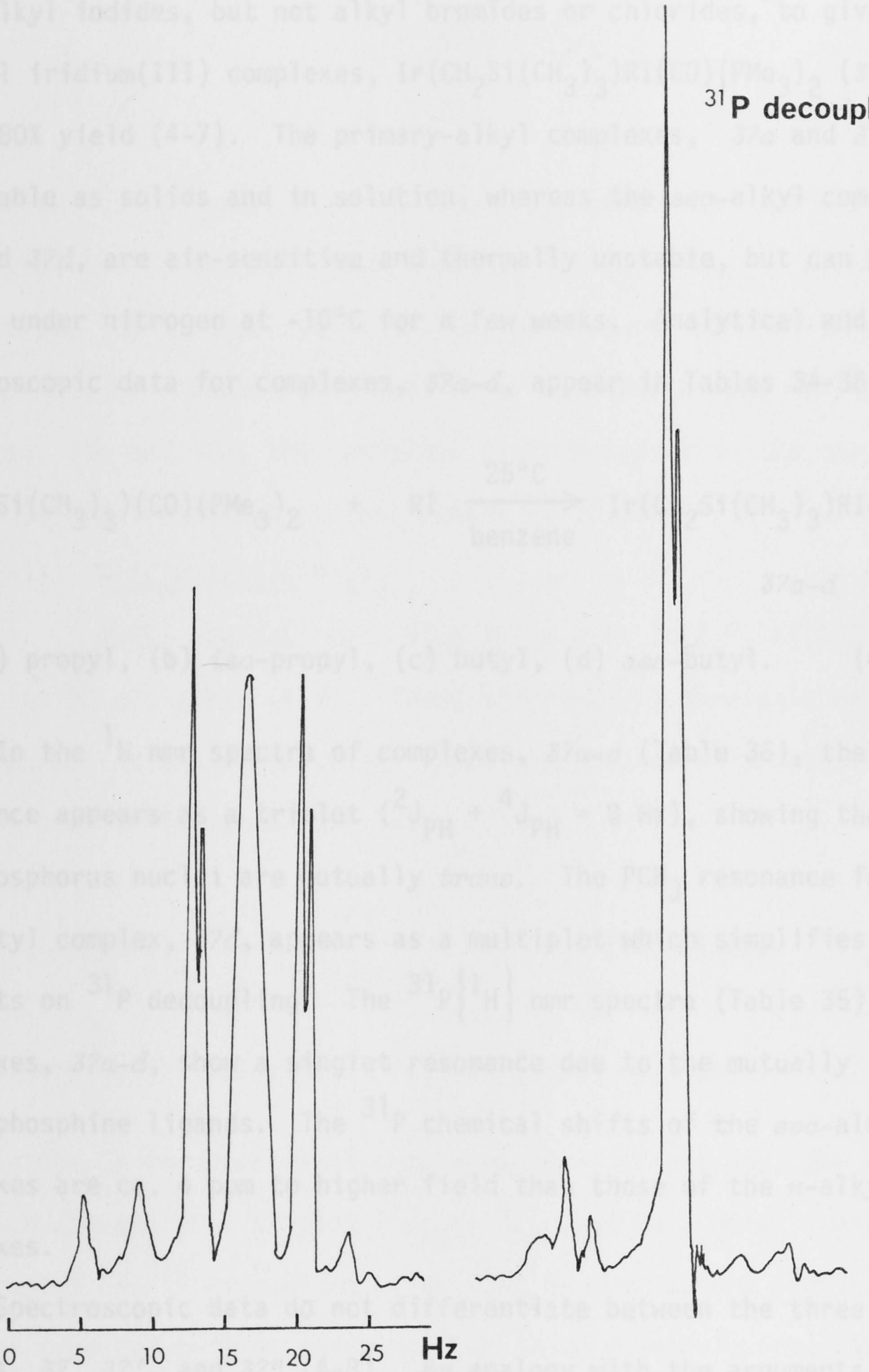


Figure 23. PCH_3 Resonance in ^1H nmr Spectrum (C_6D_6) of $Ir(CH(CH_3)C_2H_5)(CH_3)I(CO)(PMe_3)_2$.

(ii) $\underline{Ir(CH_2Si(CH_3)_3)(CO)(PMe_3)_2}$

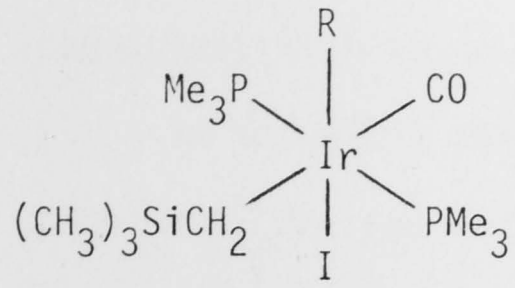
The trimethylsilylmethyl iridium(I) complex, *34*, reacts with alkyl iodides, but not alkyl bromides or chlorides, to give dialkyl iridium(III) complexes, $Ir(CH_2Si(CH_3)_3)RI(CO)(PMe_3)_2$ (*37a-d*), in 70-80% yield (4-7). The primary-alkyl complexes, *37a* and *37c*, are air stable as solids and in solution, whereas the *sec*-alkyl complexes, *37b* and *37d*, are air-sensitive and thermally unstable, but can be stored under nitrogen at -10°C for a few weeks. Analytical and spectroscopic data for complexes, *37a-d*, appear in Tables 34-36.

$$Ir(CH_2Si(CH_3)_3)(CO)(PMe_3)_2 \quad + \quad RI \xrightarrow[\text{benzene}]{25°C} \underset{37a\text{-}d}{Ir(CH_2Si(CH_3)_3)RI(CO)(PMe_3)_2}$$

R = (a) propyl, (b) *iso*-propyl, (c) butyl, (d) *sec*-butyl. (4-7)

In the ^1H nmr spectra of complexes, *37a-c* (Table 36), the PCH_3 resonance appears as a triplet ($^2J_{PH} + {}^4J_{PH}$ = 8 Hz), showing that the phosphorus nuclei are mutually *trans*. The PCH_3 resonance for the *sec*-butyl complex, *37d*, appears as a multiplet which simplifies to two singlets on ^{31}P decoupling. The $^{31}P\{^1H\}$ nmr spectra (Table 35) of complexes, *37a-d*, show a singlet resonance due to the mutually *trans* phosphine ligands. The ^{31}P chemical shifts of the *sec*-alkyl complexes are ca. 4 ppm to higher field than those of the *n*-alkyl complexes.

Spectroscopic data do not differentiate between the three isomers, *37*, *37'*, and *37"* (4-8). By analogy with the arguments presented in (i) above concerning the stereochemistry of complexes *36a-j*, it is likely that the trimethylsilylmethyl complexes have the stereochemistry depicted in *37*.



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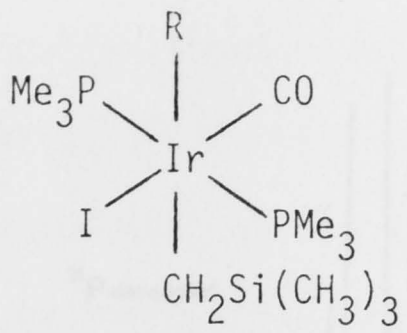
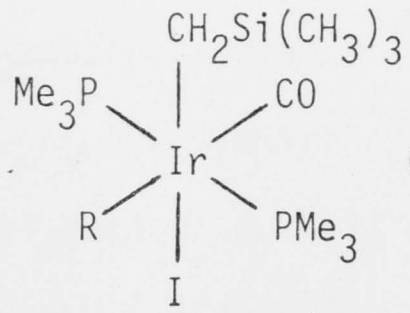


37'



37" (4-8)

In the ^{1}H nmr spectra of the *sec*-alkyl complexes, *37b* and *37d*, the triplet due to the methylene protons, ($IrC\underline{H}_2Si(CH_3)_3$), appears at δ0.06 and the singlet due to the methyl protons, ($IrCH_2Si(C\underline{H}_3)_3$) appears at δ0.50. However, in the ^{1}H nmr spectrum of the *n*-alkyl-complexes, *37a* and *37c*, the methylene protons appear in the range δ0.33-0.39 and the methyl protons appear at δ0.33.

(iii) $\underline{Ir(C_6H_5)(CO)(PMe_3)_2}$

Alkyl iodides react with *35* to give $Ir(C_6H_5)RI(CO)(PMe_3)_2$ (*38a-d*) in 70-80% yield (4-9). These iridium(III) complexes are air-stable as solids and in solution. Spectroscopic data for complexes, *38a-d*, appear in Tables 37 and 38.

$$Ir(C_6H_5)(CO)(PMe_3)_2 + RI \xrightarrow[\text{benzene}]{25^\circ C} Ir(C_6H_5)RI(CO)(PMe_3)_2 \qquad (4\text{-}9)$$

R = (a) propyl, (b) *iso*-propyl, (c) butyl, (d) *sec*-butyl.

In the ^{1}H nmr spectra of complexes *38a-c* (Table 38), the PCH_3 resonance appears as a triplet ($^{2}J_{PH} + {}^{4}J_{PH}$ = 8 Hz), which simplifies to a singlet on ^{31}P decoupling. The $^{31}P\{^{1}H\}$ nmr spectra (Table 37) show the expected singlet resonance for *trans* chemically-equivalent phosphorus nuclei. However, in the ^{1}H nmr spectrum of *38d*, the PCH_3 resonance appears as a seven line multiplet, which simplifies to two singlets on ^{31}P decoupling (Figure 24). The $^{31}P\{^{1}H\}$ nmr spectrum of *38d* appears as an AB quartet ($^{2}J_{PP}$ = 378 Hz). These date are

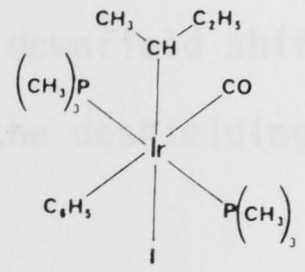


Figure 24. ^{1}H NMR Spectra of $Ir(CH(CH_3)C_2H_5)(C_6H_5)I(CO)(PMe_3)_2$.

consistent with *trans* chemically-inequivalent phosphorus nuclei.

In the alkyl chain, Ir-C(1)-C(2)-C(3)-C(4), of the *n*-alkyl complexes, *38a* and *38c*, the chemical shifts of the protons on C(1) and C(2) are about 0.3-0.6 ppm to lower field than expected (Table 39). The downfield shift of these protons suggests that they are situated in the deshielding region of the phenyl ring.

TABLE 39

Chemical Shift Differences, $\delta_{38} - \delta_{36}$ and $\delta_{38} - \delta_{37}$, Between Corresponding Protons in the Alkyl Chains, Ir-C(1)-C(2)-C(3), of *36*, *37* and *38*.

	$\delta_{38}-\delta_{36}$			$\delta_{38}-\delta_{37}$		
R	C(1)	C(2)	C(3)	C(1)	C(2)	C(3)
$CH_2CH_2CH_3$	0.3	0.6	0.1	0.33	0.6	0.1
$CH_2CH_2CH_2CH_3$	≈0.3-0.6			≈0.3-0.6		

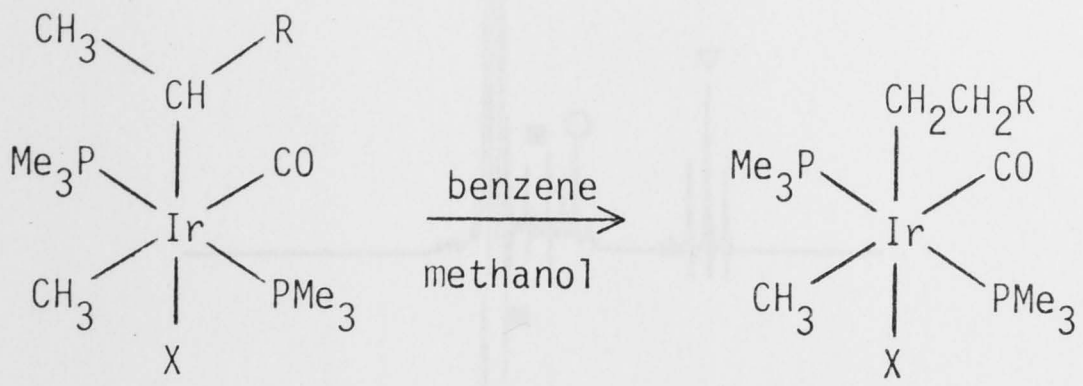
Isomerization of *sec*-Alkyl Complexes

The dialkyl iridium(III) complexes appear to be indefinitely stable in benzene solution at 25°C under a nitrogen atmosphere. However, addition of methanol to a benzene solution of the *sec*-alkyl complexes results in an alkyl group rearrangement similar to that described in Chapter Three for monoalkyl iridium(III) complexes.

(i) $Ir(CH_3)RX(CO)(PMe_3)_2$

The *sec*-alkyl complexes, *36b*, *36d*, *36h*, and *36j* undergo rearrangement in benzene/methanol at room temperature to give the isomeric *n*-alkyl complexes, *36a*, *36c*, *36g*, and *36i*, in quantitative yield (4-10). The rate of isomerization increases as the

concentration of methanol increases, e.g. for the *iso*-propyl complexes, *36b* and *36h*, the times required for complete isomerization are reduced from 10 h in benzene/methanol (6:1 volume ratio) to 1 h in benzene/methanol (1:1 volume ratio) at 25°C.

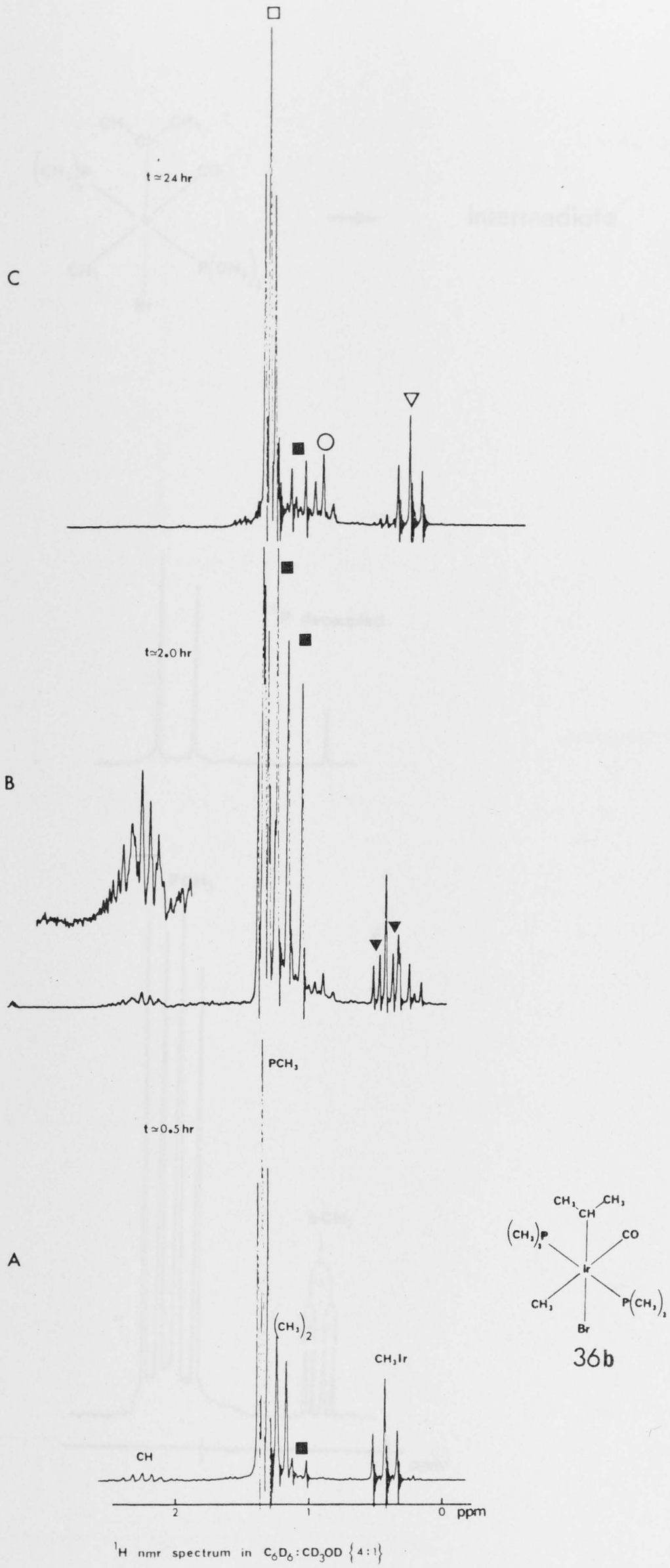


(4-10)

X = Br, I; R = CH_3, C_2H_5

The ^1H nmr spectra of the *iso*-propyl complex, *36b*, in C_6D_6/CD_3OD (4:1 volume ratio) are reproduced in Figure 25. Spectrum A (0.5 h after dissolution) shows resonances typical of the *iso*-propyl complex, *36b*. Spectrum B (after 2.0 h at 29°C) shows many overlapping resonances, but with the aid of ^{31}P decoupling these can be satisfactorily assigned to the *iso*-propyl complex, *36b*, the *n*-propyl complex, *36a*, and to an intermediate, present only during the isomerization reaction. Figure 26 reproduces the ^1H nmr spectrum of the intermediate (this spectrum is obtained by subtracting the resonances due to *36a* and *36b* from spectrum B) and shows two doublets (δ1.12, $^2J_{PH} + {}^4J_{PH}$ = 10 Hz; 1.31, $^2J_{PH} + {}^4J_{PH}$ = 9 Hz) due to the PCH_3 resonances of *cis* inequivalent-phosphine ligands and a doublet of doublets (δ0.42, $^3J_{PH}$ = 5, 10 Hz) due to the $IrCH_3$ resonance. Spectrum C (Figure 25, after 24 h) shows only resonances due to the *n*-propyl complex, *36a*, the final product of the isomerization.

The $^{31}P\{^1H\}$ nmr spectra of the *iso*-propyl complex, *36h*, in benzene/methanol (4:1 volume ratio) are shown in Figure 27. In addition to the singlet resonances of the *iso*-propyl and *n*-propyl complexes, *36h* and *36g*, respectively, two doublets (δ-37.4 and -68.1, $^2J_{PP}$ =

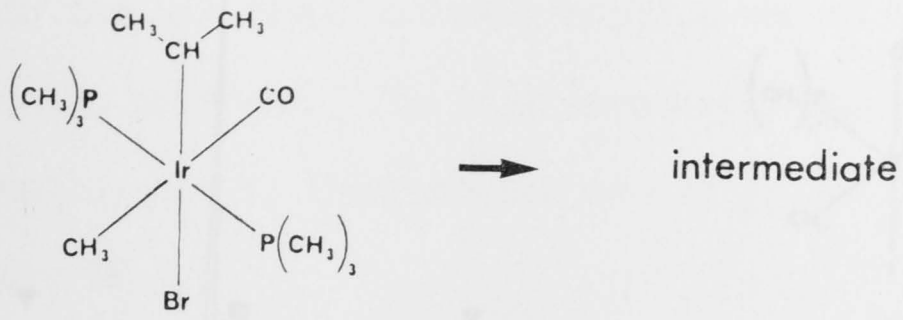


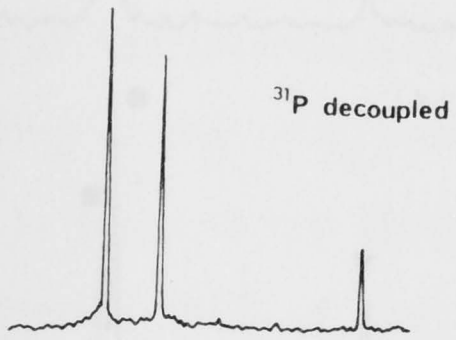
36b

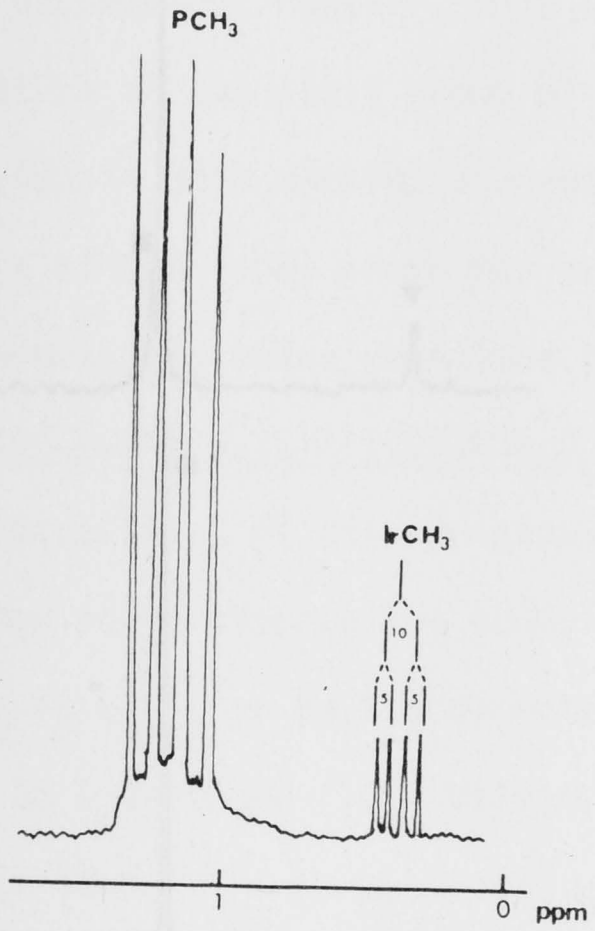
Figure 25. ^1H NMR Spectra of $Ir(CH(CH_3)_2)(CH_3)Br(CO)(PMe_3)_2$ in Benzene/Methanol.

■ PCH_3 of intermediate; ▼ $IrC\underline{H}_3$ of intermediate;

□ PCH_3 of *36a*; ○ $IrCH_2C\underline{H}_2C\underline{H}_3$ of *36a*; ▽ $IrCH_3$ of *36a*.

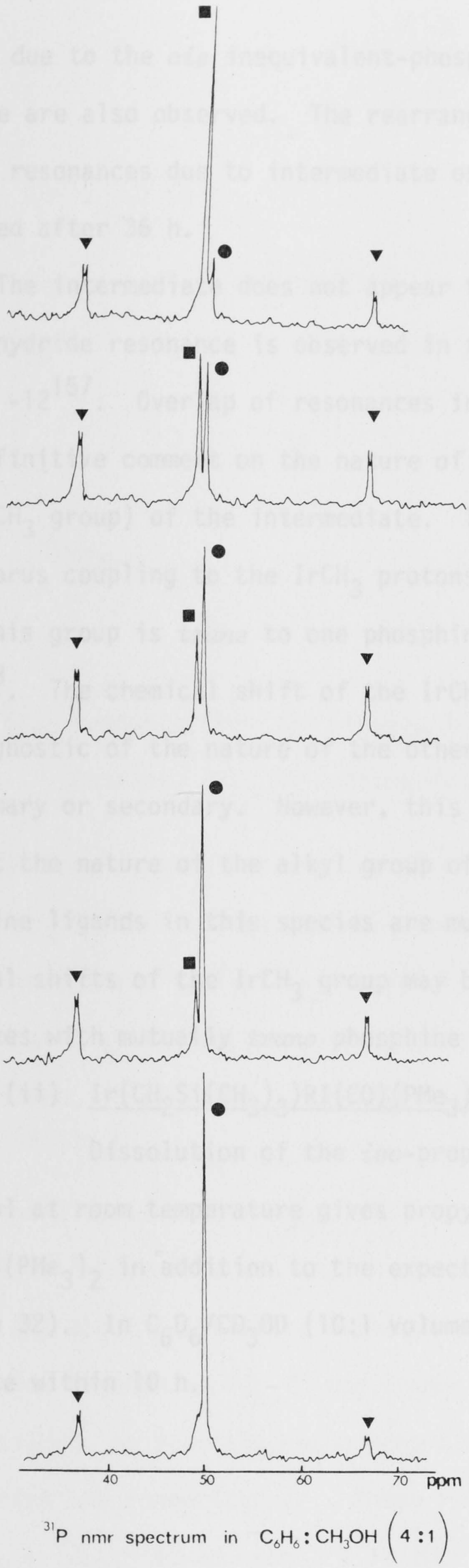






^1H nmr spectrum in $CD_2Cl_2 : CD_3OD (4:1)$

Figure 26. ^1H NMR Spectra of Intermediate present during Isomerization of $Ir(CH(CH_3)_2)(CH_3)Br(CO)(PMe_3)_2$ in Benzene/Methanol.



^{31}P nmr spectrum in $C_6H_6 : CH_3OH$ (4 : 1)

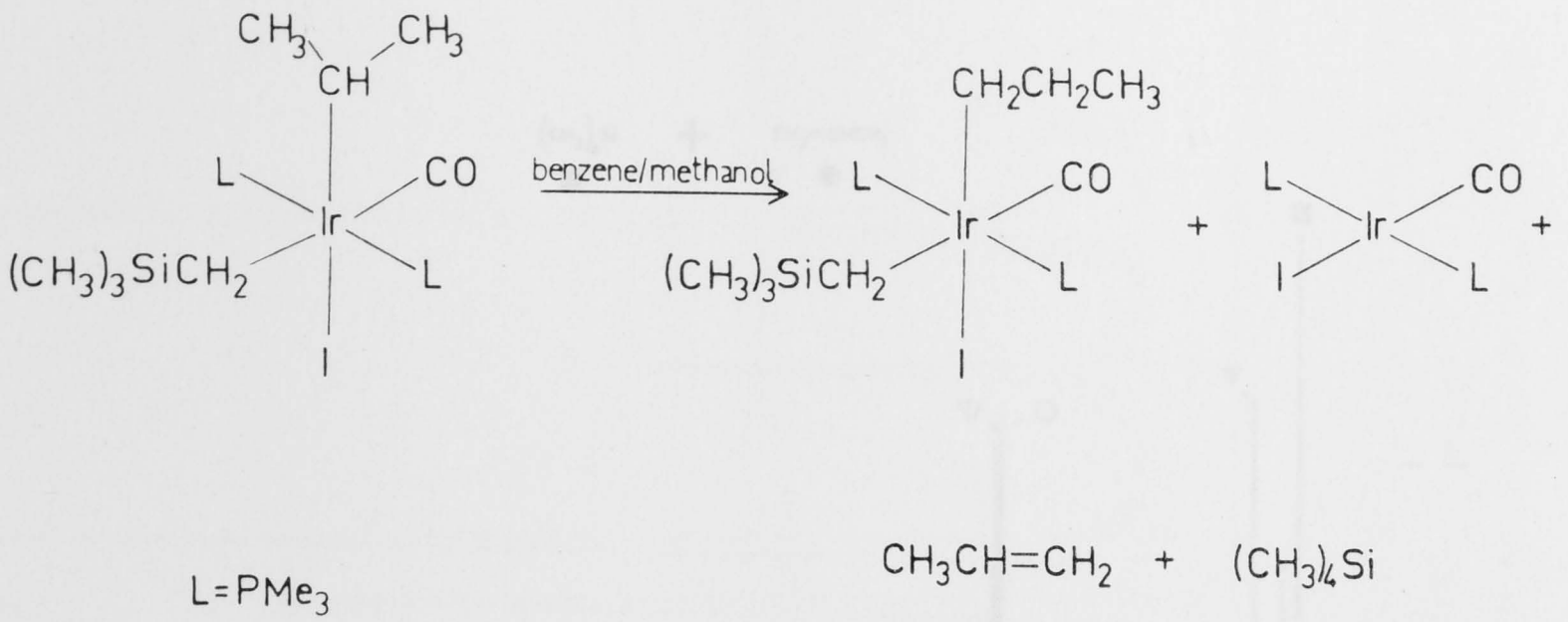
Figure 27. $^{31}P\{^{1}H\}$ NMR Spectra of $Ir(CH(CH_3)_2)(CH_3)I(CO)(PMe_3)_2$ in Benzene/Methanol.

10 Hz) due to the *cis* inequivalent-phosphine nuclei of the intermediate are also observed. The rearrangement proceeds to completion and no resonances due to intermediate or *iso*-propyl complex are observed after 36 h.

The intermediate does not appear to be an olefin-hydride complex as no hydride resonance is observed in the ^1H nmr in the region δ-9 to -12[157]. Overlap of resonances in the ^1H nmr spectra preclude any definitive comment on the nature of the alkyl group (apart from the $IrCH_3$ group) of the intermediate. The magnitudes of the phosphorus coupling to the $IrCH_3$ protons ($^3J_{PH}$ = 5, 10 Hz) suggests that this group is *trans* to one phosphine ligand and *cis* to the other[78]. The chemical shift of the $IrCH_3$ group in complexes, *36a-j*, is diagnostic of the nature of the other alkyl group, i.e. whether it is primary or secondary. However, this criterion cannot be used to predict the nature of the alkyl group of the intermediate since the phosphine ligands in this species are mutually *cis*, and the relative chemical shifts of the $IrCH_3$ group may be different from those in complexes with mutually *trans* phosphine ligands.

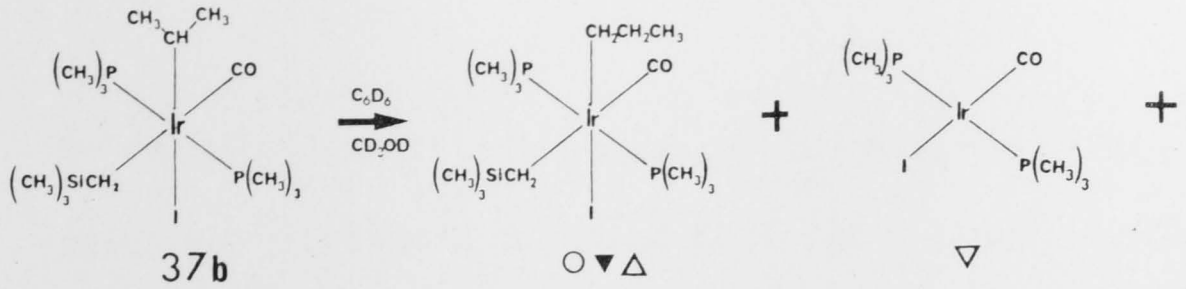
(ii) $\underline{Ir(CH_2Si(CH_3)_3)RI(CO)(PMe_3)_2}$

Dissolution of the *iso*-propyl complex, *37b*, in benzene/methanol at room temperature gives propylene, tetramethylsilane and $IrI(CO)(PMe_3)_2$ in addition to the expected *n*-propyl complex, *37a* (Scheme 32). In C_6D_6/CD_3OD (10:1 volume ratio) the reaction is complete within 10 h.



Scheme 32. Products from the Dissolution of the *iso*-Propyl Complex, *37b*, in Benzene/Methanol.

Figure 28 shows the ^{1}H nmr spectra of the *iso*-propyl complex, *37b*, in C_6D_6/CD_3OD (10:1 volume ratio). Spectrum A (0.5 h after dissolution) shows typical *iso*-propyl resonances, whereas Spectrum B (10 h after dissolution) shows resonances due to propylene, tetramethylsilane, $IrI(CO)(PMe_3)_2$ and the *n*-propyl complex, *37a*. After 24 h the $^{31}P\{^{1}H\}$ nmr spectrum of the solution shows only two singlets attributable to $IrI(CO)(PMe_3)_2$ (38%) and to the *n*-propyl complex, *37a* (62%). Figure 29 shows the ^{1}H nmr spectrum of the *iso*-propyl complex *37b* about 3.0 h after dissolution in C_6D_6/CD_3OD. The many overlapping resonances due to the products shown in Scheme 32 have been assigned, as have the resonances due to an intermediate present only during the isomerization. These resonances occur at δ1.10 (d, $^{2}J_{PH} + {}^{4}J_{PH}$ = 10 Hz, PCH_3) 1.32 (d, $^{2}J_{PH} + {}^{4}J_{PH}$ = 8 Hz, PCH_3) and 0.44 (s, $IrCH_2Si(CH_3)_3$). On the basis of ^{1}H nmr evidence the intermediate does not appear to be an olefin-hydride complex. Unfortunately, the remaining resonances of the intermediate cannot



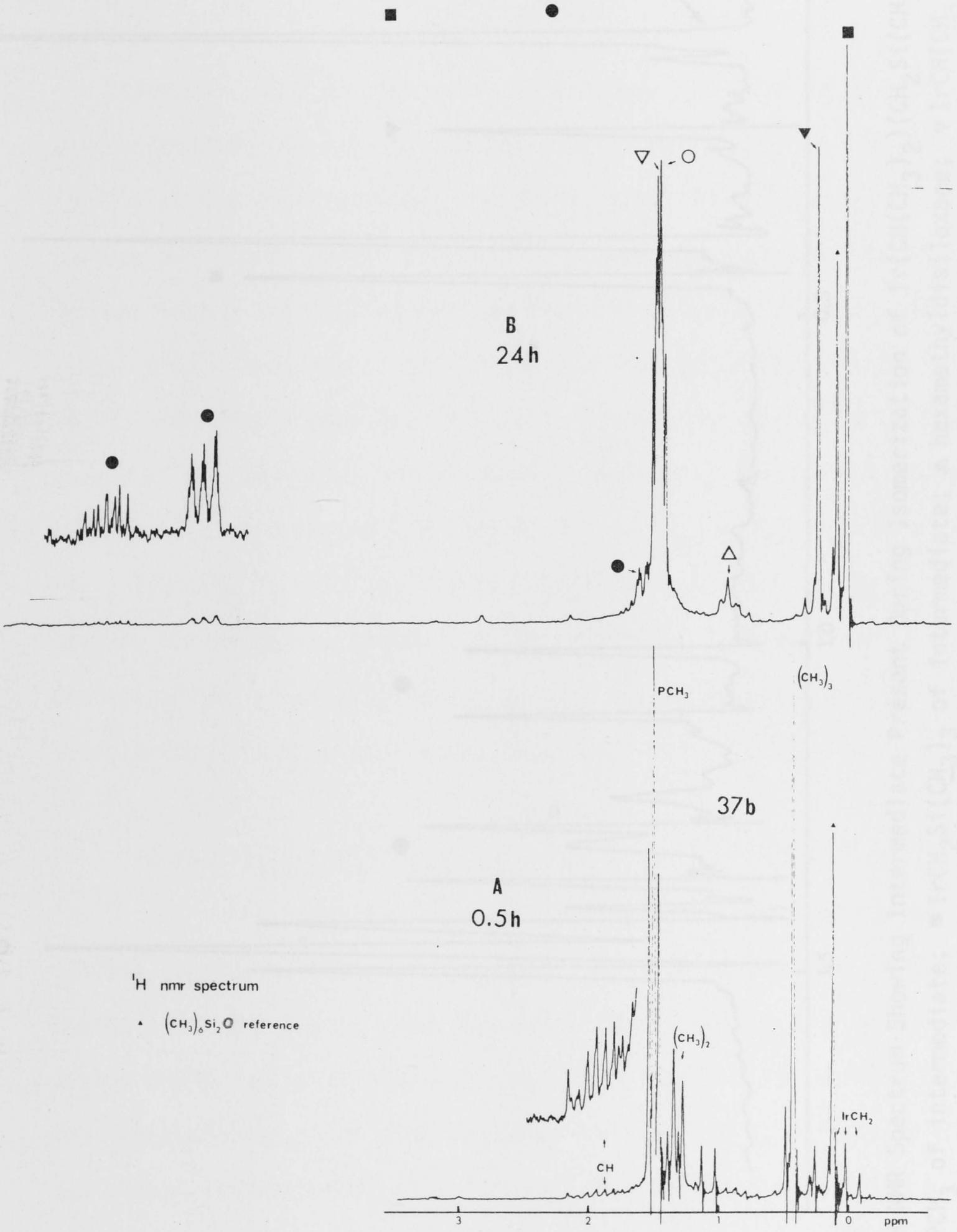


Figure 28. ^1H NMR Spectra of $Ir(CH(CH_3)_2)(CH_2Si(CH_3)_2)I(CO)(PMe_3)_2$ in Benzene/Methanol.
○ PCH_3 of *37a*; △ $IrCH_2\underline{CH}_2\underline{CH}_3$ of *37a*; ▼ $IrCH_2Si(\underline{CH}_3)_3$ of *37a*.

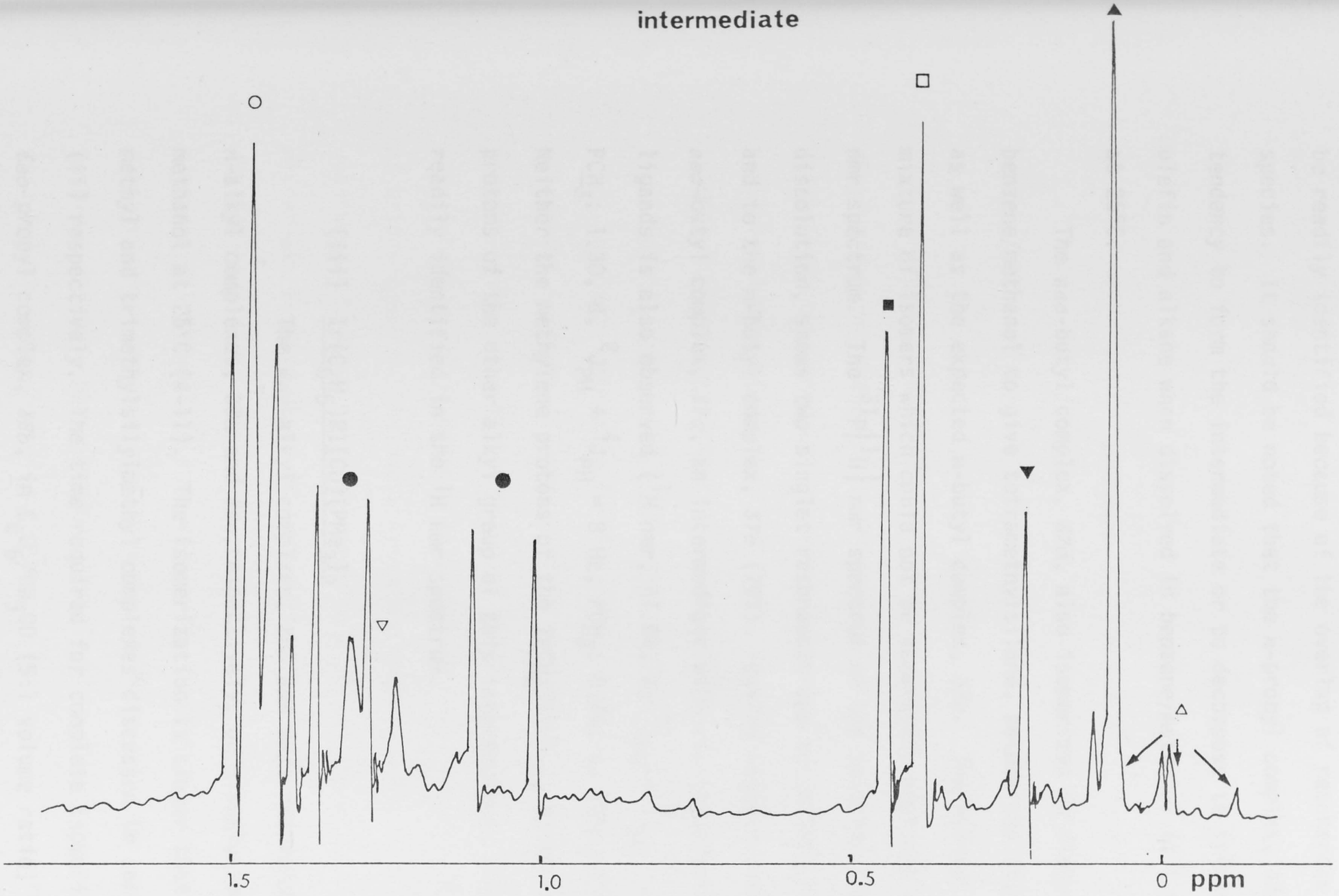


Figure 29. ^{1}H NMR Spectrum Showing Intermediate Present During Isomerization of $Ir(CH(CH_3)_2)(CH_2Si(CH_3)_3)I(CO)(PMe_3)_2$. ● PCH_3 of intermediate; ■ $IrCH_2Si(C\underline{H}_3)_3$ of intermediate; ▲ hexamethyldisiloxane; ▽ $IrCH(C\underline{H}_3)_2$ of *37b*; △ $IrC\underline{H}_2Si(CH_3)_3$ of *37b*; ○ PCH_3 of *37b*; □ $IrCH_2Si(C\underline{H}_3)_3$ of *37b*; ▼ $IrCH_2Si(C\underline{H}_3)_3$ of *37a*.

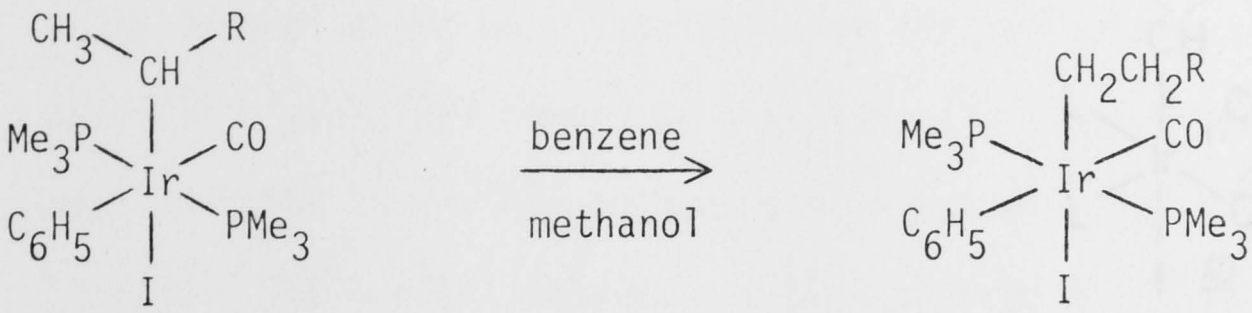
be readily identified because of the overlap of resonances from other species. It should be noted that the *n*-propyl complex, *37a*, shows no tendency to form the intermediate or to decompose to iridium(I), olefin and alkane when dissolved in benzene/methanol (4:1 volume ratio) at 25°C.

The *sec*-butyl complex, *37d*, also isomerizes on dissolution in benzene/methanol to give tetramethylsilane, butene and $IrI(CO)(PMe_3)_2$, as well as the expected *n*-butyl complex, *37c*. The butene was a mixture of isomers which could not be accurately analyzed from the ^1H nmr spectrum. The $^{31}P\{^1H\}$ nmr spectrum of the solution, 24 h after dissolution, shows two singlet resonances due to $IrI(CO)(PMe_3)_2$ (21%) and to the *n*-butyl complex, *37c* (79%). During isomerization of the *sec*-butyl complex, *37d*, an intermediate with *cis*-inequivalent phosphine ligands is also observed (^1H nmr, δ1.04, d, $^2J_{PH} + {}^4J_{PH}$ = 10 Hz, $PC\underline{H}_3$; 1.30, d, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, $PC\underline{H}_3$; 0.46, s, $IrC\underline{H}_2Si(C\underline{H}_3)_3$). Neither the methylene protons of the $IrC\underline{H}_2Si(CH_3)_3$ group, nor the protons of the other alkyl group of this intermediate, are readily identified in the ^1H nmr spectrum.

(iii) $\underline{Ir(C_6H_5)RI(CO)(PMe_3)_2}$

The *sec*-alkyl complxes, *38b* and *38d*, rearrange to the *n*-alkyl complexes, *38a* and *38c*, respectively, on dissolution in benzene/methanol at 25°C (4-11). The isomerization is slower than those of the methyl and trimethylsilylmethyl complexes discussed in sections (i) and (ii) respectively. The time required for complete isomerization of the *iso*-propyl complex, *38b*, in C_6D_6/CD_3OD (5:1 volume ratio) is 24 h. No intermediates are observed in the ^1H nmr spectra during the isomerization of the *sec*-alkyl complexes, *38b* and *38d*, in contrast to the

methyl and trimethylsilylmethyl complexes discussed in sections (i) and (ii), respectively.



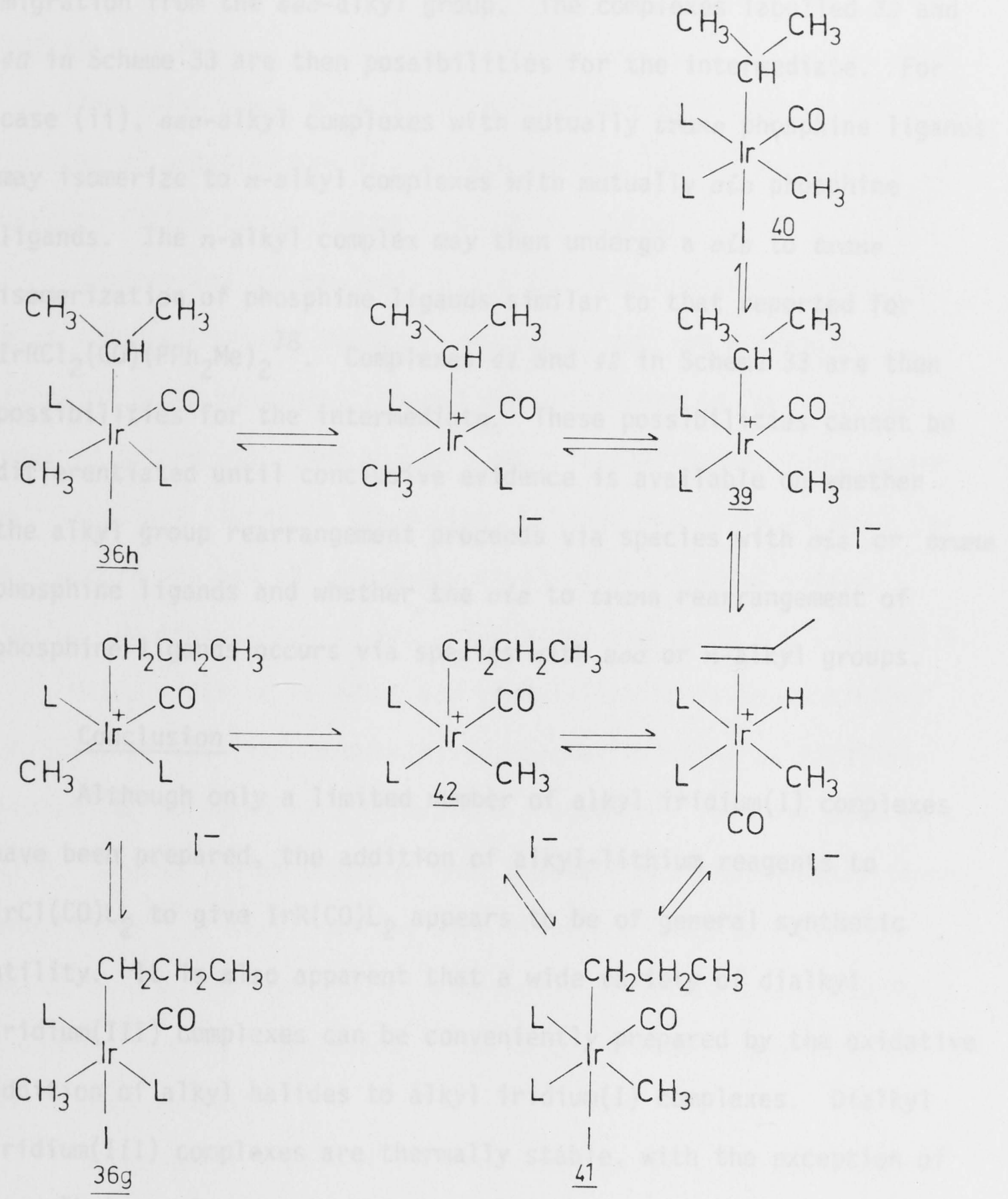
(4-11)

R = CH_3, C_2H_5

The rate at which dialkyl iridium(III) complexes undergo alkyl alkyl group rearrangement is trimethylsilylmethyl>methyl>phenyl. A detailed comparison between monoalkyl and dialkyl complexes is not possible at present but qualitatively the order appears to be trimethylsilylmethyl>methyl~monoalkyl>phenyl.

Mechanism of Alkyl Group Rearrangement

The basic mechanism for the *sec*- to *n*-alkyl group rearrangement of dialkyl iridium(III) complexes is probably similar to that proposed for the analogous rearrangements of monoalkyl iridium(III) complexes (cf. Scheme 24). It seems likely that methanol promotes dissociation of halide *trans* to the *sec*-alkyl group to give a coordinatively unsaturated species which can undergo a series of reversible β-hydride migrations to give the *n*-alkyl product. The limited amount of data available on the intermediate species present during the isomerization of dialkyl iridium(III) complexes makes it difficult to incorporate it into an overall mechanistic scheme. There are, however, two plausible pathways for the isomerization which involve an intermediate complex with mutually *cis* phosphine ligands. These are (i) a pathway in which the intermediate is a necessary part of the isomerization and (ii) a pathway involving two separate reactions (Scheme 33). For case (i), the intermediate may result from a rearrangement of the five coordinate cation formed by dissociation of halide from the *sec*-alkyl complex.



Scheme 33. Proposed Mechanism for Alkyl Group Isomerization of Dialkyl Iridium(III) Complexes.

This rearrangement may be necessary in order to facilitate β-hydride migration from the *sec*-alkyl group. The complexes labelled *39* and *40* in Scheme 33 are then possibilities for the intermediate. For case (ii), *sec*-alkyl complexes with mutually *trans* phosphine ligands may isomerize to *n*-alkyl complexes with mutually *cis* phosphine ligands. The *n*-alkyl complex may then undergo a *cis* to *trans* isomerization of phosphine ligands similar to that reported for $IrRCl_2(CO)(PPh_2Me)_2$[78]. Complexes *41* and *42* in Scheme 33 are then possibilities for the intermediate. These possibilities cannot be differentiated until conclusive evidence is available on whether the alkyl group rearrangement proceeds via species with *cis* or *trans* phosphine ligands and whether the *cis* to *trans* rearrangement of phosphine ligands occurs via species with *sec* or *n*-alkyl groups.

Conclusion

Although only a limited number of alkyl iridium(I) complexes have been prepared, the addition of alkyl-lithium reagents to $IrCl(CO)L_2$ to give $IrR(CO)L_2$ appears to be of general synthetic utility. It is also apparent that a wide variety of dialkyl iridium(III) complexes can be conveniently prepared by the oxidative addition of alkyl halides to alkyl iridium(I) complexes. Dialkyl iridium(III) complexes are thermally stable, with the exception of *sec*-alkyl complexes containing the bulky trimethylsilylmethyl group, and show no tendency to form alkane or alkene in benzene solution at 25°C. The ability of *sec*-alkyl iridium(III) complexes to undergo rearrangement to the isomeric *n*-alkyl complexes in the presence of methanol is quite general and should be taken into account when assessing the potential usefulness of dialkyl iridium(III) complexes for carbon-carbon bond forming reactions.

Experimental.

General

Manipulations of air-sensitive complexes were carried out under nitrogen or argon by use of standard Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres Corp. drybox.

Benzene and toluene were distilled from sodium benzophenone ketyl under nitrogen. Methanol was distilled from magnesium methoxide under nitrogen. Hexane was dried over sodium wire and degassed before use. NMR solvents were freeze-thawed under vacuum four times and stored in the drybox. Celite was dried at 250°C for 24 h before use and all glassware was flame-dried under vacuum. Alumina (Neutral, Grade 1) was dried under vacuum at 200°C for 24 h.

Methyl-lithium in ether and phenyl-lithium in benzene/ether (70/30) were obtained commercially, whereas trimethylsilylmethyl-lithium was prepared by a literature procedure[166] and was used as a solid. Organolithium reagents were standardized with N-benzylidene-benzylamine[167]. Alkyl halides were distilled under nitrogen (or vacuum if b.p. was over 100°C) and vacuum distilled from phosphorus pentoxide at room temperature. The latter procedure was repeated before each reaction.

^{1}H nmr spectra (100 M Hz) were recorded on a Varian HA-100 spectrometer at 29°C. Chemical shifts are reported relative to tetramethylsilane and are calculated from the position of solvent absorption. $^{31}P\{^{1}H\}$ nmr spectra (24.28 M Hz) were recorded on a Bruker 322 S spectrometer at 35°C. Phosphorus chemical shifts are reported relative to external H_3PO_4 (85%) and are positive to low field. NMR samples were prepared in the drybox. Infrared spectra (4000-200 cm^{-1}) were recorded as Nujol mulls or benzene solutions by use of CsI windows, on PE 457 or 225 spectrophotometers and calibrated

against polystyrene. Far-infrared spectra (400-100 cm^{-1}) were recorded as polythene discs on an Hitachi FIS 3 spectrophotometer. Microanalyses were carried out in the Research School of Chemistry and in the John Curtin School of Medical Research (Miss Brenda Stevenson and Dr. Joyce Fildes and their associates). Molecular weights were measured at 25°C on ca. 0.02 M solutions in dichloromethane using a Knauer vapour pressure osmometer. Melting points (uncorrected) were measured on a Gallenkamp hot-stage apparatus in capillaries sealed under vacuum.

Preparations

The complexes, $IrCl(CO)(PPh_3)_2$[168], $IrCl(CO)(PPhMe_2)_2$[106], $IrBr(CO)(PMe_3)_2$[36], $IrI(CO)(PMe_3)_2$[36] and $IrCl(CO)(PMe_3)_2$[107] were prepared by literature procedures.

(i) Carbonylmethylbis(trimethylphosphine)iridium(I), $Ir(CH_3)(CO)(PMe_3)_2$

A solution of $IrCl(CO)(PMe_3)_2$ (*11c*) (0.5 g, 1.23 mmol) in toluene (15 mL) at -78°C was treated with methyl-lithium (1.23 mmol). The solution was stirred and allowed to warm slowly (2 h) to room temperature. The orange solution was stirred for a further 2 h, solvent was then removed under vacuum and the yellow residue was extracted with two 20 mL portions of hexane which were filtered through celite. The yellow solution was stored at -78° for 48 h and the resulting yellow crystals were dried under vacuum (0.22 g, 47%). Mp 122-24°C; IR (Nujol) 1935 cm^{-1} (CO); ^1H nmr (C_6D_6) δ1.36 (t, $^2J_{PH}$ + $^4J_{PH}$ = 8 Hz, $PC\underline{H}_3$), 0.50 (t, $^3J_{PH}$ = 10 Hz, $IrC\underline{H}_3$); ^{31}P nmr (C_6H_6) δ-21.82 (s).

Anal. Calcd for $C_8H_{21}IrOP_2$: C, 24.79; H, 5.46; P, 16.00. Found: C, 24.80; H, 5.66; P, 16.01.

(ii) Carbonyl(trimethylsilylmethyl)bis(trimethylphosphine)-iridium(I), $Ir(CH_2Si(CH_3)_3)(CO)(PMe_3)_2$

A solution of *11c* (0.69 g, 1.69 mmol) in toluene (15 mL) at -78°C was treated with trimethylsilylmethyl-lithium (1.70 mmol). The solution was stirred and allowed to warm slowly (2 h) to room temperature. The orange solution was stirred for a further 2 h, solvent was removed under vacuum and the yellow residue was extracted with two 20 mL portions of hexane which were filtered through celite. The yellow crystals were dried under vacuum (0.47 g, 58%). Mp 85-86°C; IR (Nujol) 1935 cm^{-1} (CO); ^1H nmr (C_6D_6) δ1.48 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, $PC\underline{H}_3$), 0.40 (s, $IrCH_2Si(C\underline{H}_3)_3$), 0.44 (t, $^3J_{PH}$ = 14 Hz, $IrC\underline{H}_2Si(CH_3)_3$); ^{31}P nmr (C_6H_6) δ-25.14 (s).

Anal. Calcd for $C_{11}H_{29}IrOP_2Si$: C, 28.75; H, 6.36; P, 13.48. Found: C, 28.76; H, 6.77; P, 13.22.

(iii) Carbonylphenylbis(trimethylphosphine)iridium(I), $Ir(C_6H_5)(CO)(PMe_3)_2$

A solution of *11c* (0.6 g, 1.47 mmol) in toluene (15 mL) at -78°C was treated with phenyl-lithium (1.50 mmol). The solution was stirred and allowed to warm slowly (2 h) to room temperature. The orange solution was stirred for a further 4 h, solvent was removed under vacuum and the residue was extracted with three 20 mL portions of hexane which were filtered through celite. The yellow solution was stored at - 78°C for 24 h and the resulting yellow crystals were dried under vacuum (0.57 g, 86%). Mp 115-118°C; IR (Nujol) 1940 cm^{-1} (CO); ^1H nmr (CD_2Cl_2) δ1.12 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, $PC\underline{H}_3$), 7.0-7.5 (m, $IrC_6\underline{H}_5$); ^{31}P nmr (C_6H_6) δ-22.33 (s).

Anal. Calcd for $C_{13}H_{23}IrOP_2$: C, 34.74; H, 5.16; P, 13.77. Found: C, 35.62; H, 5.47; P, 13.89.

(iv) Carbonyl(trimethylsilylmethyl)bis(triphenylphosphine)-iridium(I), $Ir(CH_2Si(CH_3)_3)(CO)(PPh_3)_2$

A solution of $IrCl(CO)(PPh_3)_2$ (0.5 g, 0.64 mmol) in THF (20 mL) at 25°C was treated with trimethylsilylmethyl-lithium (1.0 mmol) and the orange solution was stirred for 18 h. Solvent was concentrated to 5 mL and applied to a column of neutral alumina (Grade 1, 2 cm by 30 cm). The column was maintained at -30°C and the product was eluted with ether (ca. 100 mL). Solvent was removed under vacuum to give a yellow solid (0.2 g) which still retained some ether (0.5-1.0 mol). IR (Nujol) 1914 cm^{-1} (CO): ^1H nmr (C_6D_6) δ0.03 (s, $IrCH_2Si(CH_3)_3$), 0.83 (t, $^3J_{PH}$ = 12 Hz, $IrCH_2Si(CH_3)_3$); ^{31}P nmr (C_6H_6) δ26.85 (s).

(v) Carbonyl(trimethylsilylmethyl)bis(dimethylphenylphosphine)-iridium(I) $Ir(CH_2Si(CH_3)_3)(CO)(PPhMe_2)_2$

A solution of $IrCl(CO)(PPhMe_2)_2$ (0.2 g, 0.38 mmol) in toluene (10 mL) at -78°C was treated with trimethylsilylmethyl-lithium (0.4 mmol). The solution was stirred and allowed to warm slowly (3 h) to room temperature. The orange solution was stirred for a further 2 h, solvent was removed under vacuum and the yellow residue was extracted with two 10 mL portions of hexane which were filtered through celite. The yellow solution was stored at -78°C for 24 h and the resulting yellow crystals were dried under vacuum (0.1 g, 45%). ^1H nmr (C_6D_6) δ1.90 (t, $^2J_{PH} + {}^4J_{PH}$ = 6 Hz, PCH_3), 0.21 (s, $IrCH_2Si(CH_3)_3$), 0.57 (t, $^3J_{PH}$ = 13 Hz, $IrCH_2Si(CH_3)_3$); ^{31}P nmr (C_6D_6) δ-10.86 (s).

(vi) Alkylcarbonylhalomethylbis(trimethylphosphine)iridium(III), $Ir(CH_3)RX(CO)(PMe_3)_2$

A solution of $Ir(CH_3)(CO)(PMe_3)_2$ (0.08 g, 0.21 mmol) in benzene (5 mL) was treated with the appropriate alkyl halide (0.1 mL)

at room temperature. The yellow solution became pale yellow to colourless over 1-10 min. The solution was stirred for 30 min (or 60 min for branched alkyl-bromides) to ensure complete reaction. Solvent was removed under vacuum and the residue was extracted with two 5 mL portions of hexane which were filtered through celite. The colourless solution was stored at -78°C for 48 h to give white crystals which were dried under vacuum. Yields were generally 60-70%. Analytical and spectroscopic data for complexes *36a-j*, appear in Tables 31-33. Although the complexes appeared to be air-stable as solids and in solution, they were stored under nitrogen at -10°C, and samples for nmr studies were prepared in the drybox.

(viii) Alkylcarbonyliodo(trimethylsilylmethyl)bis(trimethylphosphine)iridium(III), $Ir(CH_2Si(CH_3)_3)RI(CO)(PMe_3)_2$

A solution of $Ir(CH_2Si(CH_3)_3)(CO)(PMe_3)_2$ (0.08 g, 0.17 mmol) in benzene (5 mL) was treated with the appropriate alkyl iodide (0.1 mL) at room temperature. The yellow solution was stirred until it became colourless (ca. 10 min for *n*-alkyl iodides and ca. 60 min for *sec*-alkyl iodides). Solvent was removed under vacuum, and the residue was extracted with two 5 mL portions of hexane which were filtered through celite. The colourless solution was stored at -78°C for 48 h to give white crystals which were dried under vacuum. Yields were generally 70-80%. Analytical and spectroscopic data for complexes, *37a-d*, appear in Tables 34-36. The *n*-alkyl derivatives are stable as solids and in solution, whereas the *sec*-alkyl derivatives are thermally unstable but could be stored satisfactorily under nitrogen at -10°C. Solutions of these complexes for nmr studies were prepared in the drybox.

(viii) Alkylcarbonyliodophenylbis(trimethylphosphine)-iridium(III), $Ir(C_6H_5)RI(CO)(PMe_3)_2$

A solution of $Ir(C_6H_5)(CO)(PMe_3)_2$ (0.08 g, 0.18 mmol) in benzene (5 mL) was treated with the appropriate alkyl iodide (0.1 mL) at room temperature. The yellow solution was stirred until it became colourless (2-10 min). Solvent was removed under vacuum and the residue was extracted with three 5 mL portions of hexane which were filtered through celite. The colourless solution was stored at -78°C for 24 h and the resulting white crystals were dried under vacuum. Yields were generally 70-80%. Spectroscopic data for complexes, *38a-d*, appear in Tables 37 and 38. These complexes are air-stable as solids and in solution.

Analyses.

(a) *n*-Propylcarbonyliodophenylbis(trimethylphosphine)iridium(III) Calcd for $C_{16}H_{30}IIrOP_2$: C, 31.02; H, 4.88; P, 10.00. Found: C, 31.46; H, 4.99; P, 10.31.

(b) *n*-butylcarbonyliodophenylbis(trimethylphosphine)iridium(III) Calcd for $C_{17}H_{32}IIrOP_2$: C, 32.30; H, 5.09; P, 9.76. Found: C, 32.35; H, 5.11; P, 9.43.

Isomerization of *sec*-Alkyl Complexes

Samples for isomerization studies were prepared under nitrogen but it was not necessary to degas the deuterated reaction solvents.

(a) A solution of $Ir(CH_3)(CH(CH_3)_2)Br(CO)(PMe_3)_2$ (*36b*) in a mixture of C_6D_6 (0.5 mL) and CD_3OD (0.1 mL) was prepared in a 5 mm nmr tube. Successive ^1H nmr spectra were recorded at 29°C. After 0.5 h only resonances due to the *iso*-propyl complex, *36b*, were present, whereas after 24 h only resonances due to the *n*-propyl complex, *36a*, were present. Between 1 and 10 h after dissolution resonances due to an intermediate (present only during the

isomerization) were observed at δ1.12 (d, $^{2}J_{PH} + {}^{4}J_{PH}$ = 10 Hz, PCH_3) 1.31 (d, $^{2}J_{PH} + {}^{4}J_{PH}$ = 9 Hz, PCH_3), 0.42 (d of d, $^{3}J_{PH}$ = 5, 10 Hz, $IrC\underline{H}_3$) in addition to resonances due to the *iso*-propyl and *n*-propyl complexes.

Isomerization was also monitored by ^{31}P nmr at 35°C in 5 mm nmr tubes with $Ir(CH_3)(CH(CH_3)_2)Br(CO)(PMe_3)_2$ dissolved in benzene (0.5 mL) and methanol(0.1 mL). In addition to singlet resonances due to the *iso*- and *n*-propyl complexes (δ-46.5 and -45.6, respectively) two doublets (δ-36.4 and -61.4, $^{2}J_{PP}$ = 10 Hz) due to the inequivalent *cis*-phosphorus nuclei of the intermediate were observed.

(b) A solution of $Ir(CH_3)(CH(CH_3)_2)I(CO)(PMe_3)_2$ (*36h*) in a mixture of C_6D_6 (0.5 mL) and CD_3OD (0.1 mL) was prepared in a 5 mm nmr tube and isomerization was monitored by ^{1}H nmr at 29°C as in (a). Spectra were very similar to those observed in (a). Thus, in addition to resonances due to the *iso*-propyl complex, *36h*, and the *n*-propyl complex, *36g*, resonances due to an intermediate were also observed at δ0.98 (d, $^{2}J_{PH} + {}^{4}J_{PH}$ = 10 Hz, PCH_3), 1.34 (d, $^{2}J_{PH} + {}^{4}J_{PH}$ = 9 Hz, PCH_3) and 0.57 (m, $IrC\underline{H}_3$).

Isomerization was also monitored by ^{31}P nmr at 35°C in 5 mm nmr tubes as in (a). In addition to singlet resonances due to *iso*- and *n*-propyl complexes (δ-51.7 and -50.9, respectively) two doublets (δ-37.4 and -68.1, $^{2}J_{PP}$ = 10 Hz) due to the inequivalent *cis*-phosphorus nuclei of the intermediate were observed.

(c) A solution of $Ir(CH_2Si(CH_3)_3)(CH(CH_3)_2)I(CO)(PMe_3)_2$ (*37b*) in a mixture of C_6D_6 (0.5 mL) and CD_3OD (0.05 mL) was prepared in a 5 mm nmr tube. Successive ^{1}H nmr spectra were recorded at 29°C. Up to 0.3 h after dissolution only resonances due to *iso*-propyl complex, *37b*, were observed, whereas after 24 h resonances due to four species were observed: the *n*-propyl complex, *37a*; $IrI(CO)(PMe_3)_2$, δ1.47 (t, $^{2}J_{PH} + {}^{4}J_{PH}$ = 8 Hz, PCH_3); propylene, δ1.55-1.65 (m, $CH_2{=}CHC\underline{H}_3$,

4.86-5.06 (m, $C\underline{H}_2{=}C\underline{H}CH_3$), 5.50-5.90 (m, $C\underline{H}_2{=}CHCH_3$); and tetramethylsilane, δ0.0 (s). Between 0.5 and 7.0 h resonances due to an intermediate were also observed at δ1.10 (d, $^2J_{PH} + {}^4J_{PH}$ = 10 Hz, PCH_3), 1.32 (d, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3) and 0.44 (s, $IrCH_2Si(C\underline{H}_3)_3$). The complex, $IrI(CO)(PMe_3)_2$, was identified by a comparison with the ^{31}P chemical shift of an authentic sample. Propylene and tetramethylsilane were identified by a comparison with the ^1H resonances of authentic samples.

The $^{31}P\{^1H\}$ nmr spectrum (24 h after dissolution) showed two singlet resonances due to the *n*-propyl complex, *37a* (δ-52.09, 62%) and to $IrI(CO)(PMe_3)_2$ (δ-24.84, 38%).

(d) A solution of $Ir(CH_2Si(CH_3)_3)(CH(CH_3)C_2H_5)I(CO)(PMe_3)_2$ (*37d*) in a mixture of C_6D_6 (0.5 mL) and CD_3OD (0.05 mL) was prepared in a 5 mm nmr tube and isomerization was monitored by ^1H nmr at 29°C as in (c). Spectra were very similar to those observed in (c). Thus, after 0.3 h, only resonances due to the *sec*-butyl complex, *37d*, were observed, whereas after 24 h resonances due to four species were observed: the *n*-butyl complex, *37c*; $IrI(CO)(PMe_3)_2$, δ1.47 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3); butene, δ5.4 (m, olefinic protons); tetramethylsilane δ0.0 (s). Between 0.5 and 7.0 h resonances due to an intermediate were also observed at δ1.04 (d, $^2J_{PH} + {}^4J_{PH}$ = 10 Hz, PCH_3), 1.30 (d, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3) and 0.46 (s, $IrCH_2Si(C\underline{H}_3)_3$). Only the olefinic protons of the butene could be observed in the ^1H nmr spectrum. The butene may be a mixture of isomers but it was not possible to identify these conclusively from the ^1H nmr spectrum. *Cis* and *trans* butene have olefinic resonances at ca.δ5.35, whereas 1-butene has olefinic resonances at δ4.8-5.0 and δ5.5-5.9[169].

The $^{31}P\{^1H\}$ nmr spectrum (24 h after dissolution) showed two singlet resonances due to the *n*-butyl complex, *37c* (δ-52.4, 79%) and to $IrI(CO)(PMe_3)_2$ (δ-25.0, 21%).

Addition of Methyl Halide to $IrX(CO)(PMe_3)_2$

(a) Bromocarbonyliodomethylbis(trimethylphosphine)iridium(III), $Ir(CH_3)BrI(CO)(PMe_3)_2$

A solution of $IrBr(CO)(PMe_3)_2$ (0.08 g, 0.18 mmol) in benzene (5 mL) was treated with methyl iodide (0.15 mL). The yellow solution rapidly decolourized. Evaporation of volatiles and trituration with hexane gave a white solid (0.08 g, 75%). IR (Nujol) 2020 cm^{-1} (CO); IR (Polythene Disc) 192 cm^{-1} (IrBr), 280 cm^{-1} (PC_3 deform.[87]).

(b) Dibromocarbonylmethylbis(trimethylphosphine)iridium(III), $Ir(CH_3)Br_2(CO)(PMe_3)_2$

Methylbromide was added to $IrBr(CO)(PMe_3)_2$ as in (a). IR (Nujol) 2030 cm^{-1} (CO) IR (Polythene Disc) 168, 192 cm^{-1} (IrBr), 280 cm^{-1} (PC_3 deform.[87]).

(c) Bromocarbonylchloromethylbis(trimethylphosphine)iridium(III), $Ir(CH_3)BrCl(CO)(PMe_3)_2$

Methylbromide was added to $IrCl(CO)(PMe_3)_2$ as in (a). IR (Nujol) 2025 cm^{-1} (CO); IR (Polythene Disc) 168 cm^{-1} (IrBr), 280 cm^{-1} (PC_3 deform.[87]), 300 cm^{-1} (IrCl).

TABLE 31

Analytical Data for $Ir(CH_3)RX(CO)(PMe_3)_2$

Complex R	M.P. °C	Analyses: found (calculated) % C	H	P	MW(CH_2Cl_2)
X = Br					
propyl	90-95	26.18 (25.89)	5.57 (5.53)	12.26 (12.13)	530 (510)
iso-propyl	102-03	25.92 (25.89)	5.59 (5.53)		
butyl	65-66	27.22 (27.48)	5.59 (5.76)	12.38 (11.81)	
sec-butyl	85-86	27.45 (27.48)	5.78 (5.76)	12.00 (11.81)	503 (524)
pentyl	101-03	29.30 (28.99)	6.05 (6.00)	11.75 (11.50)	
2-pentyl		29.08 (28.99)	6.02 (6.00)	11.70 (11.50)	
X = I					
propyl	115-20	23.88 (23.70)	5.02 (5.06)	11.43 (11.11)	
iso-propyl	121-22	23.93 (23.70)	5.25 (5.06)	11.32 (11.11)	568 (557)
butyl		25.23 (25.22)	5.27 (5.29)	10.88 (10.83)	556 (571)
sec-butyl	85-86	25.09 (25.22)	5.35 (5.29)	11.02 (10.83)	

TABLE 32

Infrared and ^{31}P NMR[a] Data for $Ir(CH_3)RX(CO)(PMe_3)_2$

R	$\nu(CO)$ cm^{-1} NUJOL	$\nu(CO)$ cm^{-1} CH_2Cl_2	$\nu(IrBr)$[b] cm^{-1}	δ[c]
X = Br				
propyl	1995	1995	158	- 45.55
iso-propyl	2000	2005	154	- 46.45
butyl	2005,1990	1995	160	- 45.65
sec-butyl	2000	1995	167	- 46.96
pentyl	1994	1995	160	- 45.55
2-pentyl	2005	2000	156,165	
X = I				
propyl	2005	1995		- 50.88
iso-propyl	2000	1995		- 51.69
butyl				- 50.78
sec-butyl	2000			- 51.79

a. $^{31}P\{^1H\}$ nmr spectra were measured in benzene at 35°C. Chemical shifts are referenced to external 85% H_3PO_4 and are positive to low field.

b. Far-infrared spectra were measured as polythene discs.

c. Singlets.

TABLE 33

^{1}H NMR Data for $Ir(CH_3)RX(CO)(PMe_3)_2$[a,b]

R	δ A	δ B	δ C	δ D	J_{HH} Hz	δ $IrCH_3$[c]	δ Phosphine Methyls
X = Br							
propyl $\overset{A}{\widetilde{CH_2CH_2}}\overset{B}{CH_3}$	1.00 (m, 4 H)	1.30 (m, 3 H)				0.40 (t)	1.31 (t)[d]
iso-propyl $(CH_3)_2\overset{A}{CH}$	1.36 (d, 6 H)	2.32 (sp, 1 H)			6	0.60 (t)	1.40 (t)[d]
butyl $CH_2\overset{A}{\widetilde{CH_2CH_2}}CH_3$	0.94-1.40 (m)					0.42 (t)	1.32 (t)[d]
sec-butyl $\overset{A}{CH_3}\overset{B}{\widetilde{CH}}\overset{C}{CH_2}CH_3$	1.31 (d, 3 H)	1.44-2.14 (m)	0.99 (t, 3 H)		7	0.60 (t)	1.37, 1.38[e]
pentyl $CH_2\overset{A}{\widetilde{CH_2CH_2CH_2}}CH_3$	0.94-1.40 (m)					0.42 (t)	1.34 (t)[d]
2-pentyl $\overset{A}{CH_3}\overset{B}{\widetilde{CH}}CH_2\overset{C}{\widetilde{CH_2}}CH_3$	1.30 (d, 3 H)	1.44-2.04 (m)	1.01 (m)		7	0.60 (t)	1.20 (t)[d]

Cont.

TABLE 33 Cont.

R	δ A	B	C	D	J_{HH} Hz	δ $IrCH_3$	δ Phosphine Methyls
X = I							
propyl $\overbrace{CH_2CH_2}^{A}\overset{B}{CH_3}$	1.00-1.40 (m)	1.02 (t, 3 H)			8	0.49 (t)	1.42 (t)[d]
iso-propyl $(CH_3)_2\overset{A}{\overbrace{CH}}\overset{B}{}$	1.35 (d, 6 H)	2.46 (sp, 1 H)			7	0.66 (t)	1.48 (t)[d]
butyl $\overbrace{CH_2CH_2CH_2}^{A}\overset{B}{CH_3}$	1.0-1.5 (m)	1.04 (t, 3 H)			6	0.50 (t)	1.42 (t)[d]
sec-butyl $\overset{A}{CH_3}\overset{B}{CH}\overset{C}{CH_2}\overset{D}{CH_3}$	1.22 (d, 3 H)	2.04 (m, 1 H)	1.64 (m)	0.92 (t, 3 H)	7	0.56 (t)	1.38, 1.39[e]

a. ^1H nmr spectra were measured in C_6D_6 at 29°C with chemical shifts (δ) in parts per million downfield of tetramethylsilane.

b. d = doublet, m = multiplet, sp = septet, t = triplet.

c. $^3J_{PH}$ = 9 Hz.

d. $^2J_{PH} + {}^4J_{PH}$ = 8 Hz.

e. Two singlets on ^{31}P decoupling.

TABLE 34

Analytical Data for $Ir(CH_2Si(CH_3)_3)RI(CO)(PMe_3)_2$

Complex R	M.P. °C	Analyses: found (calculated) % C	H	P	I	MW (CH_2Cl_2)
propyl	120-26	27.30 (26.71)	5.92 (5.76)	10.14 (9.84)	19.75 (20.16)	627 (630)
iso-propyl	118-20	26.37 (26.71)	5.86 (5.76)			
butyl	144-46	28.68 (28.00)	6.01 (5.95)	9.83 (9.62)	19.64 (19.72)	
sec-butyl	62-63	27.85 (28.00)	5.93 (5.95)	9.85 (9.62)		

TABLE 35

Infrared and ^{31}P NMR[a] Data for $Ir(CH_2Si(CH_3)_3)RI(CO)(PMe_3)_2$

R	$\nu(CO)$ cm^{-1} NUJOL	CH_2Cl_2	δ[b]
propyl	2000	2000	- 50.29
iso-propyl	2000	2000	- 54.70
butyl	1995	2000	- 52.48
sec-butyl	1993, 1997	2000	c

a. $^{31}P\{^1H\}$ nmr spectra were measured in C_6H_6 at 35°C. Chemical shifts (δ) are referenced to external 85% H_3PO_4 and are positive to low field.

b. Singlets.

c. Not measured.

TABLE 36

^{1}H NMR Data for $Ir(CH_2Si(CH_3)_3)RI(CO)(PMe_3)_2$[a,b]

R		δ A	δ B	δ C	J_{HH} Hz	δ $IrCH_2Si(CH_3)_3$ $(CH_3)_3$	δ $IrCH_2Si(CH_3)_3$ CH_2[c]	δ Phosphine Methyls
propyl	$CH_2\overset{A}{\widetilde{CH_2}}\overset{B}{\widetilde{CH_3}}$	1.40 (m)	1.02 (m, 5 H)			0.33 (s, 9 H)	0.33 (t)	1.49 (t)[d]
iso-propyl	$(CH_3)_2\overset{A}{\widetilde{CH}}\overset{B}{\widetilde{\ }}$	1.36 (d, 6 H)	1.98 (sp)		7	0.50 (s, 9 H)	0.07 (t)	1.52 (t)[d]
butyl	$\overbrace{CH_2CH_2CH_2}^{A}CH_3$	0.88-1.40 (m)				0.33 (s, 9 H)	0.39 (t)	1.48 (t)[d]
sec-butyl	$CH_3\overset{A}{\widetilde{CH}}\overset{B}{\widetilde{CH_2}}\overset{C}{\widetilde{CH_3}}$	1.34 (d)	1.3-2.0 (m)	0.96 (t)	7	0.48 (s, 9 H)	0.06 (t)	1.52, 1.54[e]

a. ^{1}H nmr spectra were measured in C_6D_6 at 29°C with chemical shifts (δ) in parts per million downfield of tetramethylsilane.

b. d = doublet, m = multiplet, s = singlet, sp = septet, t = triplet.

c. $^{3}J_{PH}$ = 10 Hz.

d. $^{2}J_{PH} + {}^{4}J_{PH}$ = 8 Hz.

e. Two singlets on ^{31}P decoupling.

TABLE 37

Infrared and ^{31}P NMR[a] Data for $Ir(C_6H_5)RI(CO)(PMe_3)_2$

R	ν(CO) cm^{-1} NUJOL	CH_2Cl_2	δ[b]
propyl	2010	2020	- 49.98
iso-propyl	2000	2020	- 51.69
butyl	2000, 2020	2020	- 50.37
sec-butyl	2020	2020	- 51.7, - 51.8[c]

a. $^{31}P\{^1H\}$ nmr spectra were measured in C_6H_6 at 35°C. Chemical shifts are referenced to external 85% H_3PO_4 and are positive to low field.

b. Singlets.

c. Chemical shifts of central doublet of AB quartet, $^2J_{PP}$ = 378 Hz.

TABLE 38

^{1}H NMR Data for $Ir(C_6H_5)RI(CO)(PMe_3)_2$[a,b]

R		δ A	δ B	δ C	J_{HH} Hz	δ Phosphine Methyls
propyl	$\overbrace{CH_2CH_2}^{A}\overset{B}{CH_3}$	1.70 (m)	1.12 (m)			1.23 (t)[c]
iso-propyl	$(\overset{A}{CH_3})_2\overset{B}{CH}$	1.50 (d, 6 H)	2.48 (sp, 1 H)		6	1.36 (t)[c]
butyl	$\overbrace{CH_2CH_2CH_2}^{A}\overset{B}{CH_3}$	1.44-1.74 (m)	1.08 (m)			1.24 (t)[c]
sec-butyl	$CH_3\overset{A}{\overbrace{CH}}\overset{B}{\overbrace{CH_2}}\overset{C}{CH_3}$	1.47 (d, 3 H)	1.94-2.3 (m)	1.06 (t, 3 H)	7	1.37, 1.38[d]

a. ^{1}H nmr spectra were measured in C_6D_6 at 29°C with chemical shifts (δ) in parts per million downfield of tetramethylsilane.

b. d = doublet, m = multiplet, sp = septet, t = triplet.

c. $^{2}J_{PH} + {}^{4}J_{PH} = 8$ Hz.

d. Two singlets on ^{31}P decoupling.

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