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ORGANOIRIDIUM COMPLEXES AS MODELS FOR HOMOGENEOUSLY CATALYZED REACTIONS

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CONTENTS

A. INTRODUCTION

Homogeneous catalysis has been an active area of research for a number of years [1,2]. This research has been fruitful in a growing chemical production by processes which utilize homogeneous catalysts [1], and has also led to increased understanding of transformations on metallic centers [1–3]. Much of the explosive growth in organometallic chemistry can be related to the applications of homogeneous catalysis.

The Group 9 metals are among the most important homogeneous catalysts. Hydroformylation and alcohol carbonylation are major industrial processes involving Group 9 metal catalysts [1,2,4]. Each catalytic cycle is

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composed of numerous steps; the hydroformylation of C_2H_4 by $HRh(CO)_2(PPh_3)_2$ can serve as an example [5].

$HRh(CO)_2(PPh_3)_2 + C_2H_4 \rightleftharpoons HRh(CO)_2(PPh_3)(C_2H_4) + PPh_3$ (1)

$HRh(CO)_2(PPh_3)(C_2H_4) \rightleftharpoons C_2H_5Rh(CO)_2(PPh_3)$ (2)

$C_2H_5Rh(CO)_2(PPh_3) + PPh_3 \rightleftharpoons C_2H_5Rh(CO)_2(PPh_3)_2$ (3)

$C_2H_5Rh(CO)_2(PPh_3)_2 \rightleftharpoons C_2H_5C(O)Rh(CO)(PPh_3)_2$ (4)

$C_2H_5C(O)Rh(CO)(PPh_3)_2 + H_2 \rightleftharpoons C_2H_5C(O)Rh(CO)(PPh_3)_2(H_2)$ (5)

$C_2H_5C(O)Rh(CO)(PPh_3)_2(H_2) \rightarrow HRh(CO)(PPh_3)_2 + C_2H_5C(O)H$ (6)

$HRh(CO)(PPh_3)_2 + CO \rightleftharpoons HRh(CO)_2(PPh_3)_2$ (7)

The reactions may be classified as ligand addition to a sixteen electron metal complex (reactions 3 and 7), ligand substitution (reaction 1), insertion within the coordination sphere (reactions 2 and 4), oxidative addition (reaction 5) and reductive elimination (reaction 6). During catalysis, reactions (1)–(7) would be occurring so rapidly that they could not be individually observed. Thus the importance of model complexes to demonstrate and study the individual steps of catalytic reactions is apparent.

The steps for reactions catalyzed by transition metal complexes vary depending on the reaction, but have features in common: (1) the substrate is coordinated to the metal center, usually as a neutral ligand or in an oxidative addition reaction; (2) a transformation of the substrate(s) occurs while coordinated to the metal; (3) the product is eliminated from the transition metal, often in a reductive elimination reaction. Each of these are amenable to modeling reactions of transition metal complexes.

Two square planar complexes were especially important to the development of organometallic reaction chemistry. The catalytic activity of $Rh(PPh_3)_3Cl$ [6], and subsequent reactivity studies, and the stoichiometric reactions of *trans*-$Ir(CO)(PPh_3)_2Cl$ [7] have initiated many studies of organometallic reaction mechanisms. Ligand coordination and activation, oxidative addition, reductive elimination, insertion and other transformations have all been examined on iridium complexes. In this manuscript, we will consider the role of iridium complexes in each of these reaction types. The role of iridium compounds in catalysis has been previously reviewed [8].

B. LIGAND BINDING

(i) Olefins

Among the earliest systematic studies of olefin coordination to a transition metal were of complexes of *trans*-$Ir(CO)(PPh_3)_2Cl$.

trans-$Ir(CO)(PPh_3)_2Cl + \text{alkene} \rightleftharpoons Ir(CO)(\text{alkene})(PPh_3)_2Cl$ (8)

TABLE 1

Equilibrium constants for addition of alkenes to *trans*-$Ir(CO)(PPh_3)_2Cl$ at 30 ° C

Alkene	K_{eq} ($l\ mol^{-1}$)
C_2H_4	<1
CH_2=CH(CN)	1.2
CH(CN)=CH(CN)	1,500
$C_2(CN)_4$	140,000

Several equilibrium constants for alkene binding are shown in Table 1 [7]; their order has subsequently been shown to be a general order for alkene binding. The electron withdrawing ability of the alkene seems to be the predominant factor in alkene bonding. The electron density on the metal is also important to the stability of the transition metal–olefin bond. The stability of the metal–olefin bond for *trans*-$XIr(CO)(PPh_3)_2$ changes [7,9,10] in the order X = Me > I > Cl > OMe, indicating that electron donation from the metal to the olefin is important. Possible modeling of olefin polymerization by $CH_3Ir(CO)(PPh_3)_2$(olefin) and Wacker chemistry by ROIr(CO)$(PPh_3)_2$(olefin) is apparently inhibited by the weak binding of the olefin to the iridium center [10,11].

Di(ethylene) complexes were prepared by addition of ethylene to *trans*-$Ir(CO)(PMe_2Ph)_2Cl$ with displacement of Cl^- [12].

$$trans\text{-}Ir(CO)(PMe_2Ph)_2Cl + 2\ C_2H_4$$
$$\xrightarrow{BPh_4^-} [Ir(CO)(C_2H_4)_2(PMe_2Ph)_2^+][BPh_4^-] \tag{9}$$

The ethylenes were susceptible to nucleophilic attack. Such complexes may be important models for nucleophilic attack on an olefin in processes such as Wacker chemistry. Unfortunately attempts to model such reactions with *trans*-$MeOIr(CO)(PPh_3)_2$ and *trans*-$HOIr(CO)(PPh_3)_2$ have thus far been unsuccessful [10].

In several cases olefin–hydride complexes (models of hydrogenation and isomerization) have been prepared [13,14]. Reactions of activated olefins with sources of $HIr(CO)(PPh_3)_2$ ($HIr(CO)(PPh_3)_3$, $HIr(CO)_2(PPh_3)_2$ and $H_3Ir(CO)(PPh_3)_2$) led to the isolation of several complexes [13]:

$$HIr(CO)(PPh_3)_3 + \text{olefin} \rightarrow HIr(\text{olefin})(CO)(PPh_3)_2 + PPh_3 \tag{10}$$

where the olefin is fumaronitrile, dimethylmaleate, etc.; these complexes are considered good models for catalytic intermediates. Reactions of $HIr(CO)_2(PPh_3)_2$ with allene and conjugated dienes to give η^3-allyl complexes have also been reported [14]. These reactions probably involve coordination of one double bond, insertion into the Ir–H bond to form an η^1-allyl and then $\eta^1 \rightarrow \eta^3$ allyl conversion.

For eighteen electron complexes to open a coordination site for olefin bonding, a ligand dissociation must occur. Usually the ligand dissociating is a phosphine, carbonyl or other neutral ligand. For $H_2IrCl[HN(CH_2CH_2PPh_2)_2]$ in ethanolic solution Cl^- is replaced by cyclohexene forming the cationic complex [15]. In combination with reaction (9), this appears to offer another possibility for opening a coordination site.

$$H_2IrCl[HN(CH_2CH_2PPh_2)_2] + C_6H_{10} \rightarrow H_2Ir(C_6H_{10})[HN(CH_2CH_2PPh_2)_2] + Cl^- \quad (11)$$

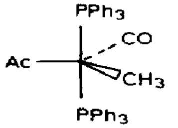
Subsequent hydrogen transfer completes a catalytic cycle for hydrogenation of cyclohexene [15].

(ii) Acetylenes

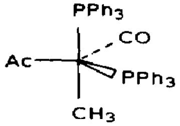
Activated acetylenes were found to readily bind to 16-electron iridium(I) complexes and provided early examples of acetylene as a two electron donor to a metal center [16].

$$Ir(CO)(PPh_3)_2Cl + RC{\equiv}CR \rightarrow Ir(CO)(PPh_3)_2Cl(RC{\equiv}CR) \quad (12)$$

More recently the reaction of activated acetylenes with alkyl complexes, *trans*-$RIr(CO)(PPh_3)_2$, have been examined leading to three different structures. Reaction of the methyl complex with $MeO_2CC{\equiv}CCO_2Me$ led initially to A which rearranged to B with time [17].



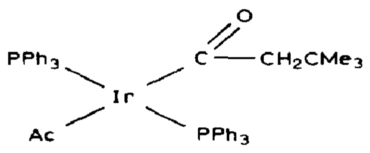
A



B

Ac = $MeO_2CC{\equiv}CCO_2Me$

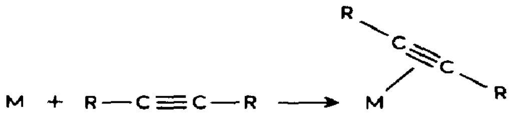
In structure B, the best σ-donors are in the axial positions and the best π-acceptors are in the equatorial positions as expected. A third structural type as shown below has been observed for the dimethylacetylenedicarboxylate adduct of the neopentyliridium complex *trans*-$Me_3CCH_2Ir(CO)(PPh_3)_2$, [18].



Ac = $MeO_2CC{\equiv}CCO_2Me$

Evidently, in this case, the extra steric interactions force the rearrangement to the four-coordinate acyl.

Coordination of a second acetylene to form the metallocyclopentadiene has been observed for *trans*-$Ir(N_2)(PPh_3)_2Cl$ with loss of N_2 [19].



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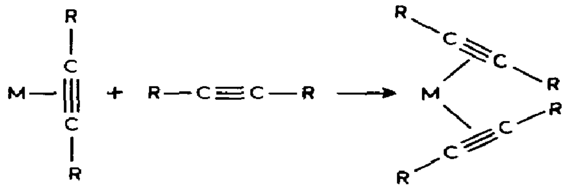

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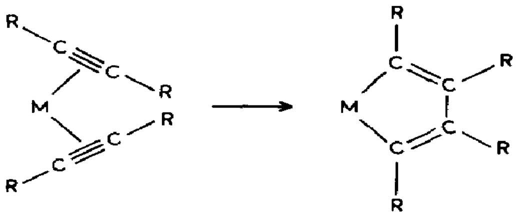


(15)

The metallocyclopentadiene structure for coordination of two acetylenes has obvious importance in catalytic oligomerization reactions.

Terminal acetylenes react with sixteen electron iridium complexes through C–H oxidative addition leading to acetylides [16,18,20]

$$\textit{trans}\text{-}MeOIr(CO)(PPh_3)_2 + HC{\equiv}CR \rightarrow \textit{trans}\text{-}RC{\equiv}C\text{-}Ir(CO)(PPh_3)_2 + MeOH \quad (16)$$

Such reactions of terminal acetylenes pertain to acetylene polymerization reactions.

(iii) Dioxygen

Dioxygen participates in an oxidative addition reaction with square planar iridium(I) complexes. However, dioxygen complexes are included in this section on ligand bonding because of similarities between O_2 and alkene bonding [21]. The dioxygen complexes of *trans*-$Ir(CO)(PPh_3)_2X$ were among the earliest which allowed the bonding of O_2 to be described.

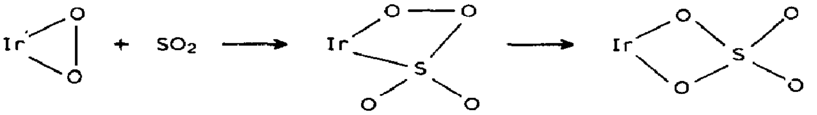
$$\textit{trans}\text{-}Ir(CO)(PPh_3)_2Cl + O_2 \rightleftharpoons Ir(CO)(PPh_3)_2(O_2)Cl \quad (17)$$

TABLE 2

Kinetic and structural data for addition of O_2 to *trans*-$Ir(CO)(PPh_3)_2X$ [22,23]

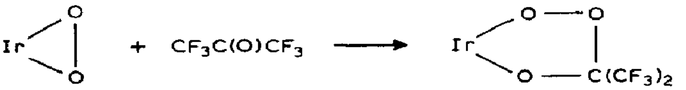
X	k (s^{-1})	ΔH^{*} (kcal mol^{-1})	ΔS^{*} (e.u.)	O–O (Å)
Cl	3.4×10^{-2}	13.1	−21	1.30
Br	0.74×10^{-1}	11.8	−24	1.36
I	0.30	10.9	−24	1.51

Despite a number of different explanations, the peroxo description of the coordinated dioxygen appears to be sufficient. The ability of dioxygen to coordinate to iridium(I) depends on the electron density at the iridium center. This is illustrated by the complexes *trans*-$Ir(CO)(PPh_3)_2X$ (X = Me, I, Cl, OMe) [9,20,21]. For the methyl complex the O_2 cannot be removed, the iodo and chloro complexes establish equilibria with the equilibrium constant for formation larger for the iodo complex, and for the methoxy complex the O_2 adduct can only be formed at low temperature. Kinetic data for O_2 addition to *trans*-$Ir(CO)(PPh_3)_2X$, as shown in Table 2, also indicate the basicity of the iridium [22]. These iridium dioxygen complexes have been used to oxidize several molecules. Oxidation of SO_2 was believed to occur through a peroxysulfate intermediate [24,25]



(18)

Use of the iridium–^{18}O complex produced sulfate with one ^{18}O and one ^{16}O coordinated to the iridium [25]. Similar oxidation of hexafluoroacetone has been reported with isolation of the presumed peroxo intermediate [26]



(19)

Kinetic studies showed dependence on the iridium complex and on the hexafluoroacetone [26]. A direct electrophilic attack of the hexafluoroacetone on the coordinated dioxygen molecule was indicated. Catalytic oxidation of other ketones has been reported under somewhat more forcing conditions [27]. Oxidation of olefins using $Ir(PPh_3)_2(O_2)(C_2H_4)Cl$ has been examined [28]. The complex decomposes to $OPPh_3$ and CH_3CHO in the absence of added olefin. In the presence of olefins, 1-octene and styrene, oxidation to ketones was observed. The data suggested that coordination of olefin and dioxygen to the same metal was not occurring in the oxidation

TABLE 3

Kinetic data for the oxidative addition of H_2 to *trans*-Ir(CO)(PPh$_3$)$_2$X [22,30]

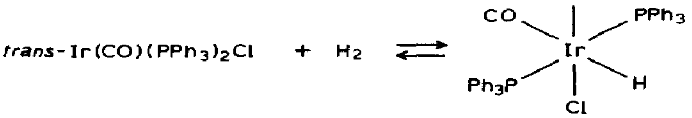
X	k	$\Delta H^{\neq}$	$\Delta S^{\neq}$
Cl	0.67	10.8	−23
Br	10.5	12.0	−14
I	fast	—	—

reaction [28]. Preliminary studies on $CH_3Ir(CO)(O_2)(PPh_3)_2$ indicate interesting oxygen transfer reactions [29].

C. OXIDATIVE ADDITION

(i) Hydrogen addition

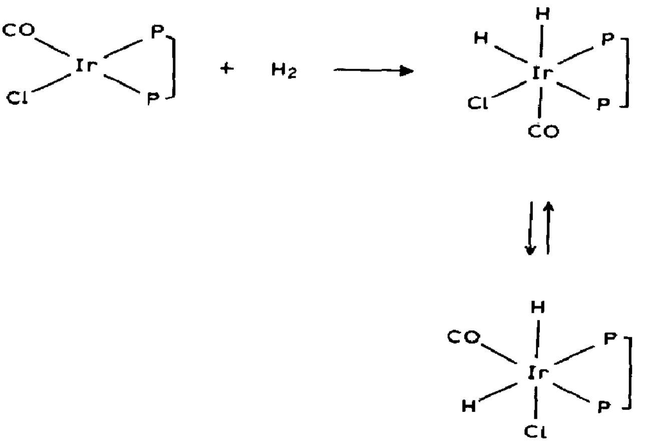
Dihydrogen adds to square planar complexes, *trans*-Ir(CO)(PPh$_3$)$_2$X, in a *cis* stereochemistry [7].



(20)

Kinetic data for H_2 addition given in Table 3 show that the basicity is important [22,30]. A three-center transition state is suggested with the hydrogen–hydrogen bond weakened both by donation of the σ-bond density to a metal p_z orbital and by electron transfer from a d_{xz} or d_{yz} metal orbital into the antibonding orbital. Temperature dependence of the kinetic isotope effect also indicated a three center transition state with substantial hydrogen tunneling [31].

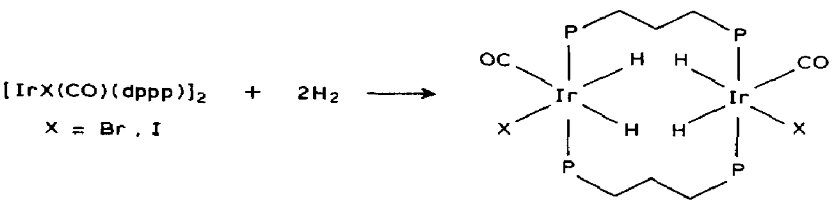
More recent work on Ir(dppe)(CO)Cl has shown that the kinetic isomer initially formed rearranges to the thermodynamic isomer [32,33]



(21)

The stereoselectivity is suggested to arise from electronic properties of the CO and Cl^- ligands. Similar studies on Ir(chiraphos)(CO)Br show a very small influence of the chiraphos ligand on the stereoselectivity of H_2 addition [33]. Electronic effects on the stereoselectivity of H_2 addition were also examined for the complex, $Ir(cod)(Ph_2POCH_2CH_2PPh_2)^+$ which produced exclusively the dihydride with one hydride *trans* to the diphenylphosphino end of the chelating ligand [34].

Use of a binuclear complex to oxidatively add two molecules of H_2 has been reported [35]



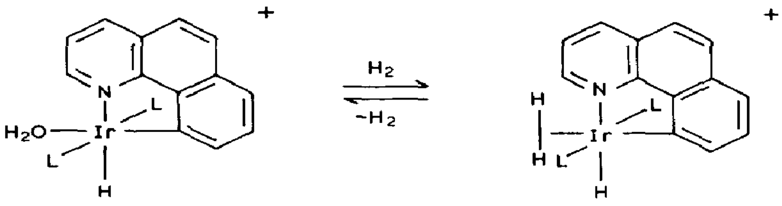
(22)

dppp = $Ph_2PCH_2CH_2CH_2PPh_2$

The reaction of the iodo complex proceeds to completion in an hour and that of the bromo complex requires 24 h, consistent with results on mononuclear complexes as shown in Table 3. The hydrogen addition shown in eqn. (22) is not reversible; warming causes cleavage to mononuclear products [35].

Addition of H_2 to iridium(I) complexes, $Ir(cod)(PPh_3)(RCN)$ (R = Me or aryl), has been instrumental in suggesting the concept of reductive addition of dihydrogen [36]. The ^{13}C resonances of the olefinic carbon atoms on cod indicate an increase in electron density at the iridium which suggests a reductive character to the H_2 addition.

Molecular hydrogen bonding to iridium complexes has also been reported [37]



(23)

L = PPh_3

That the H–H bond remains intact is shown by the magnitude of H–D coupling (29.5 Hz) when the H–D complex is formed [37]. The coordinated H_2 and H are fluxional at room temperature indicating that the molecular H_2 may be in equilibrium with the oxidatively added form.

(ii) Alkyl halide addition

Use of iridium complexes has been instrumental in determining the possible mechanisms of oxidative addition of alkyl halides to metal complexes: such reactions are involved in alcohol homologation. The addition of CH_3I shows some mechanistic differences to those of the addition of H_2 and O_2. The reaction leads to a *trans* distribution of CH_3 and I and has more negative entropies of activation [22,30]. The rate of addition to *trans*-$Ir(CO)L_2Cl$ was dependent on the ligand L as shown in Table 4. The dependence on L is consistent with the basicity of the metal being important to the rate of oxidative addition. However, the dependence on the X group of the rate of oxidative addition of CH_3I to *trans*-$Ir(CO)(PPh_3)_2X$ shows an order which is the reverse of that observed for addition of H_2 and O_2 and opposite to that expected from the basicity [38], as can be seen in Table 5. It has been suggested that steric interactions are responsible for the reversal in the dependence on X [1].

The reactions of alkyl halides with sixteen electron complexes of iridium, $Ir(CO)L_2X$, occur by nucleophilic attack of the iridium on the alkyl halide or by radical reactions [3]. Which mechanism is involved depends on L_2, X

TABLE 4

Dependence on L for the oxidative addition of CH_3I to *trans*-$Ir(CO)L_2Cl$ [22,30]

L	k_2 (M^{-1} s^{-1})
$P(OPh)_3$	1.7×10^{-5}
PPh_3	3.5×10^{-3}
P(*p*-tolyl)$_3$	1.0×10^{-2}
PEt_3	2.9×10^{-2}
PMe_2Ph	5.0×10^{-2}

TABLE 5

Second order rate constants for the addition of CH_3I to *trans*-$Ir(CO)PPh_3)_2X$ at 25 ° C [38]

X	k_2 (M^{-1} s^{-1})
NCO	1.06×10^{-3}
N_3	3.57×10^{-3}
NCS	1.90×10^{-4}
F	2.18×10^{-2}
Cl	3.5×10^{-3}
Br	1.6×10^{-3}
I	0.9×10^{-3}

TABLE 6

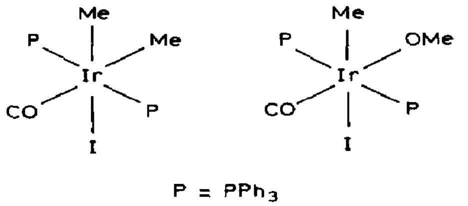
Effect of phosphine ligands on reactions of alkyl halides with $IrCl(CO)L_2$ [42]

L	Radical reaction (% of reaction) [a]	Nucleophilic attack (M^{-1} s^{-1}) [b]
PMe_3	100 (< 30 min)	5.0×10^{-2}
PMe_2Ph	100 (5 h)	1.6×10^{-2}
$PMePh_2$	10 (1 week)	3.5×10^{-3}

[a] RX = $PhCHFCH_2Br$. [b] RX = MeI.

and RY. For L = PMe_3 and X = Cl, reactions of methyl, benzyl and alkyl halides and α-haloethers proceeded by nucleophilic attack, while other saturated halides, vinyl and aryl halides and α-haloesters showed characteristics consistent with a radical chain pathway [39–42]. For radical mechanisms the phosphine ligand has a large effect on the rate [42] as is shown in Table 6.

Complexes *trans*-$Ir(CO)L_2X$, with X = Me or OMe, also undergo oxidative addition with alkyl halides. Addition of MeI leads to stable Ir(III) complexes [9,43].



Reaction with other alkyl halides leads to carbon–carbon and carbon–oxygen bond-forming reactions which will be discussed in a later section.

Acyl halides also undergo oxidative addition reactions with Ir(I) complexes leading to acyl iridium complexes, which are usually difficult to decarbonylate [44].

$$trans\text{-}Ir(CO)L_2Cl + RC(O)Cl \rightarrow RC(O)Ir(CO)L_2Cl_2 \qquad (24)$$

These reactions depend on the basicity of the metal and on the nature of R. For L = PPh_3, acetylchloride gives the six-coordinate acyl which is extremely susceptible to hydrolysis [43].

$$trans\text{-}Ir(CO)(PPh_3)_2Cl + CH_3C(O)Cl \rightarrow CH_3C(O)Ir(CO)(PPh_3)_2Cl_2$$

$$\xrightarrow{H_2O} HIr(CO)(PPh_3)_2Cl_2 + CH_3C(O)OH \qquad (25)$$

In contrast benzoylchloride does not react with *trans*-$Ir(CO)L_2Cl$ when L = PPh_3, but forms stable adducts with more basic ligands such as L =

P(p-tolyl)$_3$ or $PMePh_2$ [44]. These 18 electron complexes do not undergo decarbonylation except under forcing conditions (the benzoyl complex could be decarbonylated in refluxing xylene), presumably because of slow ligand dissociation from an octahedral Ir(III) complex. Use of *trans*-$Ir(N_2)(PPh_3)_2Cl$ for acid chloride additions led to an intermediate acyl complex which decarbonylated to the alkyl [44].

$$\textit{trans}\text{-}Ir(N_2)(PPh_3)_2Cl + RC(O)Cl \xrightarrow{-N_2} [Ir(C(O)R)(PPh_3)_2Cl_2] \rightarrow RIr(CO)(PPh_3)_2Cl_2 \qquad (26)$$

The lifetime of the intermediate acyl depends on the nature of R; for R = Me or Ph the acyl could not be observed, for R = Et or benzyl it was characterized spectroscopically [44].

(iii) Carbon–hydrogen bond activation

Iridium complexes have played a very important role in the activation of carbon–hydrogen bonds. Studies of $H_5Ir(PMe_3)_2$ showed catalysis of HD exchange between D_2 and benzene in some of the earliest studies [45,46]. Complexes of formula Cp*IrL oxidatively add carbon–hydrogen bonds of alkanes and arenes [47,48]. These compounds are prepared by photolysis of the dihydride ($Cp^*Ir(PMe_3)H_2$) or the dicarbonyl ($Cp^*Ir(CO)_2$) in the presence of hydrocarbons [47,48].

$$Cp^*Ir(PMe_3)H_2 \xrightarrow[-H_2]{h\nu} [Cp^*Ir(PMe_3)] \xrightarrow{RH} Cp^*Ir(PMe_3)(R)(H) \qquad (27)$$

$$Cp^*Ir(CO)_2 \xrightarrow[-CO]{h\nu} [Cp^*Ir(CO)] \xrightarrow{RH} Cp^*Ir(CO)(R)(H) \qquad (28)$$

The selectivity of the C–H activation was measured for [$Cp^*Ir(PMe_3)$] and is shown in Table 7 [49]. Recently a detailed examination of the reversible C–H activation and reductive elimination of alkane has been reported [50]

$$Cp^*Ir(PMe_3)(Cy)H + C_6H_6 \rightleftharpoons Cp^*Ir(PMe_3)(Ph)H + C_6H_{12} \qquad (29)$$

where Cy is cyclohexyl and Ph is phenyl. The rate of the forward reaction is first order in $Cp^*Ir(PMe_3)(Cy)(H)$, zero order in C_6H_6 and inhibited by C_6H_{12}. The activation parameters are $\Delta H^{\neq} = 35.6$ kcal mol^{-1} and $\Delta S^{\neq} = 10$ e.u. [50]. The reaction mechanism was suggested as reversible cyclohexane elimination, followed by benzene addition, with possible intermediacy of a cyclohexane–iridium complex [50]. Such a molecular complex has also been implicated in iridium activation of silicon–hydrogen bonds [5].

An extensive area of research has developed around $IrH_2S_2L_2^+$ complexes where S is a solvent and L is a phosphine [52–54]. These complexes dehydrogenate cyclic alkanes and cyclic alkenes. For example, cyclopentane is dehydrogenated to cyclopentadienyl and cyclohexanes to arenes.

$$IrH_2S_2(PPh_3)_2^+ + C_5H_{10} \xrightarrow{80\,^\circ C} CpIrHL_2^+ \qquad (30)$$

TABLE 7

Relative rate of C–H activation by [Cp* $IrPMe_3$] [49]

Hydrocarbon	Rel. rate
Benzene	4.0
Cyclopropane	2.65
Cyclopentane	1.6
Neopentane	1.14
Cyclohexane	1.0
Cyclodecane	0.23
Cyclooctane	0.09

The addition of a base allowed the dehydrogenation of cyclooctane to become catalytic, though with only a few turnovers [54].

Use of an iridium complex, $IrH_3(CO)(dppe)$, provided a route for the photochemical carbonylation of benzene [55,56]

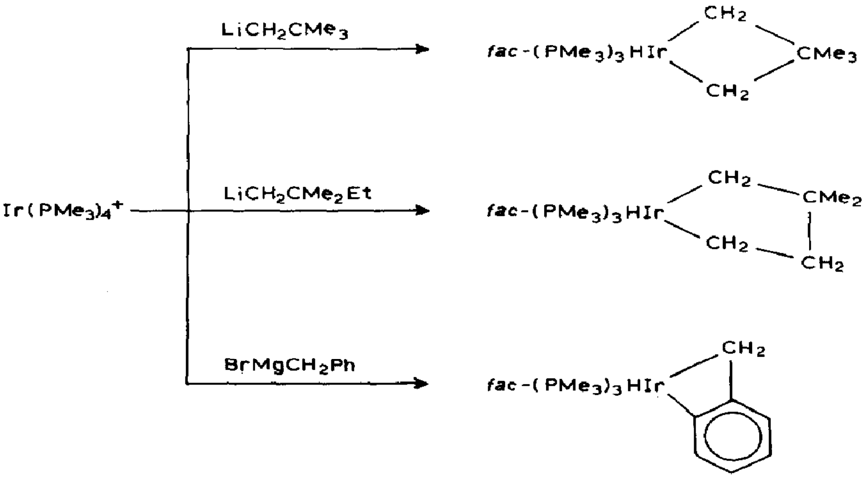
$$C_6H_6 + CO \xrightarrow[h\nu,CO]{H_3Ir(CO)dppe} C_6H_5CHO \qquad (31)$$

It was suggested that loss of H_2 occurs, a C–H bond is oxidatively added and carbonylated, and the product is provided by reductive elimination [55,56]. Iridium complexes have also been used to decarbonylate aldehydes; a decarbonylation has been demonstrated in the addition of aldehydes to $Cp^*IrMe_2(DMSO)$ [57].

$$Cp^*IrMe_2(DMSO) + RCHO \rightarrow Cp^*Ir(Me)(R)(CO) + CH_4 + DMSO \qquad (32)$$

The product is formed by loss of DMSO, oxidative addition of the C–H bond of the aldehyde, reductive elimination of CH_4 and decarbonylation [57].

Distal carbon–hydrogen activation has also been demonstrated on iridium complexes [58]. Usually these reactions lead to a metallocyclic product.

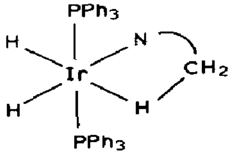


(33)

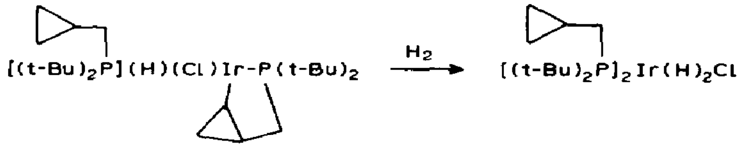
(34)

(35)

These reactions indicate that different types of carbon–hydrogen bonds can be activated. The formation of the observed product in the second reaction in > 95% yield indicates a selectivity in distal C–H activation [58]. An intermediate in such intramolecular carbon–hydrogen activation could involve a bridging hydrogen between a carbon and a metal [59]. Such an intermediate has been isolated for $[H_2IrL(PPh_3)_2]^+$ (L = 8-methylquinoline).



When $(t\text{-}Bu)_2PCH_2CHCH_2CH_2$ is reacted with $[IrCl(COD)_2]_2$, a σ-bonded cyclopropane is formed [60]



(36)

This C–H bond activation could be readily reversed by addition of H_2 [60].

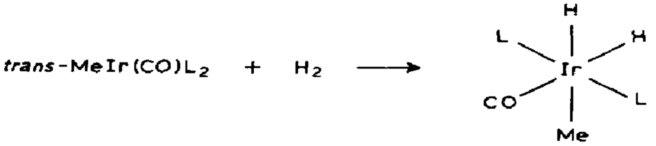
D. REDUCTIVE ELIMINATION

That reductive elimination reactions can be modeled by appropriate iridium compounds was demonstrated by the reversible reaction of *trans*-$Ir(CO)(PPh_3)_2Cl$ with H_2 [7]. The reverse of reaction (20) is the reductive elimination of H_2 from the iridium(III) compound. The scope of the reductive elimination reactions on iridium was significantly expanded by the synthesis of alkyl and alkoxy complexes, *trans*-$RIr(CO)(PPh_3)_2$ and *trans*-$ROIr(CO)(PPh_3)_2$, respectively [9,61]. These complexes oxidatively add H_2 and then eliminate alkane or alcohol [20]

$$\textit{trans}\text{-}RIr(CO)(PPh_3)_2 + 2\ H_2 \rightarrow H_3Ir(CO)(PPh_3)_2 + RH \tag{37}$$

$$\textit{trans}\text{-}ROIr(CO)(PPh_3)_2 + 2\ H_2 \rightarrow H_3Ir(CO)(PPh_3)_2 + ROH \tag{38}$$

For alkyl complexes the oxidative addition occurs readily at low temperature and the intermediate can be intercepted



(39)

The geometry is shown by two triplets for the hydrides in the ^1H NMR spectrum [62]. Such a complex has been prepared as the trifluoromethyl analogue, by a borohydride reduction of $[Ir(CF_3)Cl(MeCN)(CO)(PPh_3)_2]$. For this case the hydrides are *trans* [63]. Other hydrogen sources can also effect alkane or alcohol elimination

$$trans\text{-}MeIr(CO)L_2 + HC{\equiv}CPh \rightarrow trans\text{-}PhC{\equiv}C{-}Ir(CO)L_2 + CH_4 \qquad (40)$$

$$trans\text{-}MeOIr(CO)(PPh_3)_2 + HC{\equiv}CPh$$
$$\rightarrow trans\text{-}PhC{\equiv}CIr(CO)(PPh_3)_2 + MeOH \qquad (41)$$

In these reactions, the hydrogen on phenylacetylene is transferred to the group originally on iridium and the iridium acetylide is formed [62]. That phenylacetylene is coordinated prior to oxidative addition is indicated by the formation of the acetylene coordination product and the oxidative addition product upon addition of phenylacetylene to $[IrCl(P(i\text{-}Pr)_3)_2]$ [64]

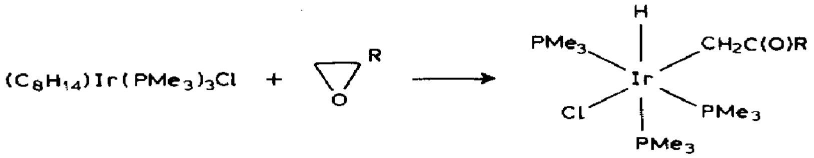
$$[IrCl(P(i\text{-}Pr)_3)_2] \xrightarrow{HC\equiv CPh} Ir(HC{\equiv}CPh)(Cl)(P(i\text{-}Pr)_3)_2$$
$$+ Ir(H)(C{\equiv}CPh)(Cl)(P(i\text{-}Pr)_3)_2 \qquad (42)$$

The mixture could be driven to the oxidative addition product by the addition of pyridine [64]. In contrast to the ready C–H bond formation from addition of hydrogen to *trans*-$MeIr(CO)(PPh_3)_2$, is the failure to eliminate methane on protonation of the electron rich Ir(I) complex, $MeIr(dppe)_2$ [65]

$$MeIr(dppe)_2 + HBF_4 \rightarrow [cis\text{-}Ir(Me)(H)(dppe)_2^+][BF_4^-] \qquad (43)$$

The slowing of reductive elimination by electron donor ligands on the metal is also shown by the characterization of *cis*-$HIr(Me)(PMe_3)_4^+$ [66].

Oxidative addition of Ir(I) to epoxides has resulted in isolation of *cis*-hydrido alkyl complexes [67]



(44)

These complexes did not undergo reductive elimination of the ketone even on heating to 100 ° C. This lack of reactivity was attributed to the necessity for a coordination site and the reluctance of the strongly binding PMe_3 to dissociate [67].

Reductive elimination of alcohol from an alkoxy, hydride complex has been reported [68]. It was suggested that a mechanism of ring-slippage or alkoxide attack on the ring was operative [68]

$$Cp^*Ir(PPh_3)(H)(OEt) \xrightarrow{L} Cp^*Ir(PPh_3)L + EtOH \qquad (45)$$

$$L = C_6H_6,\ CO,\ PPh_3$$

The alkyl and alkoxy iridium complexes can also be used to model carbon–carbon and carbon–oxygen bond-forming reactions through reactions with alkyl halides [9,43,69]. The nature of the product depends on R and R′

$$\mathrm{RIr(CO)L_2 + R'X \rightarrow [RR'Ir(CO)L_2X]} \qquad (46)$$

where R = Me, Ph, OMe; L = PPh_3, $P(p\text{-}C_6H_4OMe)_3$; R′ = Me, $CH_3C(O)$, Et; X = Cl, I. For R = Me and R′ = $CH_3C(O)$, X = Cl, acetone is formed with *trans*-$Ir(CO)(PPh_3)_2Cl$; for R = Ph and R′ = Me, X = I, toluene is formed with *trans*-$Ir(CO)(PPh_3)_2I$; for R = OMe and R′ = $CH_3C(O)$, X = Cl, $CH_3C(O)OMe$ is formed with *trans*-$Ir(CO)(PPh_3)_2Cl$; while for R = Me or OMe and R′ = Me, X = I, stable adducts are formed which do not eliminate C_2H_6 or $(CH_3)_2O$ [43,69]. Addition of alkylhalides to *trans*-MeIr $(CO)(PMe_3)_2$ also leads to dialkyl iridium complexes which do not eliminate alkanes [70]. This failure to eliminate was attributed to the difficulty in opening a coordination site with the strongly binding PMe_3 groups [70]. Similar reasoning may apply to the failure to eliminate CH_3OH from $HIr(CH_2OH)(PMe_3)_4^+$ [71], but is not readily applicable to the failure to eliminate C_2H_6 from $(CH_3)_2Ir(CO)(PPh_3)_2I$ since other groups can be readily reductively eliminated.

E. TRANSFORMATIONS

We have thus far examined the role of iridium complexes in modeling ligand binding, in oxidative addition reactions and in removal of groups from the iridium by reductive elimination reactions. Now we will examine the transformations which occur on iridium that may be pertinent to catalytic reactions. We will examine carbonylation of carbon and oxygen bonds, methylene insertions, β-elimination reactions and alkyne coupling.

(i) Carbonylations

Carbonylation of alkyl bonds has been studied on many metal centers, but added impetus is placed on iridium because of the importance of rhodium analogues in hydroformylation reactions [72,73]. Iridium species such as *trans*-$RIr(CO)(PPh_3)_2$, $RIr(CO)_2(PPh_3)_2$ and $RC(O)Ir(CO)_2(PPh_3)_2$ are direct models of species thought to be involved in hydroformylation by $HRh(CO)_2(PPh_3)_2$ [73]. For R = Me these complexes are readily formed by reaction of *trans*-$MeIr(CO)(PPh_3)_2$ with CO [9].

$$trans\text{-}\mathrm{MeIr(CO)(PPh_3)_2 \xrightarrow{CO} MeIr(CO)_2(PPh_3)_2 \xrightarrow{CO} MeC(O)Ir(CO)_2(PPh_3)_2} \qquad (47)$$

Each of these species may be isolated depending on the experimental conditions. The rapidity of the reactions (CO adds at −78 °C) has precluded detailed examination of the mechanism [9].

Carbonylation of metal–oxygen bonds is important in reactions such as carboalkoxylation of alkenes but has not been examined as frequently as carbonylation of metal–alkyl bonds. The alkoxy complexes, *trans*-$ROIr(CO)(PPh_3)_2$, have allowed carbonylation of iridium alkoxide bonds to be examined [61,74]. Reaction with CO leads to the carboalkoxydicarbonyl product, $ROC(O)Ir(CO)_2(PPh_3)_2$

$$trans\text{-}ROIr(CO)(PPh_3)_2 + 2\ CO \rightarrow ROC(O)Ir(CO)_2(PPh_3)_2 \qquad (48)$$

While the product of the carbonylation of the alkoxides is similar to that for carbonylation of the methyl complex, there are differences: (1) the carboalkoxy product is not readily decarbonylated for nucleophilic alkoxides; and (2) the mechanism of the carbonylation involves loss of OR^- from the iridium coordination sphere. When the carbonylation is done at low temperature or in the presence of $NaBPh_4$, the cation, $Ir(CO)_3(PPh_3)_2^+$ can be isolated. This cation reacts rapidly with nucleophilic alkoxides (OMe^-, OPr^-), somewhat slower with the less nucleophilic OPh^- and not at all with $OC_6F_5^-$. The following sequence has been suggested for carbonylation of these iridium alkoxides [61]

$$trans\text{-}ROIr(CO)(PPh_3)_2 + CO \rightleftharpoons ROIr(CO)_2(PPh_3)_2 \qquad (49)$$

$$ROIr(CO)_2(PPh_3)_2 + CO \rightleftharpoons Ir(CO)_3(PPh_3)_2^+ + OR^- \qquad (50)$$

$$Ir(CO)_3(PPh_3)_2^+OR^- \rightleftharpoons ROC(O)Ir(CO)_2(PPh_3)_2 \qquad (51)$$

Such a reaction where a hard base dissociates from a soft-metal center and then attacks a coordinated ligand may prove to be important in several catalytic reactions.

(ii) *β-Elimination reactions*

β-Elimination is important in catalytic isomerization and Wacker chemistry. The thermal decomposition of alkyl iridium complexes has contributed significantly to our understanding of β-elimination [75–77]. A kinetic study of the decomposition of (n-octyl)$Ir(CO)(PPh_3)_2$ showed a deuterium isotope effect of 2.28 [76]. A detailed examination of the product distribution from *trans*-alkyl $Ir(CO)(PPh_3)_2$ complexes allowed the scheme below to be suggested [77].

$$\begin{tikzcd}
(n\text{-octyl})Ir(CO)L_2 \arrow[r, rightleftharpoons] \arrow[d, shift right, "-L"'] & HIr(1\text{-octene})L_2(CO) \arrow[r, rightleftharpoons, "-1\text{-octene}"] & HIr(CO)L_2 \arrow[d, shift right, "+L"'] \\
(n\text{-octyl})Ir(CO)L \arrow[u, shift right, "+L"'] \arrow[d, shift right] & & HIr(CO)L_3 \arrow[u, shift right, "-L"'] \\
HIr(1\text{-octene})(CO)L \arrow[u, shift right] \arrow[d, shift right] & & \\
\text{isomerization} \arrow[u, shift right] & &
\end{tikzcd} \tag{52}$$

Alkane was formed in a binuclear reductive elimination. In the presence of excess L only 1-octene was observed for the octyl complex, while in the absence of excess L isomerized octene was observed [77].

A similar β-elimination has been implicated in the thermal decomposition of alkoxides which have a hydrogen β to the metal [78].

$$trans\text{-}RCH_2OIr(CO)(PPh_3)_2 \xrightarrow{PPh_3} HIr(CO)(PPh_3)_3 + RCHO \tag{53}$$

This decomposition path is available for the n-propoxy complex (propionaldehyde product) and for the i-propoxy complex (acetone product). Such reactions are important in the transfer of hydrogen from alcohols to aldehydes.

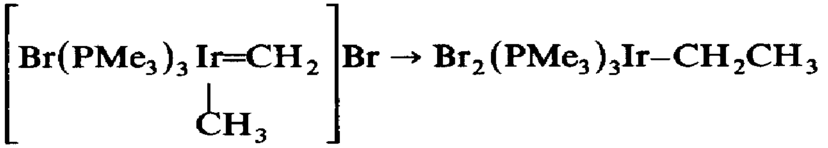
There has also been the observation of α-hydrogen elimination from iridium alkyl complexes, initiated by photolysis [79].

$$\begin{aligned}(NPP)Ir(Me)(CH_2CMe_3) \rightarrow NPPIrH_2 + NPPIr{=}CH_2 + CMe_4 \\ + H_2C{=}CHCMe_3\end{aligned} \tag{54}$$

where NPP = $N(SiMe_2CH_2PPh_2)_2$, a tridentate ligand. While mechanistic details are unknown, an α-elimination seems most reasonable.

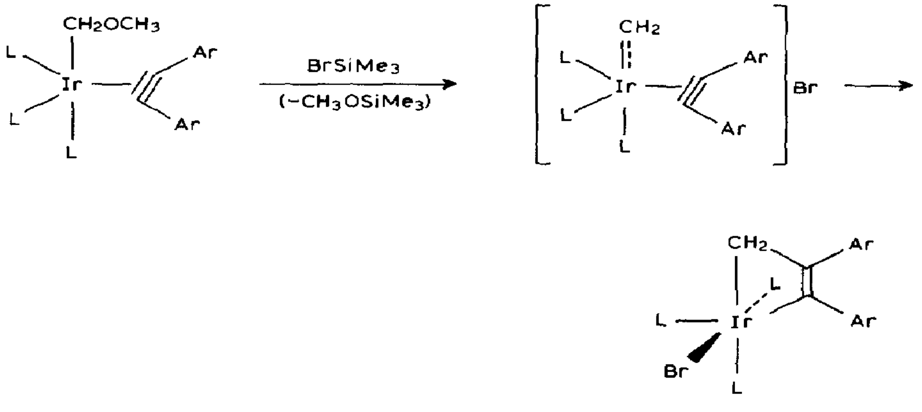
(iii) Transformations related to CO reduction

$Ir_4(CO)_{12}$ has been shown to be an effective catalyst for CO hydrogenation to methanol and methylformate [80]. In addition, mononuclear iridium centers have been used to demonstrate steps which may be important in CO reduction [66,81–83]. Combination of a methyl and methylidene to give an ethyl group has been observed [81]



$$\left[\begin{array}{c} Br(PMe_3)_3\overset{}{Ir}{=}CH_2 \\ \quad | \\ \quad CH_3 \end{array}\right]Br \rightarrow Br_2(PMe_3)_3Ir{-}CH_2CH_3 \tag{55}$$

This reaction involving C–C formation, which occurs readily, is in contrast to the difficulty in forming carbon–carbon bonds from the related dimethyl complex [70]. A slightly different form of carbon–carbon bond formation is observed between a methylidene and an acetylene with iridacyclobutane formation [84].



L = PMe3 , Ar = p-tol

(56)

Combination of an allyl and an acetylene to a cyclopentadiene has been reported on iridium [85]. The reaction of CpIr(η^3-C_3H_5)Cl with $AgBF_4$, followed by treatment with C_2Ph_2 gave CpIr(η^5-$C_5H_3Ph_2$)$^+$ [85].

$$\mathrm{CpIr}(\eta^3\text{-}C_3H_5)\mathrm{Cl} \xrightarrow{AgBF_4} \xrightarrow{C_2Ph_2} \mathrm{CpIr}(\eta^5\text{-}C_5H_3Ph_2)^+ \qquad (57)$$

The sequence from formyl → hydroxymethyl → methyl, which is quite important to CO reduction chemistry, has been demonstrated on iridium [66,82]:

$$L_4\mathrm{Ir(H)(C(O)H)}^+ \xrightarrow[THF/H_2O]{NaBH_4} L_4\mathrm{Ir(H)(CH_2OH)}^+ \xrightarrow{BH_3/THF} L_4\mathrm{Ir(H)(CH_3)}^+ \qquad (58)$$

where L = PMe_3. The formyl hydride was prepared by oxidative addition of $H_2C(O)$ to $[Ir(PMe_3)_4]^+$ and the subsequent reductions utilized boronhydrides. Protonation of the formyl hydride in CH_3CN solution led directly to the hydroxymethyl, $[Ir(PMe_3)_4(CH_2OH)(CH_3CN)]^{2+}$ [86]

$$\mathrm{Ir(PMe_3)_4(CHO)(H)}^+ \xrightarrow{HBF_4} \mathrm{Ir(PMe_3)_4(CH_2OH)(CH_3CN)}^{2+} \qquad (59)$$

Thus the formyl hydride complex can be converted to a hydroxymethyl complex by H^+ or by H^-.

A hydroxyacetyl complex of iridium has been prepared as a model for the formation of oxygenated products from CO reduction [83].

$$(C_8H_{14})\mathrm{Ir(PMe_3)_3Cl} + \mathrm{HOCH_2C(O)H} \rightarrow \mathrm{Cl(PMe_3)_3Ir(H)(C(O)CH_2OH)} \qquad (60)$$

Activation of CO for attack by nucleophiles is readily accomplished by forming cationic iridium carbonyl complexes. The early work on $[Ir(CO)_3(PPh_3)_2]^+$ [87] (eqn. 61) has been expanded by reactions with cations such as $[cis\text{-}IrX(CO)(dppe)_2]^{2+}$ [88] (eqn. 62).

$$[Ir(CO)_3(PPh_3)_2]^+ \xrightarrow{OMe^-} MeOC(O)Ir(CO)_2(PPh_3)_2 \tag{61}$$

$$[cis\text{-}IrX(CO)(dppe)_2]^{2+} \xrightarrow[-70\,^\circ C]{LiBEt_3H} [Cl(dppe)_2IrC(O)H]^+ \tag{62}$$

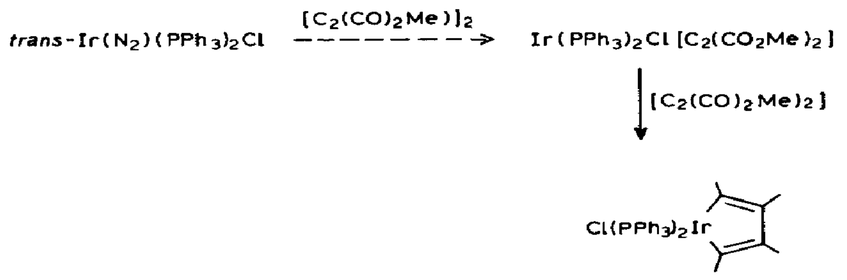
Other nucleophiles may also be utilized.

(iv) Oligomerization reactions

Iridium complexes serve as models and actual catalysts for acetylene trimerization and the aldehyde dimerization known as Tischenko chemistry [20]. Activated acetylenes can be readily bound to 16-electron iridium centers, as described in an earlier section:

$$trans\text{-}RIr(CO)(PPh_3)_2 + C_2R'_2 \rightarrow RIr(C_2R'_2)(CO)(PPh_3)_2 \tag{63}$$

where R = Cl, I, Me, OMe. For R = Cl or I, no further chemistry has been observed unless the CO is replaced by N_2 [16,19]

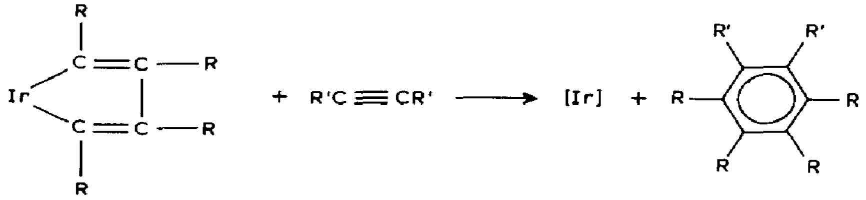


(64)

The metallocyclopentadiene was isolated and characterized. This complex was active in the cyclotrimerization of $[C_2(CO_2Me)_2]$ in boiling toluene. The inhibition by CO and the failure of the carbonyl analogues to function as a catalyst indicated the necessity for a second coordination site on the iridium [19]. In contrast, the methyl complex, $trans\text{-}CH_3Ir(CO)(PPh_3)_2$, functions as an active catalyst for acetylene trimerization under ambient conditions at 300 turnovers h^{-1}. For the methyl complex, a second coordination site may be opened by a methyl migration. Evidence for such a reaction is shown by the rearrangement of the neopentyl adduct [18]

$$\begin{aligned} &Me_3CCH_2Ir[C_2(CO_2Me)_2](CO)(PPh_3)_2 \\ &\quad\rightarrow Me_3CCH_2C(O)Ir[C_2(CO)_2Me)_2](PPh_3)_2 \end{aligned} \tag{65}$$

The neopentyl complex is much slower as a catalyst, indicating the importance of steric effects in the trimerization. An important question in acetylene trimerization is the mode of addition of the third acetylene. The failure of the metallocyclopentadiene to react with maleic anhydride was used to exclude a Diels–Alder reaction [19]. However, for the methyl complex addition of an acetylene which is not coordinated or cyclotrimerized by itself leads to incorporation of one acetylene into the substituted benzene



(66)

Thus in this case, coordination may not be required and a Diels–Alder step could be occurring.

F. CONCLUSION

Iridium complexes have made and continue to make important contributions to our understanding of organometallic reactions. The earlier work on molecular binding to iridium is now shifting towards emphasis on transformations which may occur, with expectations of isolating complexes along the reaction coordinate. The combination of structural stability and kinetic inertness allows many "intermediates" to be isolated and examined. We may expect the use of iridium complexes as models for catalytic reactions to continue for many years.

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