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POLYNUCLEAR IRIDIUM HYDRIDO COMPLEXES

TANIA M. GOMES CARNEIRO, DOMINIQUE MATT and PIERRE BRAUNSTEIN

Laboratoire de Chimie de Coordination, UA 416 CNRS, Université Louis Pasteur,
4 rue Blaise Pascal, F-67070 Strasbourg Cédex (France)

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CONTENTS

ABBREVIATIONS

bipy	2,2′-bipyridine
Bu	butyl
cod	cyclooctadiene
Cp	η^5-cyclopentadienyl
Cp′	η^5-pentamethylcyclopentadienyl
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
dppm	bis(diphenylphosphino)methane
Et	ethyl
Me	methyl
Ph	phenyl

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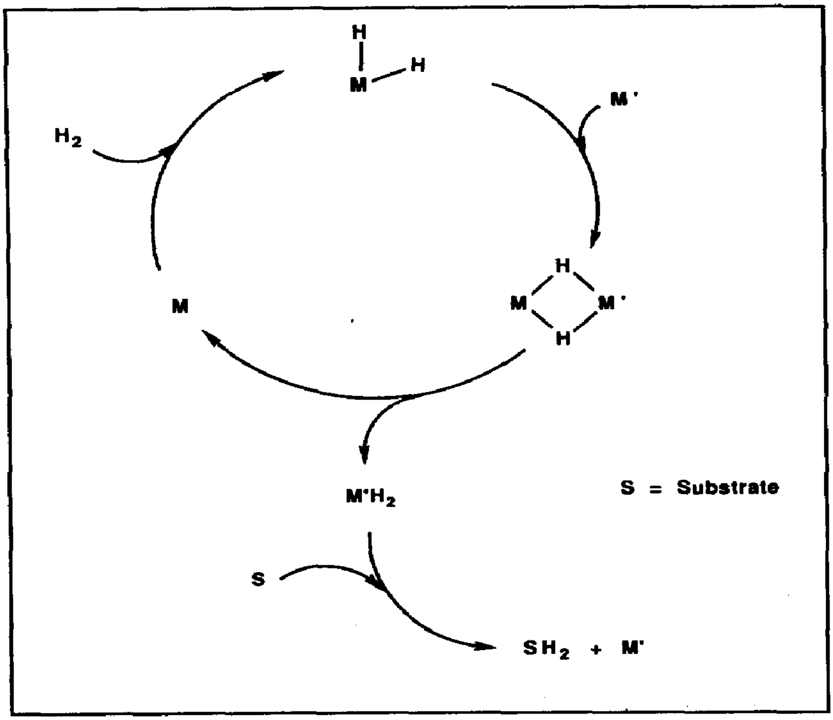
PN	1-(2-pyridyl)-2-(diphenylphosphino)ethane
Pr^i	isopropyl
Py	pyridine
THF	tetrahydrofuran
tolyl	$Me(C_6H_4)$
triphos	$MeC(CH_2PPh_2)_3$

A. INTRODUCTION

The increasing interest in hydrido complexes of the transition metals arises from their roles in many homogeneous catalytic processes, where they can be directly used as catalysts or can be invoked as key intermediates during the process. Iridium hydride complexes have proved to be the most active homogeneous hydrogenation catalysts. This might be thought surprising as it is well documented that the third row transition metals are catalytically less active than those of the first and second rows. In iridium hydride complexes the M–H bonds are thought to be stronger than those formed with the first and second row metals. These hydride complexes are stabilized by the presence of ligands, in most cases tertiary phosphines, where the basicity is as important a factor as the steric bulk.

An example of an iridium hydride complex used in a catalytic process is $[IrH_5(PPh_3)_2]$ which is a catalyst for the hydrogenation, isomerization, hydroformylation and disproportionation of olefins [1]. Also a variety of olefins can be catalytically hydrogenated using $[IrH_5(PPh_3)_2]$ in the presence of CF_3CO_2H, probably involving an intermediate such as $IrH_2(CF_3CO_2)(PPh_3)_2$ [2,3].

It is well known that when an organometallic complex contains two (or more) metals in sufficiently close proximity, the system can display, through mutual interactions, chemical and physical properties different from those observed in the mixing of corresponding mononuclear moieties. Bimetallic systems offer, at the same time, the possibility of bifunctional activation of an organic substrate, as well as that of concerted reactions progressing successively upon each of the metal centres. However, the interaction of the substrate molecule first with one centre could give rise to phenomena of synergy or allotropy, which could facilitate reactions with a second substrate molecule. These aspects are particularly important in the design of new bimetallic catalytic systems [4]. Hydrido-bridged bimetallic complexes could also be envisaged as intermediates in hydride transfer reactions between a mononuclear hydrido complex and a hydrido acceptor. This may lead to very efficient reagents for the selective reduction of unsaturated substrates such as for example AlH_2I which is generated in situ by reacting $LiAlH_4$ with CuI [5]. Furthermore, although they have been little exploited for



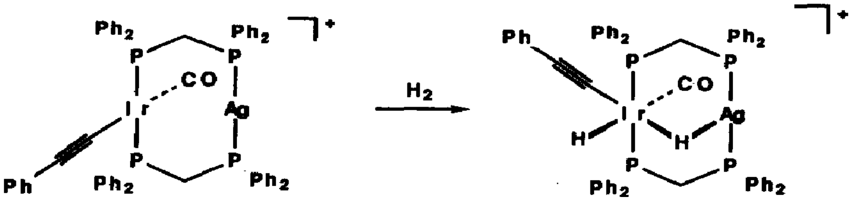
Scheme 1.

catalytic reactions, hydrido-bridged bimetallic systems are of considerable interest for such reactions, particularly if they associate a metal capable of reacting and transferring molecular hydrogen (for example rhodium or iridium) and another metal known to promote hydride formation and reduction of organic substrates (see Scheme 1).

By reacting stable metal hydride complexes with reagents containing metals such as copper, silver or gold, it is possible to generate and stabilize hydrido-bridged complexes of metals for which a mononuclear hydride is unknown or difficult to handle. This could offer the advantage of performing reactions with activated species.

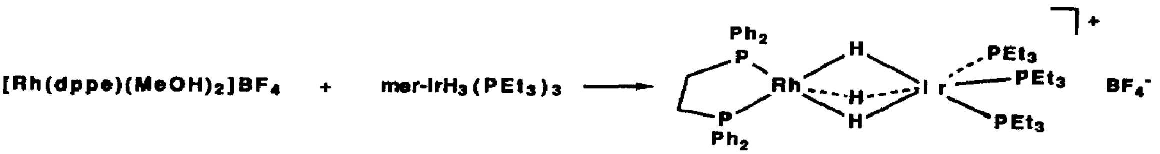
Several recent reviews have covered the areas of synthesis, spectroscopic and structural characterization and theoretical treatments of hydride complexes in considerable detail [1,6–11]. It is not proposed to discuss further these general areas here, and the reader is referred to these reviews for information. Here, we will be uniquely concerned with the binuclear or polynuclear hydride complexes of iridium, which may or may not display M–M bonding. These compounds are usually obtained by the following methods of synthesis: the action of molecular hydrogen on an appropriate substrate; the reaction of a hydride-containing donor complex with another metal acceptor centre; or by hydrogen elimination reactions from mononuclear polyhydrides. As the last method only concerns mononuclear complexes it will not be discussed further here. An example of each of the first two synthetic methods is outlined below.

The reaction of a bimetallic complex with molecular hydrogen is the less common of the two routes, and the degree of scope and flexibility in forming the metal framework is limited. In most cases the metal skeleton is already in place and the reaction with H_2 results either in the formation of hydride ligands on the metal centres or in an increase in the number of hydride ligands present in the molecule. An example is shown below:



The bridging nature of the hydride ligand was postulated on the basis of $^{31}P\{^1H\}$ and ^1H NMR data (see also eqn. (37)) [48].

The reaction of a hydride-containing donor complex with an acceptor complex is the more common and general synthetic route employed, as it allows the metal and hydride stoichiometries to be easily varied. Normally the donor and acceptor complexes are mononuclear in nature, but the reaction may give rise to a binuclear or polynuclear hydride complex. An example is illustrated below:



The bridging nature of the hydride ligands in this complex was inferred from NMR data as the ligands could not be located in the X-ray structural determination [16–18].

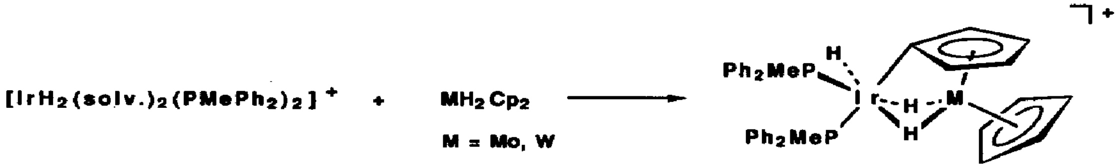
Binuclear and polynuclear hydride complexes of iridium are formed with transition metals from a wide range of groups in the Periodic Table. Examples can be found with metals from groups 6–12, although the large majority are to be found in groups 9, 10 and 11. The nuclearity of these complexes ranges from simple binuclear species through to pentanuclear complexes, although in all cases only one other metallic element, apart from iridium, is to be found in the complex. Both terminal and bridging hydride ligands may be present in this class of compound, where the number of hydrides so far observed ranges from one to seven. Obviously, in a given complex, both bonding modes (terminal and bridging) may be present simultaneously. However, there are no fixed rules for where the hydride ligand(s) will be found and which spectroscopic techniques need to be employed to elucidate this. Identification of the bonding mode of the hydride ligand(s) can be provided by IR and NMR, the latter normally proving the more useful spectroscopic method. Neutron diffraction is a powerful technique for the location of hydride ligands, but this technique relies on obtaining crystals of a suitable size, which is not always possible.

In the following, the complexes will be treated in group order in the Periodic Table and in order of increasing nuclearity. A listing of the complexes, together with some relevant information concerning selected bond lengths and/or spectroscopic data, is presented in Table 1.

B. BIMETALLIC IRIDIUM HYDRIDO COMPLEXES WITH GROUP 6 METALS

Examples of Ir–group 6 metal hydrido complexes have been reported with both molybdenum and tungsten. However, no example of an analogous chromium-containing complex was found in the literature.

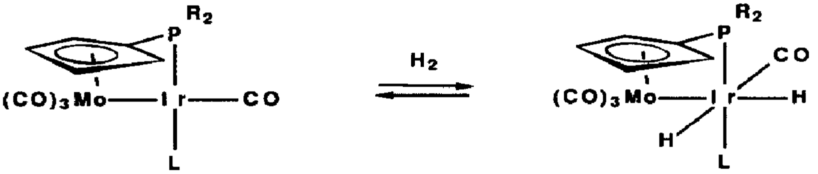
Reaction of solvento complexes $[Ir(H)_2(solvent)_2L_2]^+$ (L = PEt_3, PMe_2Ph, $PMePh_2$, PCy_3) with the hydrido complexes $[MH_2Cp_2]$ (M = W or Mo) yielded complexes of the type $[CpM(\mu\text{-}H)_2\{\mu\text{-}(\eta^5,\eta^1\text{-}C_5H_4)\}IrHL_2]^+$ (eqn. (1)) [12,13,15]:



(1)

The structures of the complexes where M = Mo, W and L = $PMePh_2$ have been determined using X-ray crystallographic methods [12]. Of note is the difference in the Ir–M bond distances (Ir–W = 2.706(1) Å, Ir–Mo = 2.641(1) Å). As the atomic radii of molybdenum and tungsten are comparable it is suggested that this is due to a stronger M–M interaction in the Ir–Mo complex. In the tungsten complex the two bridging hydrides and one terminal hydride were located by X-ray diffraction. Both the bridging distances (M = W; W–H = 1.8(1), 2.1(2) Å; Ir–H = 1.7(1), 2.1(1) Å) and the terminal distance (M = W, Ir–H = 1.5(1) Å) are in the normal range found for this class of complex. The hydrides were positioned by classical methods for the tungsten complex and for the molybdenum complex using potential energy calculations (HYDEX program) [22].

Bimetallic complexes of the type $[L(CO)Ir\{\mu\text{-}[P(p\text{-}MeC_6H_4)_2(C_5H_4)]\}\text{-}Mo(CO)_3]$ (L = CO, PMe_3 or PPh_3) react reversibly with H_2 to form iridium dihydrido complexes which were characterized by spectroscopic methods (eqn. (2)) [14]:

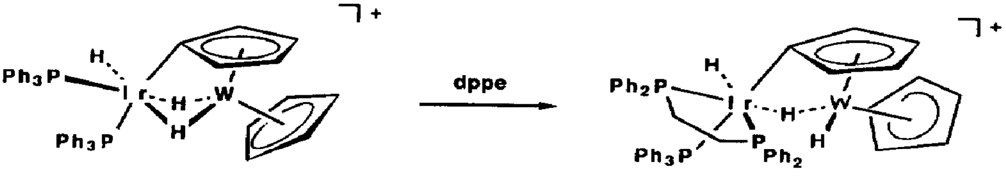


(2)

R = p-tolyl
L = CO, PPh₃, PMe₃

From the values of J(P–H) each hydride is thought to be *cis* with respect to two phosphines. All the compounds have different rates of formation, $PPh_3 < CO < PMe_3$, and here steric hindrance is thought to be an important factor.

A similar reaction with $[IrH_2(PPh_3)_2(acetone)_2]^+$ was carried out by Howarth et al. [15]. Addition of dppe to the tungsten-containing complex $[CpW(\mu\text{-}H)_2\{\mu\text{-}(\eta^5,\eta^1\text{-}C_5H_4)\}IrH(PPh_3)_2]$ yielded $[CpHW(\mu\text{-}H)\{\mu\text{-}(\eta^5,\eta^1\text{-}C_5H_4)\}IrH(PPh_3)(dppe)]$ which was characterized using X-ray crystallographic methods and ^1H NMR data (eqn. (3)):



(3)

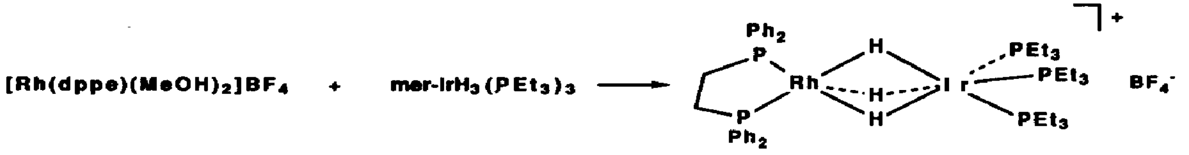
The nominally six-coordinate iridium(III) exhibits a distorted octahedral geometry, while that around tungsten is quite close to the expected pseudotetrahedral arrangement.

C. BIMETALLIC IRIDIUM HYDRIDO COMPLEXES WITH GROUP 9 METALS

(i) Complexes of stoichiometry IrM

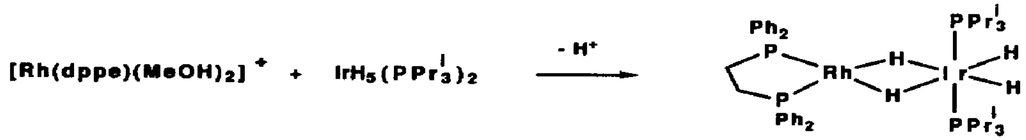
Venanzi and coworkers have synthesized a range of bimetallic Ir–Rh complexes with bridging hydride and chloride ligands. Some of these complexes also contain terminal hydride ligands. They reported that the reaction of $[(dppe)Rh(MeOH)_2]BF_4$ with $[IrH_3(PEt_3)_3]$ in the presence of $Na[BPh_4]$

yielded the binuclear triply hydrido-bridged complex [(dppe)Rh(μ-H)$_3$-Ir(PEt$_3$)$_3$][BPh$_4$] (eqn. (4)) [16–18]:



The positions of the hydride ligands could not be established by X-ray diffraction [16] and were inferred from ^{1}H NMR data. Of note is the rather short Ir–Rh distance (2.636(2) Å), suggesting a significant degree of M–M interaction. This can be attributed partly to the small size of the bridging hydrides and partly also to the residual positive charge on the complex.

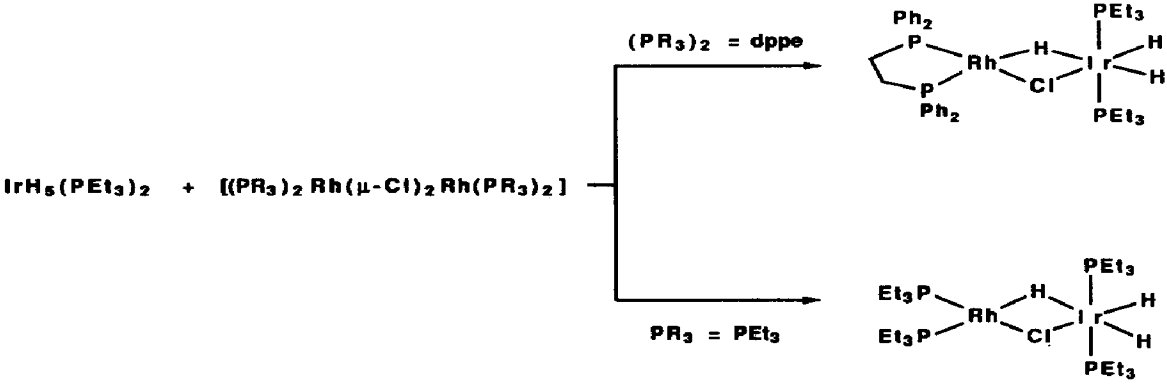
It was also reported that the reaction between [(dppe)Rh(MeOH)$_2$]$^+$ and [IrH$_5${PPr$^i_3$}$_2$] gave the dihydrido-bridged complex [(dppe)Rh(μ-H)$_2$IrH$_2${PPr$^i_3$}$_2$] (eqn. (5)) which was characterized by NMR and X-ray crystallographic methods [19]:



(5)

The positions of the hydride ligands were found using ^{1}H NMR spectroscopy as they could not be located using the X-ray data. The rhodium centre has the expected distorted square-planar geometry while the iridium exhibits distorted octahedral coordination with two phosphine ligands *trans* to each other. The coordination geometry is consistent with two bridging hydride ligands and two terminal hydride ligands in a planar arrangement. The M–M distance of 2.662(1) Å is again quite short.

The binuclear complexes [(PR$_3$)$_2$Rh(μ-H)(μ-Cl)IrH$_2$(PEt$_3$)$_2$] are formed in the reaction between [IrH$_5$(PEt$_3$)$_2$] and [(PR$_3$)$_2$Rh(μ-Cl)$_2$Rh(PR$_3$)$_2$] (PR$_3$ = PEt$_3$; 2PR$_3$ = dppe) (eqns. (6) and (7)) [17,20]:

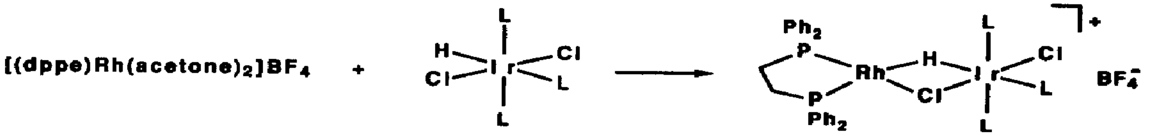


(6)

(7)

The structure of the complex with PEt_3 was determined by X-ray techniques. The Rh–Ir distance (2.899(1) Å) suggests only a weak M–M interaction, which is consistent with the presence of the larger chloride bridge. Some catalytic studies revealed that the complex with $2PR_3$ = dppe catalyses the hydrogenation of 1-hexene at room temperature under 5 atm H_2 [17].

In another publication the results of some reactions between $[(dppe)Rh(acetone)_2]BF_4$ and various phosphine-containing chlorohydrido iridium complexes were presented [18]. Thus the reaction between $[(dppe)Rh(acetone)_2]BF_4$ and *mer,trans*-$[IrHCl_2L_3]$ (L = PMe_2Ph, PEt_2Ph and PEt_3) yielded complexes of the type $[(dppe)Rh(\mu\text{-}H)(\mu\text{-}Cl)IrClL_3]BF_4$ (eqn. (8)):

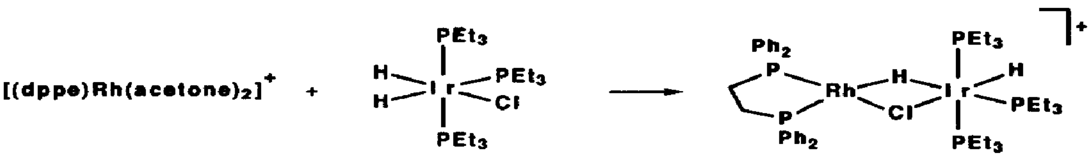


L = PMe₂Ph

L = PEt₂Ph

(8)

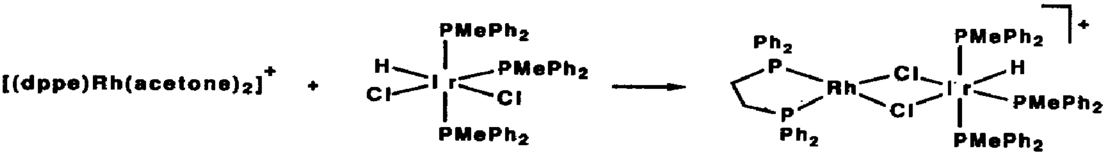
The structure of the complex with L = PEt_3 was determined by X-ray crystallography. Of note here is the unsymmetrical nature of the hydride bridge, as determined from the X-ray data. The M–H distances (Ir–H = 1.67(8) Å, Rh–H = 1.85(8) Å) support the argument that Ir–H bonds are stronger than those formed with first and second row metals. An isoelectronic complex $[(dppe)Rh(\mu\text{-}H)(\mu\text{-}Cl)IrH(PEt_3)_3]BF_4$ was synthesized from the reaction between $[(dppe)Rh(acetone)_2]BF_4$ and *mer,cis*-$[IrH_2Cl(PEt_3)_3]$ and characterized by X-ray diffraction (eqn. (9)):



(9)

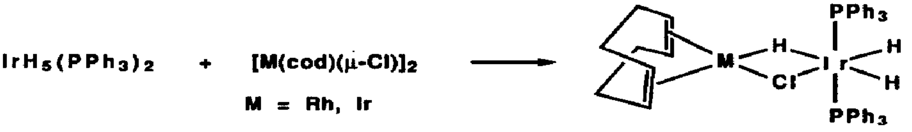
The hydride ligands were positioned using a computer program for calculating the minimum energy position. The distances are consistent with those for bridging (Ir–H = 1.80 for a fixed Rh–H = 1.80 Å value) and terminal (Ir–H = 1.61 Å) hydride ligands [18].

A point worth mentioning here is the symmetric nature of the chloride bridge in $[(dppe)Rh(\mu\text{-}H)(\mu\text{-}Cl)IrCl(PEt_3)_3]BF_4$ (Rh–Cl = 2.386(3) Å, Ir–Cl = 2.381(3) Å) compared with its unsymmetrical nature in $[(dppe)Rh(\mu\text{-}H)(\mu\text{-}Cl)IrH(PEt_3)_3]BF_4$, (Rh–Cl = 2.394(5) Å, Ir–Cl = 2.510(5) Å). This is thought to be due to the strong *trans* influence of the terminal hydride ligand. The Ir–Rh distances of 2.903(1) and 2.969(1) Å suggest that there is a degree of M–M interaction in both complexes. In a similar reaction the bis-chloro-bridged complex $[(dppe)Rh(\mu\text{-}Cl)_2IrH(PMePh_2)_3]BF_4$ was synthesized from $[(dppe)Rh(acetone)_2]BF_4$ and *mer,cis*-$[IrHCl_2(PMePh_2)_3]$ (eqn. (10)):


(10)

The product was characterized using NMR spectroscopic data. A discussion of the preference for one hydride and one chloride bridge in this class of compound was also presented. The bridging ligands are not very strongly bound, and the bridges may be easily cleaved by donor ligands such as CO and CH_3CN.

From the reaction of $[IrH_5(PPh_3)_2]$ and $[M(cod)(\mu\text{-}Cl)]_2$ (M = Rh, Ir) (eqn. (11)) complexes of the type $[(cod)M(\mu\text{-}H)(\mu\text{-}Cl)IrH_2(PPh_3)_2]$ were obtained [21]:


(11)

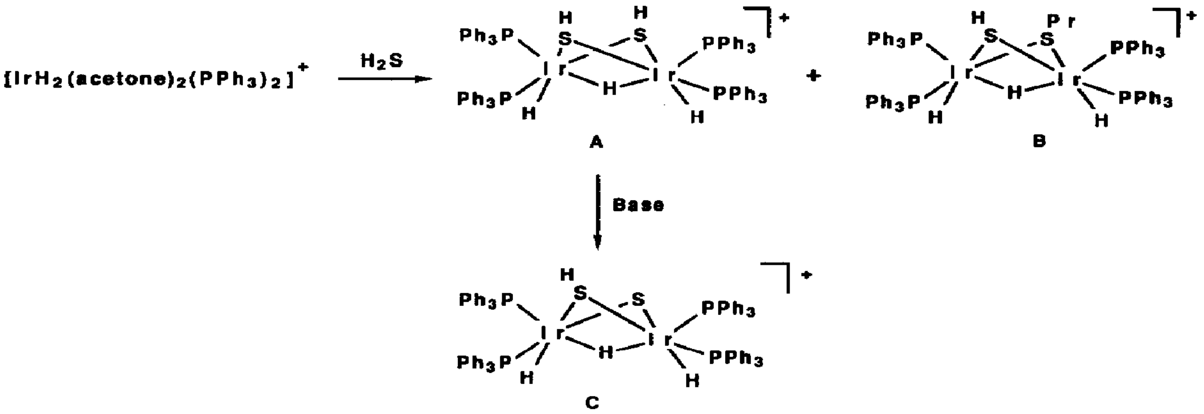
The structure of the di-iridium complex was determined by X-ray diffraction. One metal shows distorted square-planar geometry, while the other exhibits a distorted octahedral arrangement. The Ir–Ir distance (2.827(2) Å) is consistent with a significant degree of metal–metal interaction. Again the bridges can be easily cleaved with donor ligands such as PPh_3.

Crabtree and coworkers isolated the complex $[(PPh_3)_2HIr(\mu\text{-}H)_3IrH(PPh_3)_2]PF_6$ resulting from the deactivation of $[Ir(cod)(PPh_3)_2]PF_6$ during the catalytic hydrogenation of olefins (eqn. (12)) [10]:


(12)

The structure determination revealed that the two iridium atoms are in a distorted octahedral geometry with an extremely short Ir–Ir distance (2.52 Å). This is attributed to the presence of the three bridging hydrides which, as the M–H distance must be of the order of 1.6 Å, results in the two iridium atoms being in close proximity. From NMR spectroscopic data it is shown that each iridium atom bears one terminal hydride ligand and that both iridium atoms share the "face" formed by the other three bridging hydride ligands. A similar complex with L_2 = dppm was structurally characterized by Wang and Pignolet [10(b)]. In this complex, one of the shortest Ir–Ir distances (2.514(1) Å) is present, indicating significant metal–metal interaction.

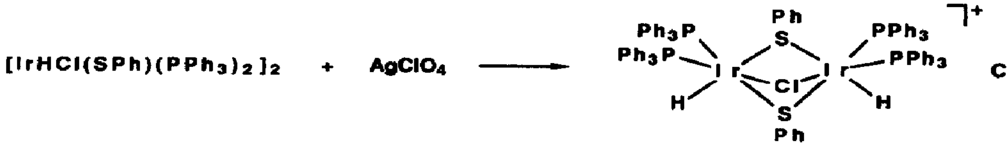
Pignolet et al. reported that the reaction of H_2S with $[Ir(H)_2(acetone)_2(PPh_3)_2]BF_4$ in acetone led to the formation of the hydrido and sulphydryl-bridged complexes $[Ir_2(SH)_2(H)_3(PPh_3)_4]BF_4$ (**A**) (major product) and $[Ir_2(SH)(SPr^i)(H)_3(PPh_3)_4]$ (**B**) (minor product) (eqn. (13)). Deprotonation of the bridging SH ligand of complex **A** produced $[Ir_2S(SH)(H)_3(PPh_3)_4]$ (**C**):



(13)

The complexes were characterized by X-ray diffraction, and ^1H and ^{31}P NMR spectroscopy. In all cases, the coordination geometry about each iridium atom is pseudooctahedral with a terminal and a bridging hydride, not located by X-ray diffraction. The ^{31}P and ^1H NMR data indicate the presence of three isomers for **A**, three isomers for **B** and two isomers for **C** with respect to the orientation of the SR groups (R = H, Pr^i) relative to the metal–metal axis [23].

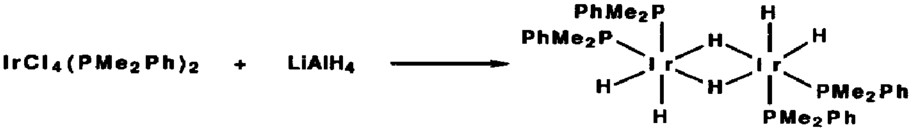
Roberts et al. reported that the reaction of the dinuclear complex $[IrHCl(SPh)(PPh_3)_2]_2$ with $AgClO_4$ in acetone yielded the triply bridged complex $[(Ph_3P)_2HIr(\mu\text{-}SPh)_2(\mu\text{-}Cl)Ir(H)(PPh_3)_2]ClO_4$ (eqn. (14)) [24]:



(14)

An X-ray diffraction study revealed the geometry of the complex and an Ir–Ir distance of 3.377(1) Å. This is much too long for any metal–metal interaction to be present. The terminal hydride ligands were not located in the structure determination but the presence of Ir–H bonds is supported by IR and NMR data.

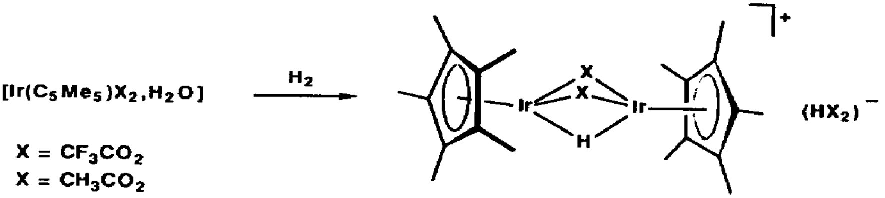
Reaction of $[IrCl_4(PMe_2Ph)_2]$ with $LiAlH_4$ (eqn. (15)) and subsequent work-up with wet THF yielded the centrosymmetric di-iridium complex $[(PhMe_2P)_2H_2Ir(\mu\text{-}H)]_2$ which was structurally characterized by X-ray diffraction [25]:



(15)

The hydride ligands were located and the bonding distances ($Ir\text{–}H_{br}$ = 1.69(6), 1.66(6) Å; $Ir\text{–}H_{term}$ = 1.75(7), 1.53(7) Å) fall in the expected range. The difference in the Ir–P bond lengths is accounted for in terms of the *trans* influence of terminal (term) vs. bridging (br) hydride ligands (Ir–P = 2.315(2) Å for the phosphorus atom in the Ir_2H_4 plane, Ir–P = 2.231(3) Å for the phosphorus atom out of this plane). The Ir–Ir distance (2.739(1) Å) is shorter than the value predicted for an Ir(III)–Ir(III) single bond (2.804 ± 0.014 Å) [26], suggesting a significant degree of M–M interaction, which again must be partly attributable to the small size of the hydride bridging ligand.

Complexes of the type $[MCp'(\mu\text{-}Cl)(Cl)]_2$ and $[MCp'(\mu\text{-}X)(X)]_n$ (M = Rh, Ir; X = CH_3CO_2 or CF_3CO_2) are hydrogenation catalysts for olefins. Maitlis and coworkers isolated a series of complexes from the reaction of these complexes with H_2, which were characterized by spectroscopic (NMR and IR) and microanalytical techniques (eqn. (16)) [27]:



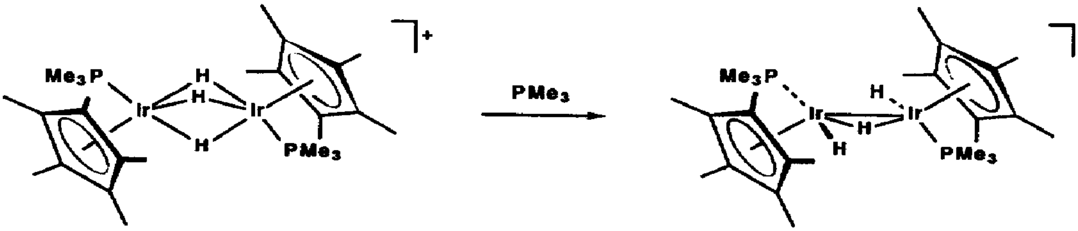
(16)

Complexes such as $[\{MCp'\}_2HCl_3]$, $[\{MCp'\}_2HX_2]Y$, $[\{MCp'\}_2H_2X]Y$ and $[\{IrCp'\}_2H_3]Y$ (Y = PF_6, $H(OCOCF_3)_2$ or $H(OCOMe)_2$ (M = Rh, Ir) were also characterized.

Complexes of formula $[\{MCp'\}_2HX_2][HX_2]$ (M = Rh, Ir; X = CH_3CO_2)

were isolated from the reaction of $[MCp'(CH_3CO_2)_2]_n$ with isopropyl alcohol, and also $[\{MCp'\}_2H(OH)X]^+$ was isolated from the hydrolysis of $[\{MCp'\}_2HX_2]^+$ (M = Rh, X = $OCOCH_3$ or $OCOCF_3$; M = Ir, X = $OCOCH_3$).

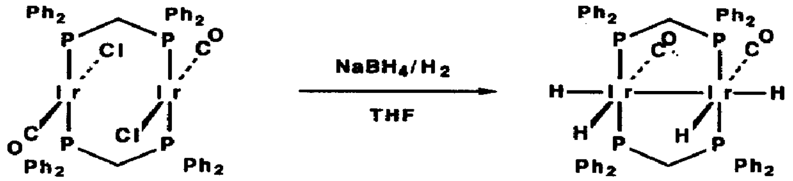
The crystal structure determination of $[\{Cp'HIrPMe_3\}_2(\mu\text{-}H)]PF_6$, which was obtained from the reaction of $[(Cp'Ir)_2(\mu\text{-}H)_3]PF_6$ with PMe_3, was carried out by Burns et al. (eqn. (17)) [28]:



(17)

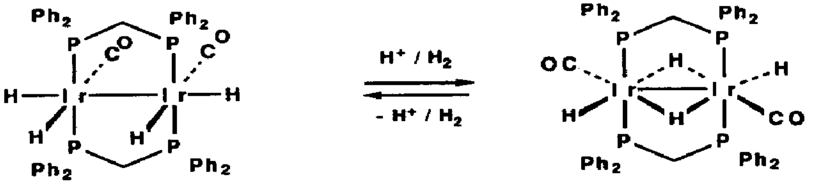
The hydride ligands were located in the structure determination and the Ir–H distances (range, 1.47(5)–1.80(4) Å) fall within the range of normal Ir–H bond distances observed for this class of complex. Also of note is the long Ir–Ir bond distance (2.983(1) Å) and the approximately tetrahedral geometry about the iridium centres.

Cowie and coworkers [29] reported a series of "A-frame" di-iridium complexes derived from *trans*-$[IrCl(CO)(dppm)]_2$. The reaction of this complex with $NaBH_4$ under an atmosphere of H_2 yielded the binuclear tetrahydride $[Ir_2(H)_4(CO)_2(dppm)_2]$ (eqn. (18)):



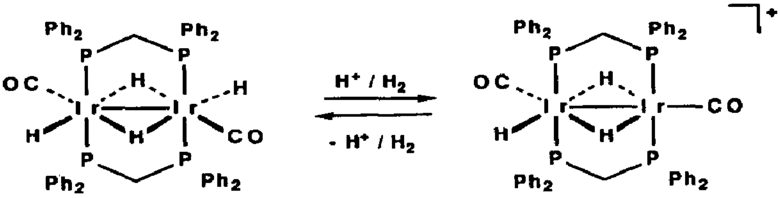
(18)

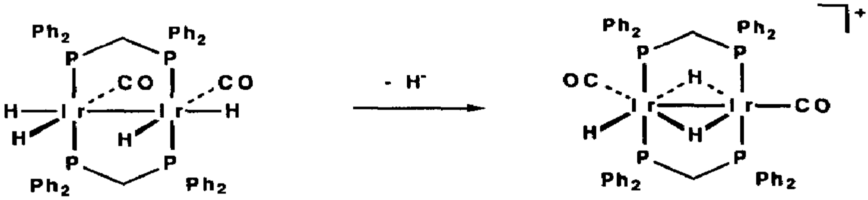
The action of the acids $HBF_4 \cdot Et_2O$ or CF_3CO_2H on this latter complex under an H_2 atmosphere causes a reversible rearrangement to the isomeric complex $[Ir_2(H)_2(CO)_2(\mu\text{-}H)_2(dppm)_2]$ (eqn. (19)):



(19)

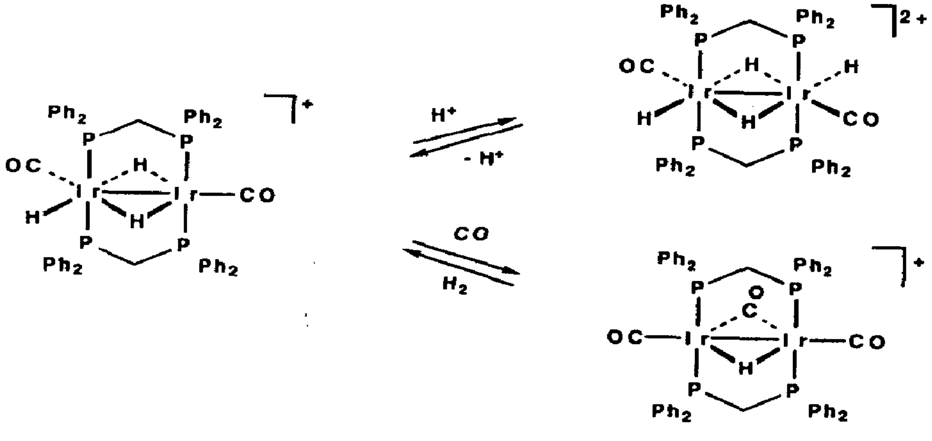
However, if the addition of $HBF_4 \cdot Et_2O$ to $[Ir_2(H)_2(CO)_2(\mu\text{-}H)_2(dppm)_2]$ is performed under an atmosphere of N_2, the cationic trihydride $[Ir_2(H)(CO)_2(\mu\text{-}H)_2(dppm)_2]BF_4$ is formed (eqn. (20)). This complex can also be isolated from the reaction of $[Ir_2(H)_4(CO)_2(dppm)_2]$ with $[Ph_3C][BF_4]$ (eqn. (21)) or by reaction with chlorinated solvents such as $CHCl_3$ or CH_2Cl_2 [29]:


(20)


(21)

This complex was characterized using X-ray crystallographic techniques [29]. The two bridging and the terminal hydrides were not located in the X-ray study but their positions were inferred from the positions of the other ligands in the structure. The Ir–Ir distance (2.855(2) Å) is normal for a single bond and is consistent with the values observed for other Ir–Ir-bonded dppm systems [30–32].

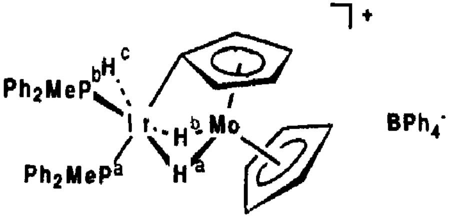
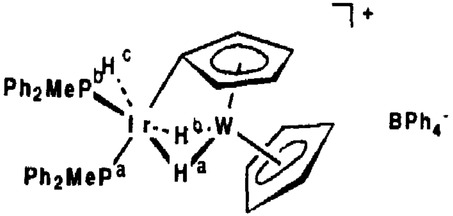
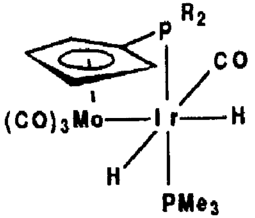
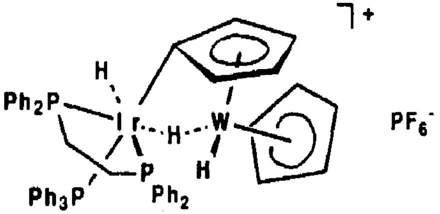
Protonation of $[Ir_2(H)(CO)_2(\mu\text{-}H)_2(dppm)_2]^+$ with $HBF_4\text{–}Et_2O$ yielded $[Ir_2(H)_2(CO)_2(\mu\text{-}H)_2(dppm)_2][BF_4]_2$ (eqn. (22)). This reaction is reversible in the presence of $KOBu^t$. Reaction with CO gave $[Ir_2(CO)_2(\mu\text{-}H)(\mu\text{-}CO)(dppm)_2]^+$ which reacts with H_2 to regenerate the starting material (eqn. (23)) [29]:


(22)

(23)

TABLE 1

Selected structural and NMR data of polynuclear iridium hydrides

Complex	Equation number	Ir–M distance (Å)	^{1}H NMR of hydrides * δ (ppm), *J* (Hz)	^{31}P{^{1}H} NMR δ (ppm), *J* (Hz)	Ref.
	(1)	2.641(1)	H^a −14.3 H^b −17.0 H^c −22.1 ^2J(P^{b}H^b) = 48.6 ^2J(H^{a}H^b) = 5.1	P^a −2.2 P^b 1.2 ^2J(P^{a}P^b) = 11.8	12
	(1)	2.706(1)	H^a −17.4 (CD$_2$Cl$_2$) H^b −18.6 H^c −23.7 ^2J(P^{b}H^b) = 53.7 ^2J(H^{a}H^b) = 3.7	P^a 2.1 P^b −7.0 ^2J(P^{a}P^b) = 11.8	12, 13
	(2)		H −10.43 (C$_6$D$_6$) H −13.81 ^2J(HH) = 3.4 ^2J(PH) = 11.0 and 14.6	P 11.6 (CD$_2$Cl$_2$) P −48.9 ^2J(PP) = 308	14
	(3)	3.0771(7)	H −11.2 (CD$_2$Cl$_2$, 183 K) H −14.0 H −22.5		15

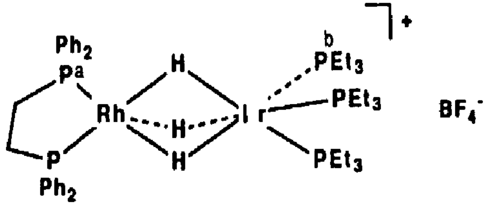
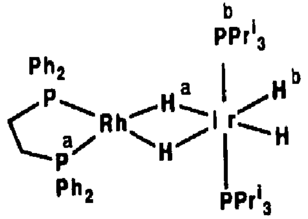
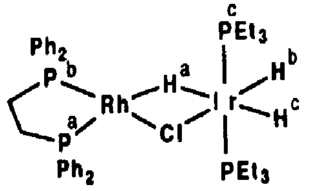
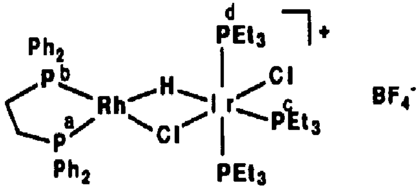
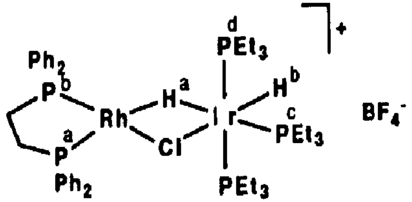
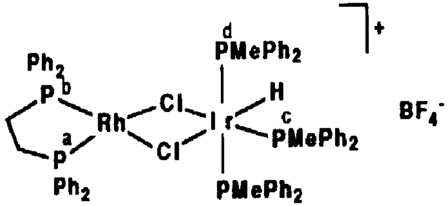
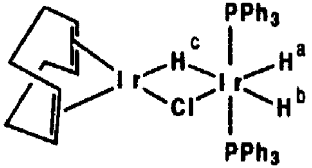
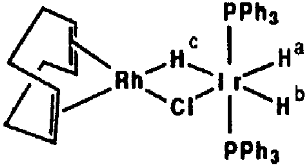
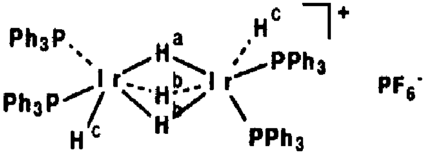
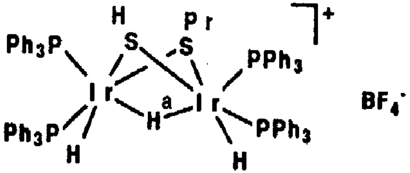
	(4)	2.636(2)	H_3 −12.0 (acetone-d_6) J(RhH) = 22 $^2J(P_{Rh}H)$ = 10	P^a 80.0 (acetone-d_6) P^b −8.5 ^3J(RhP) = 6.8 $^4J(P^aP^b)$ = 8.3	16
	(5)	2.662(1)	H^a −8.5 (C_6D_6) H^b −19.0	P^a 69 (C_6D_6) P^b 64 $J(RhP^a)$ = 160	19
	(6)		H^a −12.2 (toluene-d_8) H^b −24.2 H^c −12.7 $^2J(H^aH^b)$ = 2 $^2J(H^aH^c)$ = 16 $^2J(H^bH^c)$ = 7 $^2J(P^aH^a)$ = 61	P^a 58.8 (toluene-d_8) P^b 80 P^c 4.2 $J(P^aRh)$ = 172.8 $J(P^bRh)$ = 202.5 $^4J(P^aP^c)$ = 3.3	20
	(8)	2.903(1)	H −14.2 (CD_2Cl_2) $^2J(P^cH)$ = 93	P^a 68.2 (CD_2Cl_2) P^b 77.8 P^c −26.3 P^d −32.0 $^4J(P^aP^c)$ = 46	18
	(9)	2.969(2)	H^a −14.9 (acetone-d_6) H^b −21.9 $^2J(P^cH)$ = 72	P^a 66.6 (acetone-d_6) P^b 74.0 P^c −12.1 P^d −15.0 $^4J(P^aP^c)$ = 41 $J(P^aRh)$ = 184 $J(P^bRh)$ = 199 $^4J(P^bP^c)$ = 3	18

TABLE 1 (continued)

Complex	Equation number	Ir–M distance (Å)	^{1}H NMR of hydrides * δ (ppm), *J* (Hz)	^{31}P{^{1}H} NMR δ (ppm), *J* (Hz)	Ref.
	(10)		H −21.8 (CD_2Cl_2)	P^a 75.8 (CD_2Cl_2) P^b 78.9 P^c −19.7 P^d −8.6	18
	(11)	2.827(1)	H^a −22.47 (C_6D_6) H^b −11.36 H^c −9.1 $^2J(PH^a) = 16.4$ $^2J(H^aH^c) = 1.6$		21
	(11)		H^a −21.84 (C_6D_6) H^b −11.13 H^c −14.17		21
	(12)	2.518	H^a −8.4 (acetone-d_6) H^b −6.9 H^c −23.9 $^2J(PH^a) = 65$ $^2J(PH^b) = 86$	P 15.3 (acetone-d_6) P 18.5 $^2J(P^aP^b) = 95$	10(a), 10(c)
	(13)	2.822(1)	H^a −16.0 (CD_3CN) H −15.1 H −16.9 $^2J(P_{trans}H^a) = 59$	Mixture of isomers	23

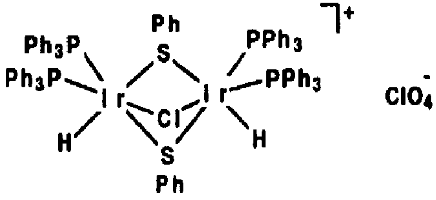
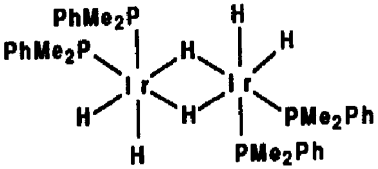
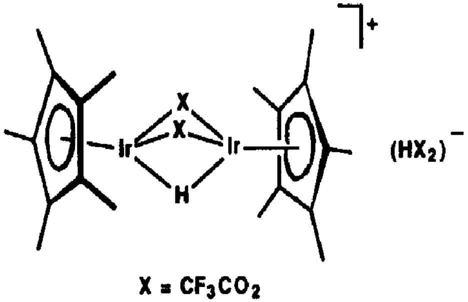
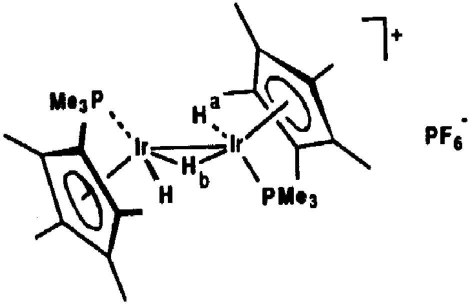
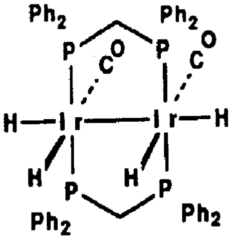
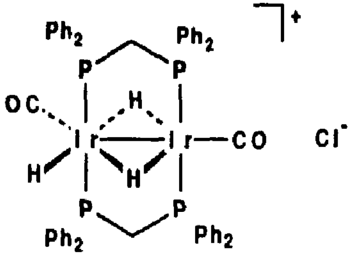
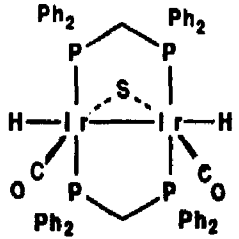
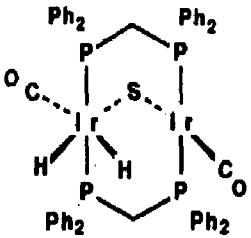
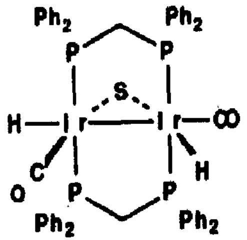
	(14)	3.377(1)	H −23.36 ($CDCl_3$)		24
	(15)	2.739(1)	H −13.36 (CD_2Cl_2, 233 K)	P 1.5 (CD_2Cl_2)	25
	(16)		H −10.46 (CD_2Cl_2)		27
	(17)	2.983(1)	H^a −19.16 (CD_2Cl_2, 193 K) H^b −23.02	P −47.03 (CD_2Cl_2)	28
	(18)		H −10.94 (CD_2Cl_2) H −11.39 $^2J(HH)$ = 4.7	P −3.4 (CD_2Cl_2, 233 K)	29

TABLE 1 (continued)

Complex	Equation number	Ir–M distance (Å)	^1H NMR of hydrides * δ (ppm), J (Hz)	$^{31}P\{^1H\}$ NMR δ (ppm), J (Hz)	Ref.
	(20)	2.855(2)	H −10.23 (CD_2Cl_2) H −10.49 H −11.18	P 14.9 (CD_2Cl_2, 233 K) P −1.0	29
			H −10.18 (C_6D_6)	P −8.5 (C_6D_6)	33(b)
			H −10.5 (acetone-d_6) H −11.3	P 0.9 (acetone-d_6) P −8.9	33(b)
			H −10.07 (C_6D_6) H −11.68	P −6.8 (C_6D_6) P −13.2	33(b)

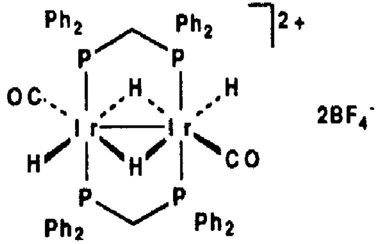
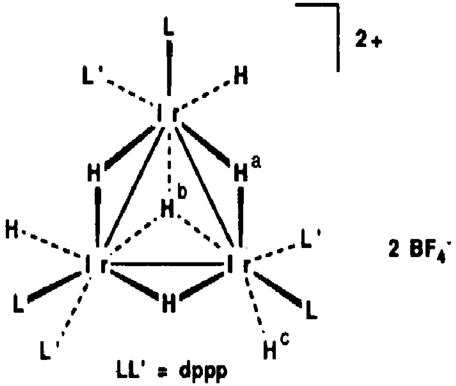
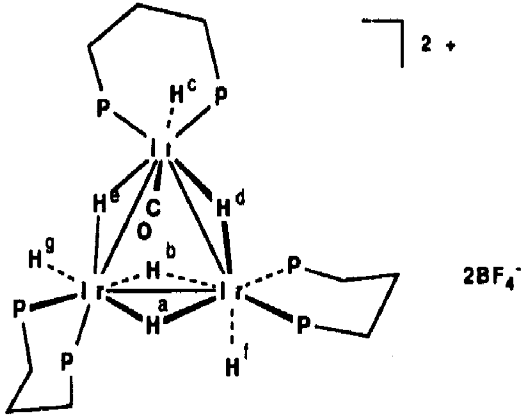
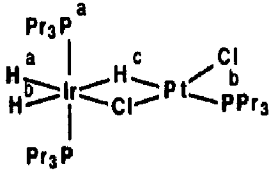
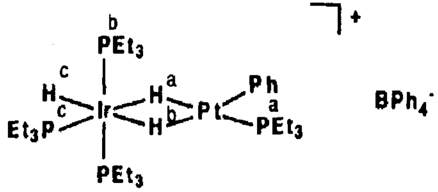
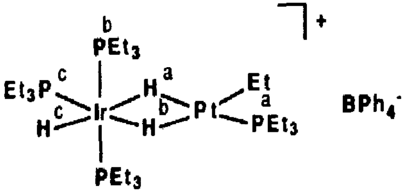
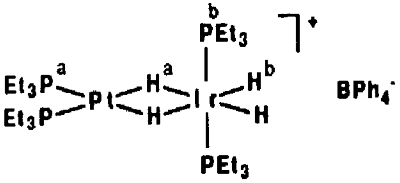
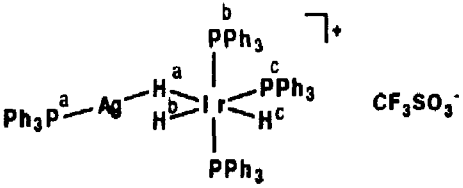
	(22)		H −9.20 (CD_3NO_2) H −19.22	P 9.0 (CD_2Cl_2, 233 K)	29
	(24)	2.757(1) 2.765(1) 2.793(1)	H^a −7.98 (acetone-d_6) H^b −8.83 H^c −15.0 $^2J(P_{trans}H^a) = 68$ $^2J(P_{trans}H^b) = 37$	P 1.0 (acetone-d_6) P −7.9 Fluctional behaviour	10(b)
	(25)	2.665(1) 3.142(1) 3.153(1)	H^a −8.60 (acetone-d_6) H^b −12.35 H^c −12.84 H^d −16.75 H^e −17.38 H −18.33 H −20.87	P −7.9 (CH_2Cl_2, 338 K) P −12.1 P −16.7 P −20.1 P −29.5	34
	(26)		H^a −25.2 (toluene-d_8) H^b −13.9 H^c −11.6 $^2J(H^aH^c) = 1$ $^2J(P^bH^c) = 122$	P^a 2.2 (toluene-d_8) P^b 45 $^4J(P^aP^b) = 3.6$	35

TABLE 1 (continued)

Complex	Equation number	Ir–M distance (Å)	^{1}H NMR of hydrides * δ (ppm), *J* (Hz)	^{31}P{^{1}H} NMR δ (ppm), *J* (Hz)	Ref.
	(27)	2.687(2)	H^a −9.04 (CD_2Cl_2) H^b −7.05 H^c −15.27 *J*(PtH^a) = 662 *J*(PtH^b) = 671	P^a 16.3 P^b −4.5 P^c 6.0 *J*(PtP^a) = 3656	36, 37 38
	(27)	2.682(1)	H^a −5.05 (acetone-d_6) H^b −11.5 H^c −14.6 *J*(PtH^a) = 823 *J*(PtH^b) = 512	P^a 22.8 (acetone-d_6) P^b −5.2 P^c 2.4 *J*(PtP^a) = 3614	36–38
	(30)		H^a −5.37 (acetone-d_6) H^b −22.41 *J*(PtH^a) = 786 *J*(H^aP^a) = −6 *J*(H^aH^b) < 3	P^a 21.5 (acetone-d_6) P^b 20.9 *J*(PtP^a) = 2601	36–38
	(31)	2.758(2)	H^a −8.56 (CD_2Cl_2) H^b −11.54 H^c −11.09 $^{2}J(P^aH^a) = 33$ $J(^{109}AgH^a) = 116$ $J(^{109}AgH^b) = 23$ $J(^{109}AgH^c) = 15$	P^a 17.8 (CH_2Cl_2) P^b 5.2 P^c 10.3 $J(^{109}AgP^a) = 617$	40, 41

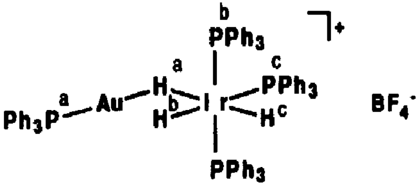
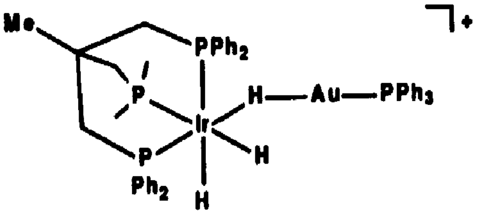
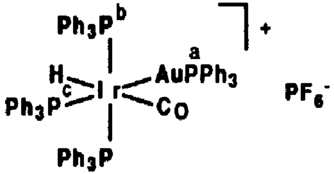
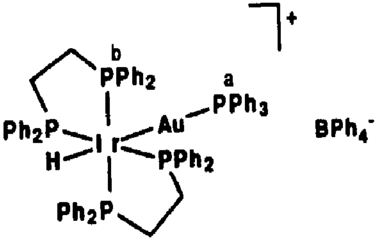
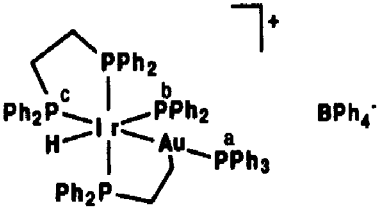
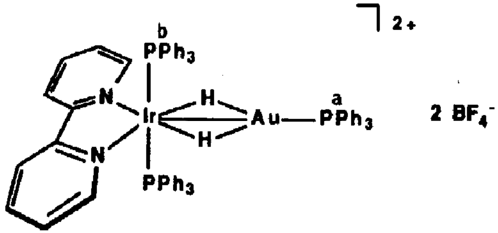
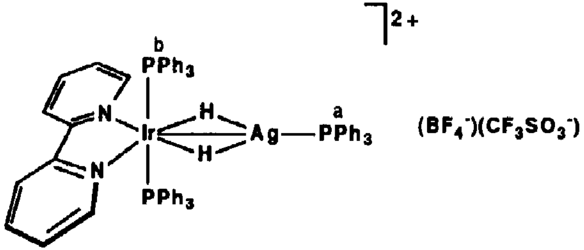
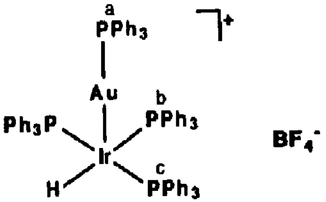
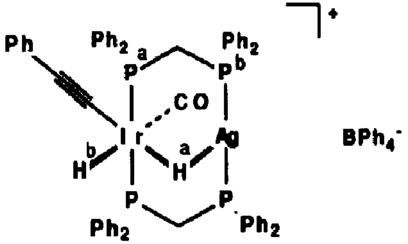
	(31)	2.765(1)	H^a −4.49 (CD_2Cl_2) H^b −9.2 H^c −11.1 $^2J(P^aH^a) = 79.3$ $^2J(P^aH^b) = 15.9$	P^a 48.2 (CH_2Cl_2) P^b 2.8 P^c 13.9 $^4J(P^aP^c) = 19.5$	40, 41
			H −8.0 (CD_2Cl_2) Fluctional $^2J(P^{Au}H) = 25$	P^{Au} 52.9 (CH_2Cl_2, 183 K) P^{Ir} −3.0 $^4J(PP) = 15$	61
	(32)	2.6628(4)	H −8.93	P^a 36.8 (243 K) ** P^b 4.1 P^c 6.2 $^3J(P^aP^c) = 6$	42, 43
	(33)		H −20.3 $^2J(P^aH) = 12$	P^a 27.6 ** P^b 15.4	43
	(33)		H −11.3 $^2J(P^bH) = 107.6$	P^a 39.8 ** P^b 13.7 P^c 31.9 P 28.9 P 33.4	43

TABLE 1 (continued)

Complex	Equation number	Ir–M distance (Å)	^{1}H NMR of hydrides * δ (ppm), *J* (Hz)	^{31}P{^{1}H} NMR δ (ppm), *J* (Hz)	Ref.
	(34)	2.699	H −13.3 (CDCl$_3$)	P^a 46.5 (CH$_2$Cl$_2$) P^b 3.0	42
	(35)		H −16.3 (CDCl$_3$) *J*(P^{a}H) = 12.5 *J*(^{109}AgH) = 55	P^a 18.0 (CH$_2$Cl$_2$) P^b 3.7	45
	(36)		H −6.10 (acetone-*d*$_6$, 273 K) ^3JP^{a}H) = 4.1 ^2J(P^{b}H) = 99.5	P 19.5 (acetone-*d*$_6$, 273 K) P −6.6 P^c 28.1	42
	(37)		H^a −9.6 (CDCl$_3$) H^b −11.85 *J*(AgH^a) = 17 *J*(H^{a}H^b) = 2	P^a −1.6 (CDCl$_3$) P^b 16.3	48

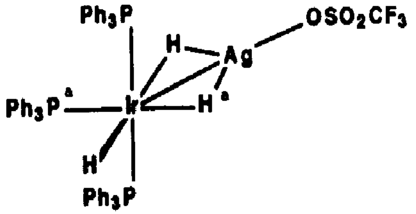
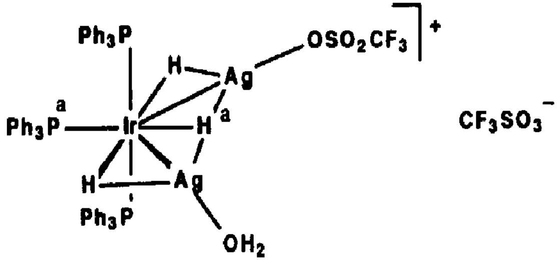
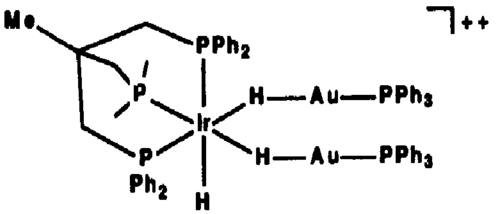
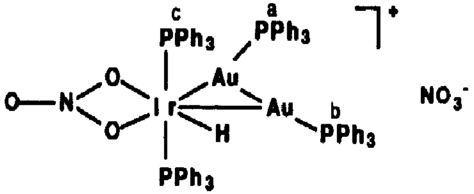
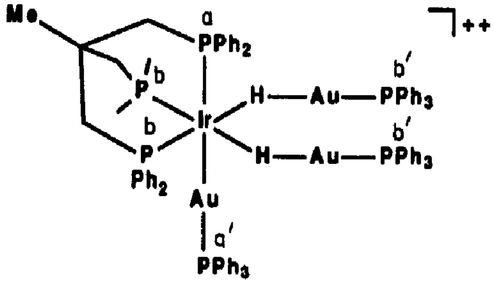
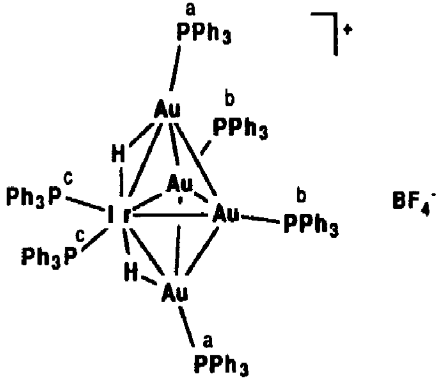
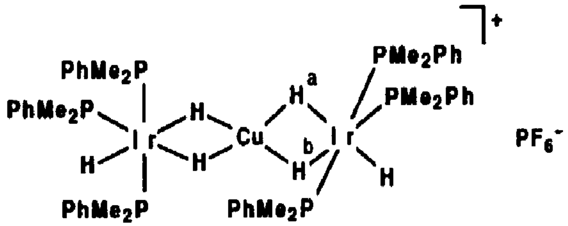
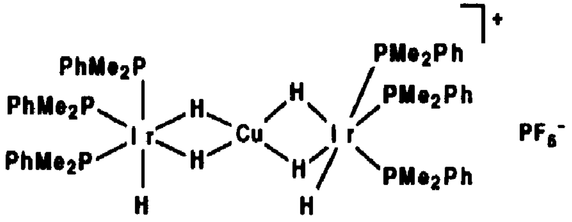
			H^a −9.52 (CD_2Cl_2) H −11.55 H −12.05 $J(P^aH^a) = 156$		49(b)
	(38)	2.764(4) 2.808(4)	H^a −10.28 (CD_2Cl_2) H −9.11 $^2J(P^aH^a) = 88$	P^a 4.6 P 2.6	49
			H −6.3 (CD_2Cl_2) $^2J(P^{Au}H) = 26$ $^2J(P^{Ir}H) = 47$	P^{Au} 49.7 (CD_2Cl_2) P^{Ir} −43.3 $^4J(PP) = 17$ Fluctional	61
	(39)	2.673(1) 2.697(1)	H −25.3 (acetone-d_6, 183 K)	P^a 7.9 (acetone-d_6, 183 K) P^b 35.9 P^c 7.3	46
			H −5.6 (CD_2Cl_2, 233 K) $^2J(P^bH) = 16$ $^2J(P^{b'}H) = 12$	P^b −0.6 (CD_2Cl_2, 233 K) P^a 6.5 $P^{a',b'}$ 50.2 $^4J(P^{Au}P^b) = 15$ $^4J(P^{Au}P^a) = 41$	61

TABLE 1 (continued)

Complex	Equation number	Ir–M distance (Å)	^{1}H NMR of hydrides * δ (ppm), *J* (Hz)	^{31}P{^{1}H} NMR δ (ppm), *J* (Hz)	Ref.
	(40)	2.637 2.687 2.695 2.753	H −5.71 (acetone-d_6)	P^a 47.3 (CH_2Cl_2– $CHClF_2$, 128 K) P^b 41.8 P^c 35.8 P^a ⇌ P^b	50
	(41)		H^a −9.36 (CD_3CN) H^b −11.28 H^c −11.69	P −33.45 (CD_3CN) P −34.03	51
	(42)	2.502(4) 2.529(4)	H −11.89 (CD_3CN, 289 K)	P −37.3 (CD_3CN) Fluctional behaviour	51

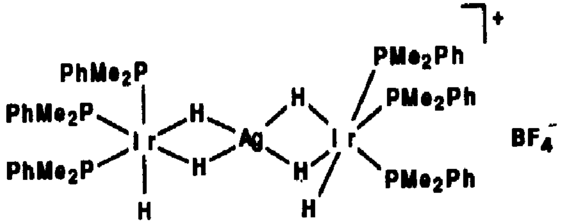
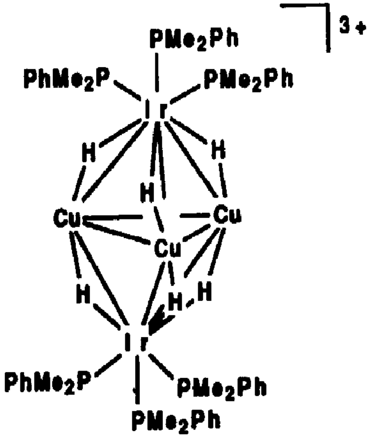
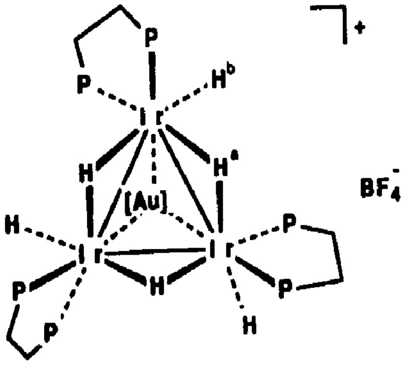
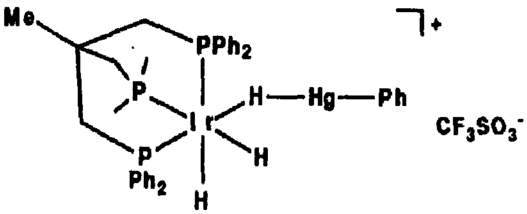
			H −11.59 $J(AgH) = 49.5$ $J(P_{trans}H) = 72$	P −37.3 $J(AgP) = 23$	51
 $\dot{C}u$ = Cu(MeCN)	(43)	2.793(9)	–	–	52
 [Au] = $AuNO_3$	(44)	$Ir–Ir_{av.}$ 2.842(1) $Ir–Au_{av.}$ 2.705(1)	H^a −8.86 ($CDCl_3$) H^b −15.04	P 32.1 (CH_2Cl_2) P 44.3	53

TABLE 1 (continued)

Complex	Equation number	Ir–M distance (Å)	^{1}H NMR of hydrides * δ (ppm), *J* (Hz)	^{31}P{^{1}H} NMR δ (ppm), *J* (Hz)	Ref.
	(45)	–	H −7.50 (CD$_2$Cl$_2$, 183 K) $J(^{199}$HgH) = 312	P-5.5 (CH$_2$Cl$_2$, 213 K) Fluctional behaviour	54

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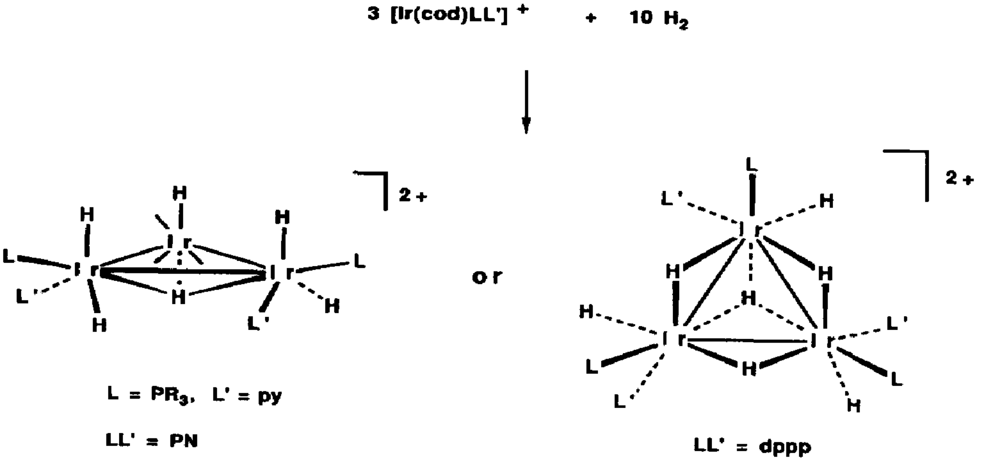
* δ values preceded by H or P without label indicate that no assignment was made. Solvents are given in parentheses when available from the original publication. ** Values given relative to trimethylphosphate.

A reaction with molecular hydrogen is observed with toluene or THF solutions of the A-frame complex $[Ir_2(\mu\text{-}S)(CO)_2(dppm)_2]$ [33]. The isomeric complexes formed, $[Ir_2(\mu\text{-}S)(H)_2(CO)_2(dppm)_2]$ (see Table 1), were characterized by ^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopy. Although H_2 attack seems to occur at one metal centre to give an $Ir^I\text{–}Ir^{III}$ complex, further exchange of hydride ligands between the two metals is extremely facile.

(ii) Complexes of stoichiometry Ir_3

Trinuclear hydrido-bridged iridium complexes of the type $[(H_2LL'Ir)_3(\mu_3\text{-}H)]PF_6$ were isolated from the use of $[Ir(cod)LL']PF_6$ ($L = PPr^i_3$, PCy_3; L' = pyridine [10(a)], LL' = dppp [10(b)], LL' = PN [34]) as an olefin hydrogenation catalyst (eqn. (24)):

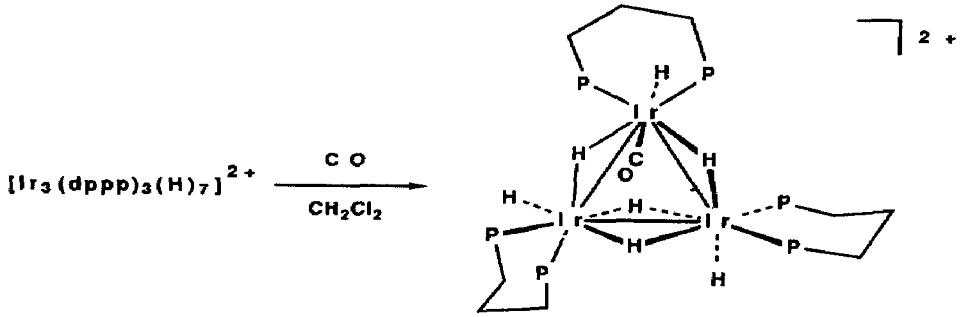


(24)

The complex with $L = PCy_3$ and L' = pyridine was isolated and characterized using X-ray diffraction techniques [10(a)]. This showed a triangular arrangement of iridium atoms with an average Ir–Ir distance of 2.76 Å. The hydride positions were inferred, using a combination of X-ray and ^1H NMR data, as they were not located in the diffraction study. The reasons why the stoichiometrically related complex with the symmetrical ligand LL' = dppp displays doubly bridging hydrides remain unclear.

Another trinuclear hydrido-bridged iridium complex, $[Ir_3(dppp)_3(H)_7\text{-}$

$(CO)]^{2+}$, was obtained by reaction of $[Ir_2(dppp)_3(H)_7]^{2+}$ with CO in CH_2Cl_2 (eqn. (25)):



(25)

The hydride positions were deduced from structural and ^1H NMR data. The complex possesses four doubly bridging hydrides and three terminal hydrides, and the molecular structure consists of a isosceles triangle, the total symmetry being C_1.

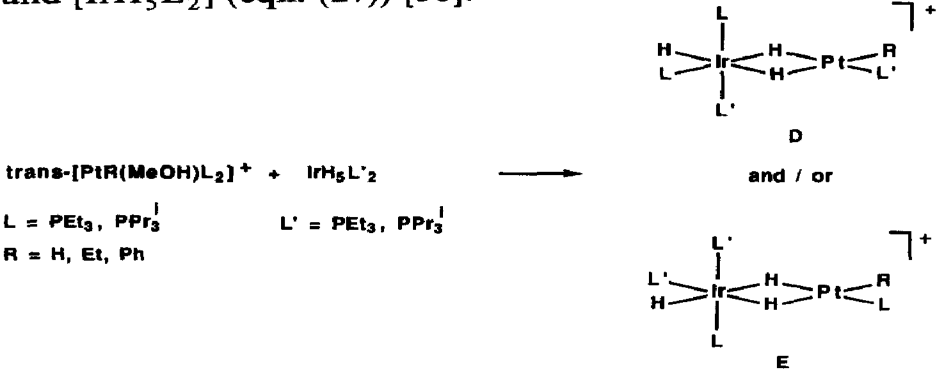
D. BIMETALLIC IRIDIUM HYDRIDO COMPLEXES WITH GROUP 10 METALS

The reactions of $[IrH_5(PPr_3)_2]$ with $[M_2Cl_4(PPr_3)_2]$ (M = Pt and Pd) have been studied and were found to yield a hydrido-bridged bimetallic complex in the case of platinum (eqn. (26)) [35]:

(26)

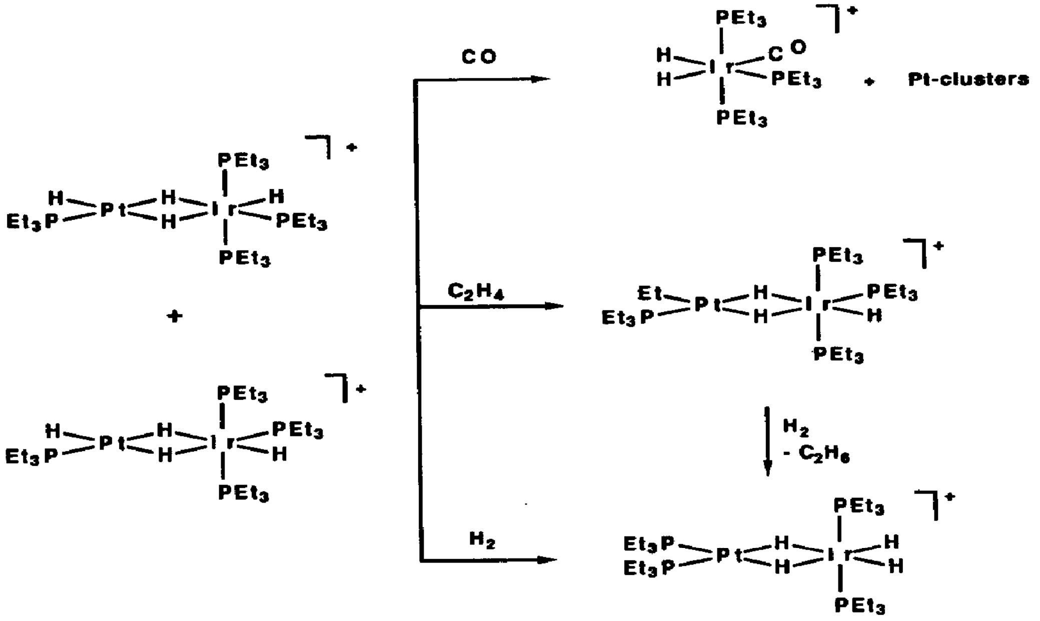
The product $[(PPr_3)_2(H)_2Ir(\mu\text{-}Cl)(\mu\text{-}H)PtCl(PPr_3)]$ was characterized using multinuclear NMR spectroscopic techniques. It is not very stable and disproportionates upon standing in toluene for about 30 min at room temperature. Analogous reactions were observed with $[Pd_2Cl_4(PPr_3)_2]$, but the decomposition is so rapid that no bimetallic species could be characterized.

Venanzi and coworkers [36–39] have published a series of reports on Ir–Pt hydrido complexes. Bimetallic hydrido-bridged cationic species of the type $[L'RPt(\mu\text{-}H)_2IrHL_2L']^+$ were prepared from *trans*-$[PtR(MeOH)L_2]^+$ and $[IrH_5L_2]$ (eqn. (27)) [36]:



(27)

These species give mixtures of isomers of type **D** and **E** in solution, and it has not been possible to establish whether both forms exist also in the solid state. It is noteworthy that ligand exchange occurred during the reaction. The isomeric mixture of complexes obtained according to eqn. (27) reacts with CO to yield $[IrH_2(CO)(PEt_3)_3]^+$ (eqn. (28)), whereas the reaction with C_2H_4 (eqn. (29)) gives $[(PEt_3)(Et)Pt(\mu\text{-}H)_2IrH(PEt_3)_3]^+$ and the reaction with H_2 gives $[(PEt_3)_2Pt(\mu\text{-}H)_2IrH_2(PEt_3)_2]^+$ (eqn. (30)):



(28)

(29)

(30)

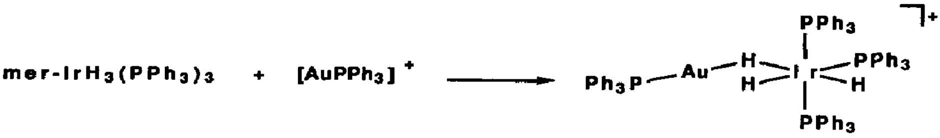
The majority of these complexes were characterized using multinuclear NMR techniques, but a structure determination was carried out on the complex $[(PEt_3)(Ph)Pt(\mu\text{-}H)_2IrH(PEt_3)_3]BPh_4$ [37,38], which adopts a **D**-type structure in the solid state. None of the hydride ligands could be located, but their positions were proposed on the basis of NMR and crystallographic data. A degree of metal–metal interaction is suggested from the Ir–Pt distance of 2.687(2) Å. An X-ray crystallographic study of the ethyl complex $[(PEt_3)(Et)Pt(\mu\text{-}H)_2IrH(PEt_3)_3]BPh_4$ [38] was also performed, and this complex was characterized, as solid, as an **E**-type structure. For the latter complex an X-ray study and a neutron diffraction analysis were undertaken [39]. The hydride ligands were poorly located in the X-ray study but the distances obtained from the neutron study ($Ir–H_{br}$ = 1.879(3), 1.882(3) Å; $Ir–H_{term}$ = 1.586(3), 1.591(3); $Pt–H_{br}$ = 1.726(3), 1.736(3) Å) are similar to those found in other complexes of this type. The Ir–Pt distance differed in the X-ray (2.685(1) Å) and neutron (2.677(1) Å) studies but this difference was attributed to the different temperatures of the two experiments, namely, 298 K and 22 K respectively.

E. BIMETALLIC IRIDIUM HYDRIDO COMPLEXES WITH GROUP 11 METALS

Bimetallic iridium hydrido complexes have been synthesized with all three metals of group 11. These complexes encompass a range of Ir–M ratios and, although the majority are Ir–Au complexes, there is a fair number of copper- and silver-containing molecules reported in the literature.

(i) Complexes of stoichiometry IrM

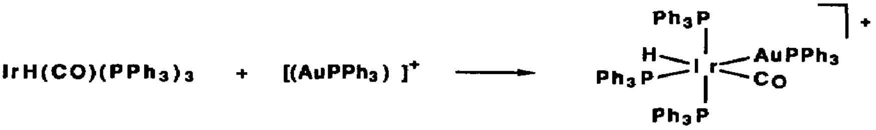
Compounds of the type $[\mathrm{AuCl(PR_3)}]$ (R = Ph, Et) reacted with $\mathrm{AgBF_4}$–THF to yield the solvento complexes $[\mathrm{Au(THF)(PR_3)}]^+$ which, upon further reaction with *mer*-$[\mathrm{IrH_3(PPh_3)_3}]$, yielded complexes of the general formula $[(\mathrm{R_3P})\mathrm{Au}(\mu\text{-H})\mathrm{IrH_2(PPh_3)_3}]^+$ (eqn. (31)) [40,41]:



(31)

An X-ray structural analysis of the compound was performed and revealed a bent $\mathrm{R_3P{-}Au{-}Ir}$ geometry (P–Au–Ir = 155.3(1)°). This, together with NMR evidence, led the authors to propose a bridging hydride ligand between the iridium and gold atoms, which are in relatively close proximity (Ir–Au = 2.765(1) Å). This complex provided the first example of three-centre two-electron bonding in an $\overline{\mathrm{Ir{-}H{-}Au}}$ system. The silver analogue could also be obtained (Ir–Ag = 2.758(2) Å) and it was shown that the $J(^{109}\mathrm{Ag},{}^{1}\mathrm{H})$ values obtained from the two-dimensional $^{109}\mathrm{Ag},{}^{1}\mathrm{H}$ NMR spectra are useful in distinguishing bridging from terminal hydrides [41].

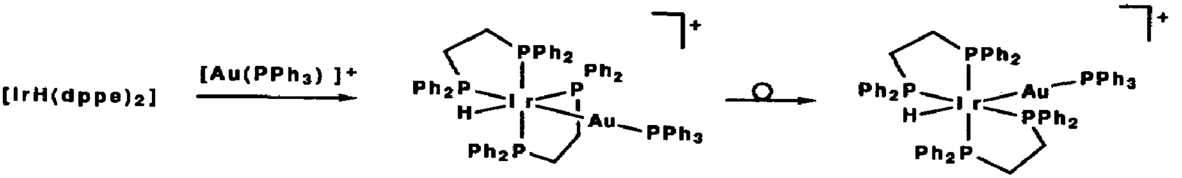
In contrast, no direct Au–hydride interaction is to be found in the complex $[\mathrm{AuIrH(CO)(PPh_3)_4}]\mathrm{PF_6}$ formed by reaction of $[\mathrm{Au(PPh_3)NO_3}]$ with $[\mathrm{IrH(CO)(PPh_3)_3}]$ (eqn. (32):



(32)

This complex, first synthesized by Pignolet et al. [42], was structurally characterized by Mingos et al. [43]. The hydride ligand is terminally bound to the iridium atom (Ir–H = 1.70(1) Å) and the absence of a bridging mode is supported by the P–Ir–Au angle of 165.53(7)°. The slight divergence from linearity is accounted for in terms of steric considerations. Also of note is the relatively short Ir–Au distance (2.662(1) Å). Thus in this case the Ir–Au interaction may be viewed as a two-centre two-electron M–$AuPPh_3$ bond.

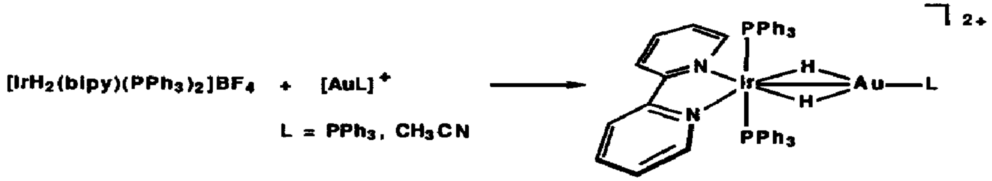
Another product with *cis* geometry was obtained by reaction of $[IrH(dppe)_2]$ with $[AuCl(PPh_3)]$, followed by subsequent metathesis with $[NH_4]PF_6$. The *cis* isomer appears to be the kinetic product of the reaction, as heating to 60°C for a period of 3 h yielded the *trans* isomer (eqn. (33)) [43]:



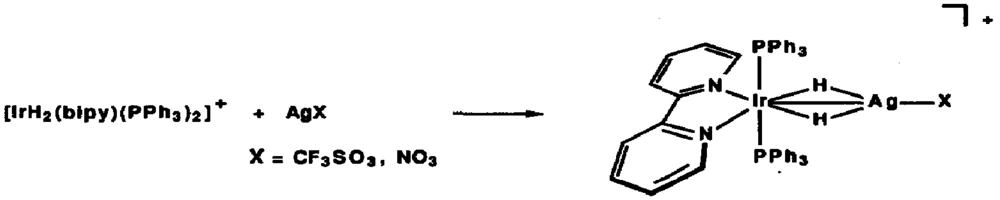
(33)

Both products were characterized by multinuclear NMR spectroscopy.

Pignolet and coworkers have published a series of papers on gold- and silver-containing iridium hydride complexes [42,44,45]. The reaction of $[Au(PPh_3)NO_3]$ with $[Ir(H)_2(bipy)\text{-}(PPh_3)_2]BF_4$ yielded $[AuIr(H)_2(bipy)\text{-}(PPh_3)_3][BF_4]_2$ (eqn. (34)); a similar reaction performed with a silver salt instead of a gold salt gave the complex shown in eqn. (35):



(34)

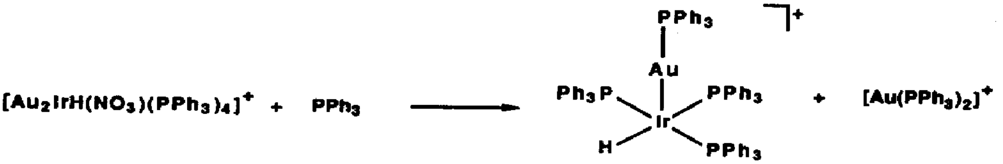


(35)

The gold complex with L = PPh_3 was structurally characterized by X-ray diffraction [42]. The positions of the hydride ligands were not directly found but were inferred from the relative geometries of the other ligands and from NMR evidence. The two hydrides bridge the Au–Ir bond (2.699(1) Å) which is comparable in length with those observed in a variety of AuIr cluster compounds [46,47]. The silver complexes were characterized using IR and NMR spectroscopy and conductivity measurements. It is thought that the hydrides bridge the two metal atoms, with the iridium atom having an octahedral coordination geometry. The silver atoms is also ligated by either a coordinating anion in the case of the NO_3 complex or a solvent molecule in the case of the CF_3SO_3 complex. These silver complexes showed evidence, based on $^{31}P\{^1H\}$ NMR data, of a dissociative equilibrium of the type

$$[AgIr(H)_2(bipy)(PPh_3)_2]^{2+} \rightleftarrows Ag^+ + [Ir(H)_2(bipy)(PPh_3)_2]^+$$

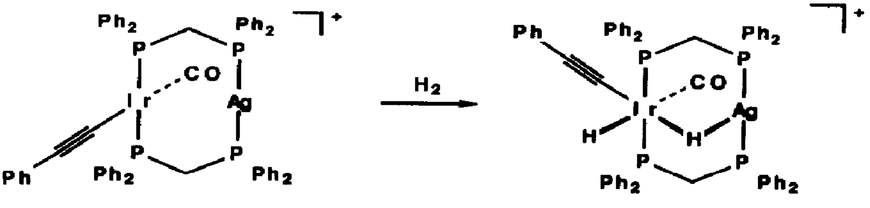
Pignolet et al. also reported that the reaction of PPh_3 with $[Au_2IrH(NO)_3(PPh_3)_4]BF_4$ yielded $[AuIrH(PPh_3)_4]X$ (X = mixture of BF_4 and NO_3) (eqn. (36)), which is relatively unstable in solution at 25 °C [42]:



(36)

It was proposed on the basis of ^{31}P and ^1H NMR and IR spectroscopy that the hydride is terminally bonded to the iridium atom which would be in a square-based pyramidal geometry. This complex and that in eqn. (32) constitute further examples of a monotransition metal–Au hydride where no Au–hydride interaction occurs. It is noteworthy that the isolobal analogy between $[Au(PPh_3)]^+$ and H^+ makes this complex an analogue of the transient species $[IrH_2(PPh_3)_3]^+$ [59]. The action of CO on this Au–Ir complex yielded $[AuIrH(CO)(PPh_3)_4]^+$, also prepared by the reaction given in eqn. (32).

Shaw and coworkers isolated a series of mixed Ir–Cu, Ir–Ag and Ir–Au complexes which contained the bridging dppm ligand [48]. The silver complex $[(OC)(PhC_2)Ir(\mu\text{-dppm})_2Ag]BPh_4$ reacts with H_2 in $CDCl_3$ solution (eqn. (37)) to yield the dihydride, $[(OC)(PhC_2)(H)Ir(\mu\text{-dppm})_2(\mu\text{-}H)Ag]BPh_4$, which was characterized on the basis of $^{31}P\{^1H\}$ and $^1H\{^{31}P\}$ NMR data:

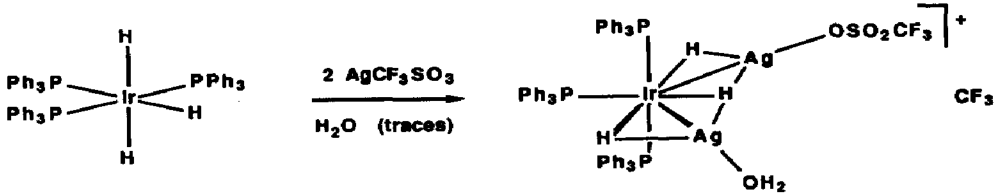


(37)

A similar reaction is proposed for the Ir–Cu complex, $[(CO)(PhC_2)Ir(\mu\text{-}dppm)_2CuCl]$, to give $[(CO)(PhC_2)(H)Ir(\mu\text{-}dppm)_2(\mu\text{-}H)CuCl]$, which was characterized in solution using ^1H and ^{31}P NMR spectroscopy.

(ii) Complexes of stoichiometry IrM_2

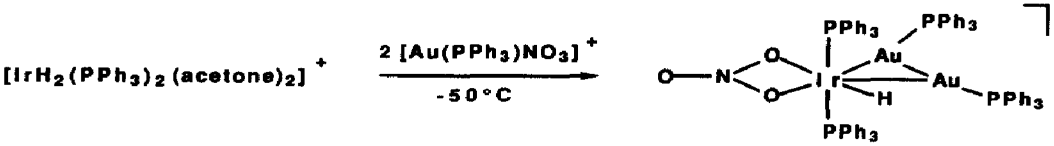
The Ir–disilver complex $[(Ph_3P)_3Ir(\mu_3\text{-}H)(\mu\text{-}H)_2Ag_2(OSO_2CF_3)(H_2O)]$-$[CF_3SO_3]$ was isolated from the reaction between *mer*-$[IrH_3(PPh_3)_3]$ and two equivalents of $AgCF_3SO_3$ (eqn. (38)) and structurally characterized by X-ray diffraction [49]:



(38)

It is noteworthy that this reaction proceeds without any side redox reaction occurring. The three metal atoms are in a "bent" arrangement with the central iridium atom bonded to the two silver atoms (Ir–Ag = 2.808(4) and 2.764(4) Å). The positions of the hydride ligands were inferred from the coordination geometries of the other ligands together with NMR evidence. Of note is the coordination of one CF_3SO_3 anion and of an H_2O molecule to the silver atoms. In solution the complex exhibits dynamic behaviour involving exchange/equivalence of two hydride and two phosphine ligands. The third hydride (the μ_3-H ligand) appears to remain stationary during this process. Interestingly, this trinuclear complex could also be synthesized by a stepwise build-up, i.e. by the reaction of Ag^+ with a complex formulated as $[(Ph_3P)_3IrH_3Ag(OSO_2CF_3)]$, itself resulting from the reaction of one equivalent of $AgCF_3SO_3$ with *mer*-$[IrH_3(PPh_3)_3]$ (see Table 1) [49(b)]. However, $[(Ph_3P_3IrH_3Ag(OSO_2CF_3)]$ does not react with $[AuPPh_3]^+$. The reactivity of this Ir–Ag complex thus appears to be lower than that of its Ir–Au analogue in eqn. (31), which forms addition compounds with $AgCF_3SO_3$ as well as with $[AuPPh_3]^+$ [49(b)]. With the former electrophile, the product isolated was formulated as $[(Ph_3P)_3IrH_3(AuPPh_3)Ag(OSO_2CF_3)][F_3SO_3]$ on the basis of analytical and spectroscopic data.

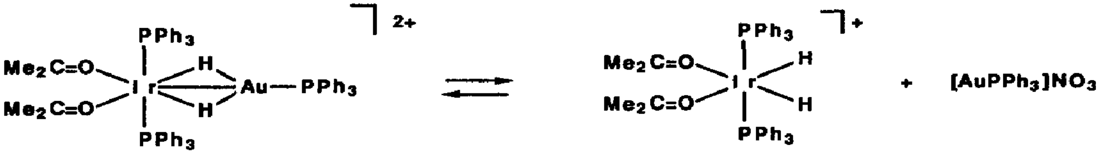
Pignolet and coworkers isolated and structurally characterized the unstable Ir–digold complex $[IrAu_2(H)(PPh_3)_4NO_3]BF_4$ [46]. This resulted from the reaction of two equivalents of $[Au(PPh_3)NO_3]$ with $[Ir(PPh_3)_2(H)_2(acetone)_2]BF_4$ in acetone at −78 °C. Initially, $[(acetone)_2(PPh_3)_2Ir(\mu\text{-}H)_2Au(PPh_3)]^{2+}$ was formed (NMR evidence), but warming to −10 °C the monohydrido complex $[IrAu_2(H)(PPh_3)_4(NO_3)]BF_4$ was isolated in good yield (eqn. (39)):

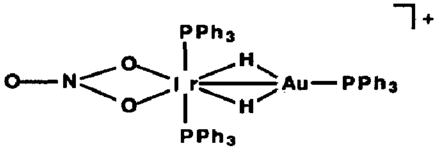


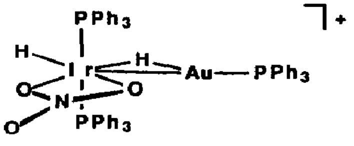
(39)

The X-ray crystal structure showed the iridium atom to be seven-coordinate with a distorted pentagonal-bipyramidal geometry. Although the hydride ligand was not located, it appears to be terminally bonded to the iridium atom, as there is no lengthening of the Ir–O bond *trans* to this hydride, a phenomenon usually observed for ligands *trans* to bridging hydrides. The three metal atoms form an approximately equilateral triangular arrangement, illustrated by the metal–metal distances, Ir–Au = 2.673(1) and 2.697(1) Å and Au–Au = 2.728(1) Å.

The authors could characterize by NMR several reaction intermediates shown below:

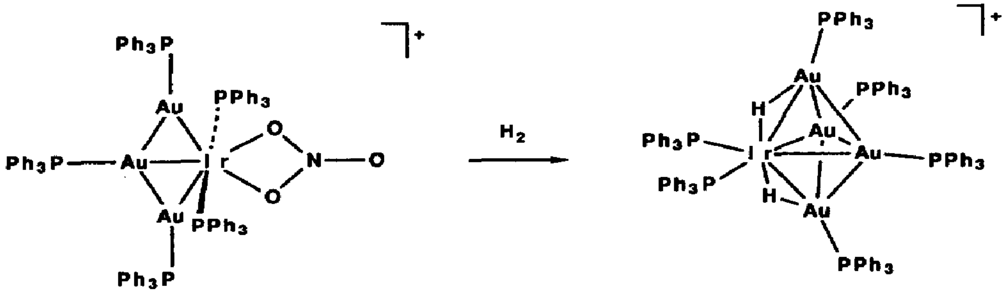






(iii) Complexes of stoichiometry IrM_4

The dihydride Ir–Au cluster complex $[IrAu_4(H)_2(PPh_3)_6]BF_4$ was synthesized from the reaction of an acetone solution of $[IrAu_3(PPh_3)_5(NO_3)]BF_4$ with 1 atm of H_2 (eqn. (40)) [50]:

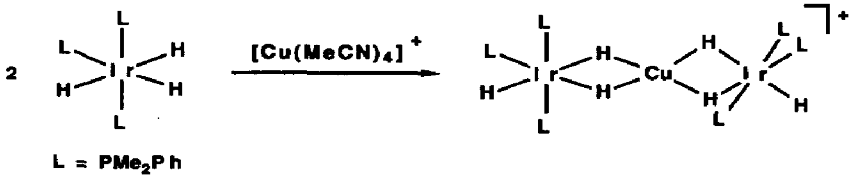


(40)

The complex was characterized in solution by ^1H and ^{31}P NMR spectroscopy and in the solid state by X-ray diffraction. The $IrAu_4$ core consists of an approximately trigonal bipyramidal structure, with the $Ir(PPh_3)_2$ unit occupying an equatorial position (Ir–Au = 2.637(1)–2.753(1) Å; Au–Au = 2.794(1)–3.142(1) Å). The positions of the two hydride ligands could not be determined from the X-ray analysis. The suggested assignment is that they bridge the Ir–Au bonds of the two apical gold atoms.

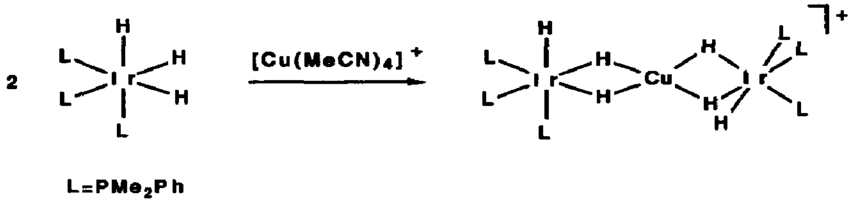
(iv) Complexes of stoichiometry Ir_2M

Caulton and coworkers reported that the reaction of two equivalents of *mer*-$[IrH_3(PMe_2Ph)_3]$ with one equivalent of $[Cu(MeCN)_4]PF_6$ yielded a complex of formulation $[\{$*mer*-$IrH_3(PMe_2Ph)_3\}_2Cu]PF_6$ (eqn. (41)) [51]:



(41)

A similar reaction was also reported to occur with *fac*-$[IrH_3(PMe_2Ph)_3]$ to give $[\{$*fac*-$IrH_3(PMe_2Ph)_3\}_2\}Cu]PF_6$ (eqn. (42)) [51]:

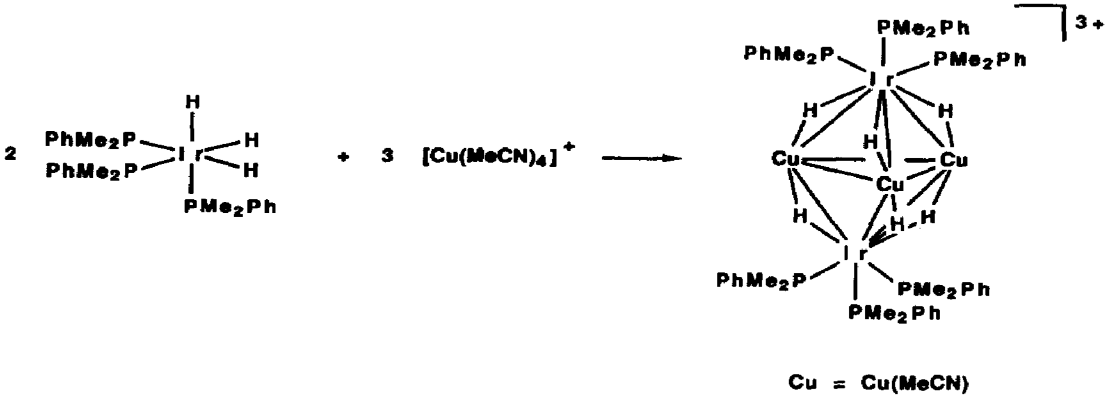


(42)

No conversion could be found between the two species in an acetonitrile solution over a period of several hours at 25 °C. The latter complex was characterized by a single-crystal X-ray study which revealed a linear trinuclear chain (Ir–Cu = 2.502(4), 2.529(4) Å). It is suggested that four of the hydride ligands, which were not located in the X-ray study, bridge the iridium and copper atoms, with the remaining two hydride ligands, being terminally bound to the iridium atoms. As only one hydride signal is observed in the ^1H NMR spectrum it is thought that the complex is fluctional about the copper atom and the hydrides can easily exchange positions. A silver(I) adduct of *fac*-IrH_3P_3 and $AgBF_4$ was synthesized by similar means and formulated as $[\{$*fac*-$IrH_3(PMe_2Ph)_3\}_2Ag]BF_4$ [51]. It is proposed that the structure is similar to that found for the copper complex but on this occasion no evidence for fluctionality about the silver atom was found from NMR data.

(v) Complexes of stoichiometry Ir_2M_3

In a subsequent publication, Caulton and coworkers published an extension of the above work [52]. Reaction of *fac*-$[IrH_3(PMe_2Ph)_3]$ and $[Cu(MeCN)_4]PF_6$ at −78 °C in a 2 : 3 molar ratio resulted in the isolation of the complex of formula $[Ir_2Cu_3H_6(MeCN)_3(PMe_2Ph)_6][PF_6]_3$ (eqn. (43)):

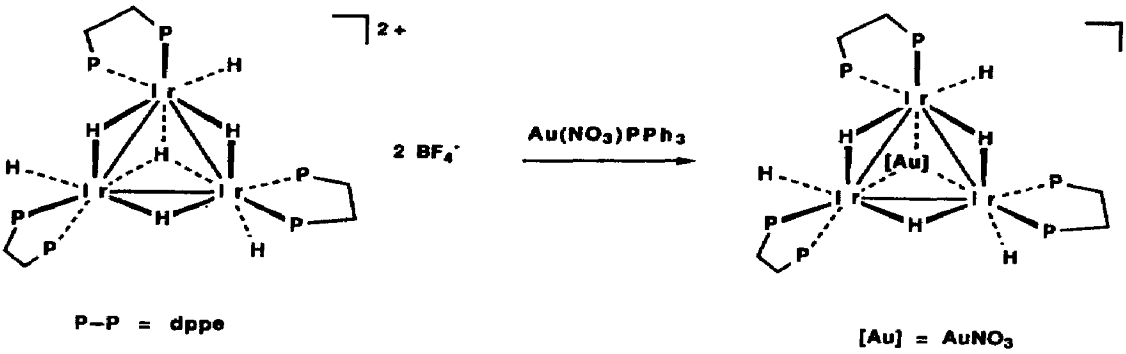


(43)

An X-ray crystal structure of this complex shows the metal atoms to be in a trigonal bipyramidal arrangement with the two iridium atoms in the axial positions (Cu–Ir = 2.793(9) Å, Cu–Cu = 2.570(22) Å). Although the hydride atoms were not located using the X-ray diffraction data, they were placed in positions *trans* to the Ir–P vectors on the basis of AA′A″XX′X″ patterns in the ^1H and ^{31}P NMR spectra. Thus they can be considered as μ-H ligands bridging the Ir–Cu bonds.

(vi) Complexes with stoichiometry Ir_3M

Reaction of $[Au(PPh_3)NO_3]$ with the trinuclear complex $[Ir_3(\mu_3\text{-}H)(\mu\text{-}H)_3H_3(dppe)_3](BF_4)_2$ yielded the cationic Ir–Au hydrido cluster $[AuIr_3(\mu_2\text{-}H)_3H_3(NO_3)(dppe)_3]BF_4$ (eqn. (44)) [53]:

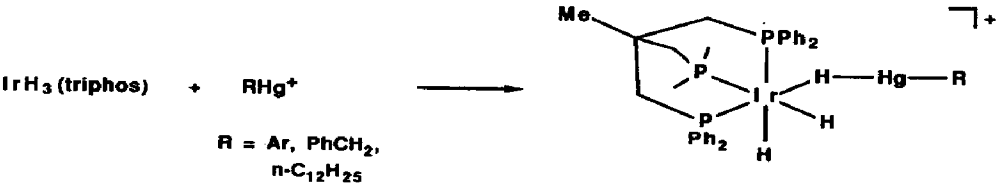


(44)

The X-ray crystal structure of this complex revealed the $AuIr_3$ unit to be approximately tetrahedral (Ir–Ir = 2.805(1)–2.861(1) Å, Ir–Au = 2.696(1)–2.718(1) Å) and the AuL^+ unit has effectively replaced the μ_3-H of the precursor compound. No hydrides were located in the structure but proof of their existence comes from ^1H and ^{31}P NMR data. The coordinated NO_3 ligand is readily replaced by PPh_3 to yield the complex $[AuIr_3(\mu_2\text{-}H)_3(H)_3(PPh_3)(dppe)_3]BF_4$ characterized by NMR spectroscopic techniques.

F. BIMETALLIC IRIDIUM HYDRIDO COMPLEXES WITH GROUP 12 METALS

The only complexes so far reported in this class are formed with mercury. Thus Venanzi and coworkers reported the low temperature reaction of $[IrH_3(triphos)]$ with RHg^+ species (R = n-$C_{12}H_{25}$, CH_2Ph, 2,4,6-$Me_3C_6H_2$, Ph, 2,4,6-$Cl_3C_6H_2$, 4-ClC_6H_4) (eqn. (45)) [54]:



(45)

The compounds formed are of the type $[(triphos)(H_{3-x})Ir(\mu\text{-}H)_xHgR]CF_3SO_3$ and were characterized using NMR techniques. On the basis of the NMR data it is proposed that the iridium and mercury atoms are linked by a hydride bridging ligand, although this could be a fluctional system. The compounds have low thermal stability and readily decompose.

G. CONCLUDING REMARKS

The examples described above and which were taken from iridium hydride chemistry clearly illustrate the rapid progress made in the past few years in the preparation and characterization of bimetallic or polymetallic hydrido species. Thus the application of Venanzi's molecular association scheme in which mononuclear hydrido complexes are regarded as Lewis bases towards acceptor complexes has led to the preparation of many heterometallic hydrido compounds. Although hydrido-bridged iridium complexes have so far been a little disappointing with respect to catalytic hydrogenations, bimetallic hydrido systems remain conceptually interesting if one recalls Muetterties' [55] efficient $[HRh\{P(OR)_3\}_2]_2$ dihydride (for catalytic applications) or if one considers the combinations recently realized between transition metals and the classical reducing agent AlH_4^- (see for example ref. 56) and which constitute potential new stoichiometric and catalytic hydrogenation agents.

Considering the increasing number of polyhydrido mononuclear complexes that have now been authenticated as H_2 complexes, it can be anticipated that binuclear and polynuclear hydrido-rich complexes will also be prepared or identified as complexes of molecular hydrogen. Such considerations would be of particular interest in connection with the involvement of hydrido complexes in catalytic hydrogenation reactions or for H_2 storage devices [57]. It is noteworthy that a large majority of heterometallic hydrido iridium complexes (and all clusters of this type) contain group 11 metals. The increasing number of heterometallic complexes containing two or more AuL units linked to each other should also be noted [11,58,59]. These observations are particularly interesting in relation to the isolobal analogy between the fragments LM^+ ($M = Cu$, Ag, Au) and H^+ and between LMH or LM–ML and H_2. A significant interaction between adjacent hydride ligands may also be related to the stereodynamic behaviour of polyhydride complexes. This view could therefore be extended to heterometallic systems containing d^{10} ions isolobal with the proton. For example, the fluctional behaviour of $[IrH_4(PR_3)_3]^+$ [60(a)], a protonation product of $[IrH_3(PR_3)_3]$ [60], and of $[IrAg_2H_3(PPh_3)_3]^{2+}$ [49(a)] obtained by addition of Ag^+ to $[IrAgH_3(PPh_3)_3]^+$ which is itself related to $[IrH_4(PR_3)_3]^+$ by the isolobal analogy should be remembered. Novel and interesting properties are likely to be associated with such systems.

Just as electron counting rules do not allow the site occupied by a hydrido ligand, e.g. terminal, doubly or triply bridging, in a cluster compound to be predicted, they cannot predict the bonding mode, η^1, μ^2 or μ^3 respectively of an ML^+ ($M = Cu$, Ag, Au) unit in a heterometallic complex. Since these cations do not donate an electron to the cluster, structural changes are in principle not expected and in general are not observed in the metal core geometry of the fragment to which they have been added. However, energy considerations may lead to isomerization of the metal core. Further studies are clearly needed to understand better the structural properties and the reactivity of polynuclear iridium hydrido complexes.

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