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TRANSITION METAL COMPLEXES WITH BRIDGING HYDRIDE LIGANDS

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CONTENTS

A. INTRODUCTION

The coordination chemistry of hydrogen, acting as a ligand in a transition metal complex, has progressed almost explosively during the last ten years [1].

The striking advances in borane chemistry that took place during the period 1940–1960 revealed a wealth of new types of compounds and spurred the development of improved theoretical models for the description of the chemical bond [2]. Similarly, the discovery of a large number of stable compounds containing hydrogen bonded to a transition metal centre immediately induced a flurry of activity in this area in the expectation of another "hydride chemistry boom", an expectation which is being amply fulfilled [3].

Furthermore, just as the Group III hydride chemistry added a new dimension to preparative organic chemistry [4], the use of transition metal hydrides has revolutionized the industrial processes used for the production of a wide range of organic chemicals. Transition metal organometallic chemistry is becoming all-pervading in the regio- and stereo-selective synthesis of organic compounds [5].

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TABLE 1

Some organometallic reactions involving transition metal hydrido complexes

(1) Homogeneous hydrogenation (typical "catalyst": $[RhCl(PR_3)_3]$)
(2) Alkene polymerization (typical "catalyst": $TiCl_3/AlR_3$)
(3) Alkene dimerization (typical "catalyst": $RhCl_3$)
(4) Alkene carbonylation (typical "catalyst": $[CoH(CO)_4]$)
(5) Wacker acetaldehyde synthesis (typical "catalyst": $PdCl_2/CuCl_2$)
(6) Hydrocyanation (typical "catalyst": $[Ni\{P(OR)_3\}_4]$)

A selection of some of the industrially significant organometallic reactions involving transition metal hydrides is shown in Table 1.

The high dissociation energies of M–H bonds in some mononuclear transition metal complexes are now firmly established. As can be seen from the data shown in Table 2 [6], these are of the same order of magnitude as the M–Cl bonds and much higher than metal–alkyl or aryl bonds in comparable systems.

While a wide range of cluster compounds containing bridging hydride ligands has been known for some time [7], only in the last few years has it become apparent that hydride ligands show a marked tendency to act as bridging atoms in binuclear complexes [8]. Thus, a fairly large number of compounds containing one, two, three, and even four bridging hydrogen atoms have been reported in recent literature [1]. Their schematic formulation is shown in Fig. 1.

Hydride bridges in binuclear compounds are often accompanied by other

TABLE 2

M–H bond enthalpy contributions, $\bar{D}$, for some transition metal hydrido complexes [6]

	$\bar{D}$ ($kJ\ mol^{-1}$)
$[MnH(CO)_5]$	ca. 300
$[FeH(CO)_4]^-$	ca. 310
$[CoH(CO)_4]$	ca. 290
Compared with	
$[Mn(CH_3)(CO)_5]\{Mn–CH_3\}$	ca. 130
$[MnCl(CO)_5]\{Mn–Cl\}$	ca. 300

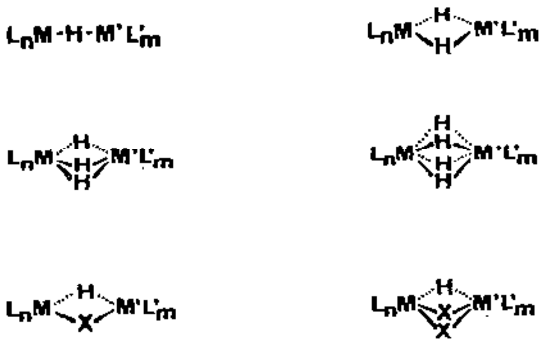

Fig. 1. Schematic formulation of mono-, di-, tri- and tetrahydrido-bridged transition metal complexes.

bridging atoms or groups, e.g. halides, phosphides, and carbon monoxide. The schematic formulation of complexes of this type is also shown in Fig. 1.

Some actual examples of monohydrido-bridged complexes, taken from the earlier literature, **1** [9], **2** [10], **3** [11], and **4** [12] are schematically shown in Fig. 2 and a selection of dihydrido-bridged complexes of recent publication, **5** [13], **6** [14], **7** [15], and **8** [16] are shown in Fig. 3. Many trihydrido-bridged compounds, e.g. **9** [16], **10** [17], and **11** [18] and one tetrahydrido-bridged

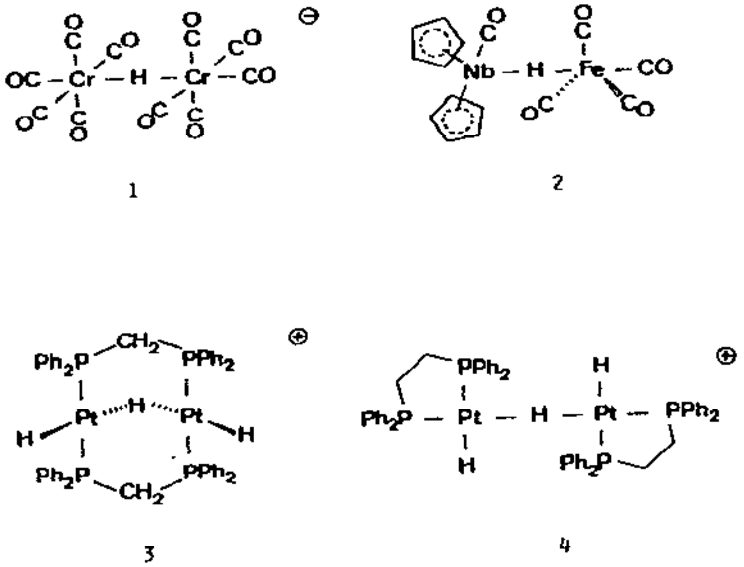

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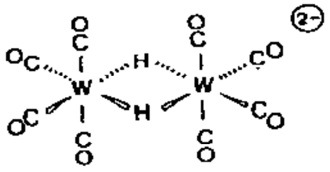
Fig. 2. Some binuclear monohydrido-bridged transition metal complexes.



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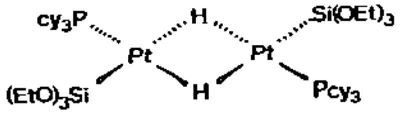

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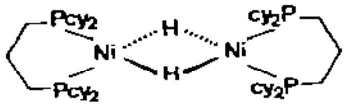

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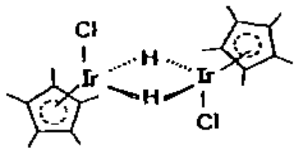

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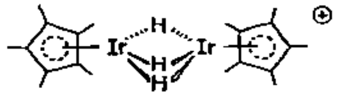
Fig. 3. Some binuclear dihydrido-bridged transition metal complexes.

complex **12** [19] have also been reported and are shown in Fig. 4. Finally, hydrido bridges frequently occur together with other bridging ligands as can be seen from examples **13** [16], **14** [20], **15** [16], and **16** [21] shown in Fig. 5.

Most of the interest in binuclear complexes containing bridging hydride ligands has centred around their structural features and on the nature of the bonding in the M–H–M bridging unit.



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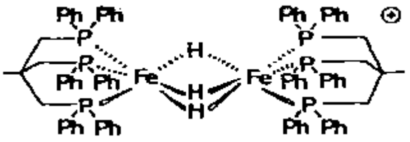

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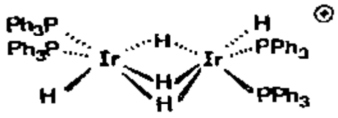

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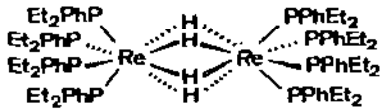

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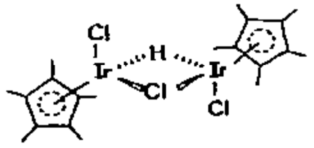
Fig. 4. Some binuclear tri- and tetrahydrido bridged transition metal complexes.



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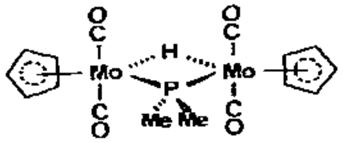

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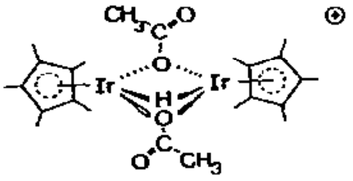

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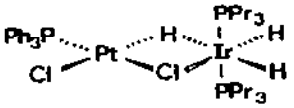

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Fig. 5. Some binuclear hydrido-bridged and heteroatom-bridged transition metal complexes.

B. STRUCTURAL STUDIES

The most reliable structural information has been obtained by neutron diffraction [1]. Several interesting features have emerged from these investigations.

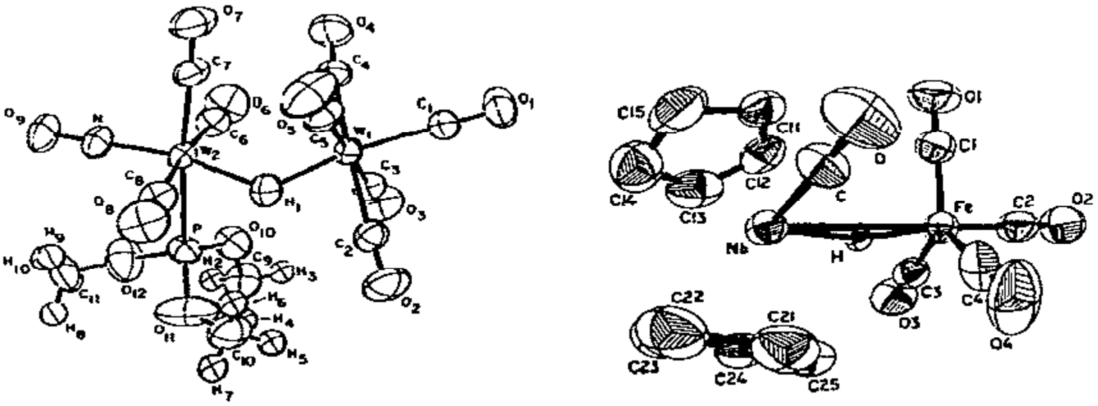


Fig. 6. The crystal structures of $(OC)_5W(\mu_2\text{-}H)W(CO)_3(NO)\{P(OMe)_3\}$ and $(\eta^5\text{-}C_5H_5)_2(OC)Nb(\mu_2\text{-}H)Fe(CO)_4$.

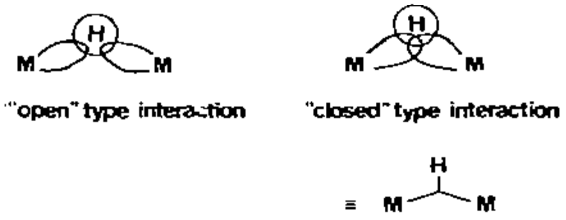


Fig. 7. The "open" and "closed" type of M–H–M bonds.

(i) Monohydrido-bridged species

It is now evident that, at the static limit, the M–H–M unit is not linear. The crystal structures of two compounds showing this distortion from linearity, i.e. $[\{(MeO)_3P\}(ON)(OC)_3W(\mu_2\text{-}H)W(CO)_5]$ [22] and **2** [10], are shown in Fig. 6.

This deviation from linearity is accounted for in terms of a direct metal–metal interaction [8]. As shown in Fig. 7, when a significant deviation from linearity is observed the M–H–M bond is described as "closed" by analogy with the terminology developed for borane chemistry [8].

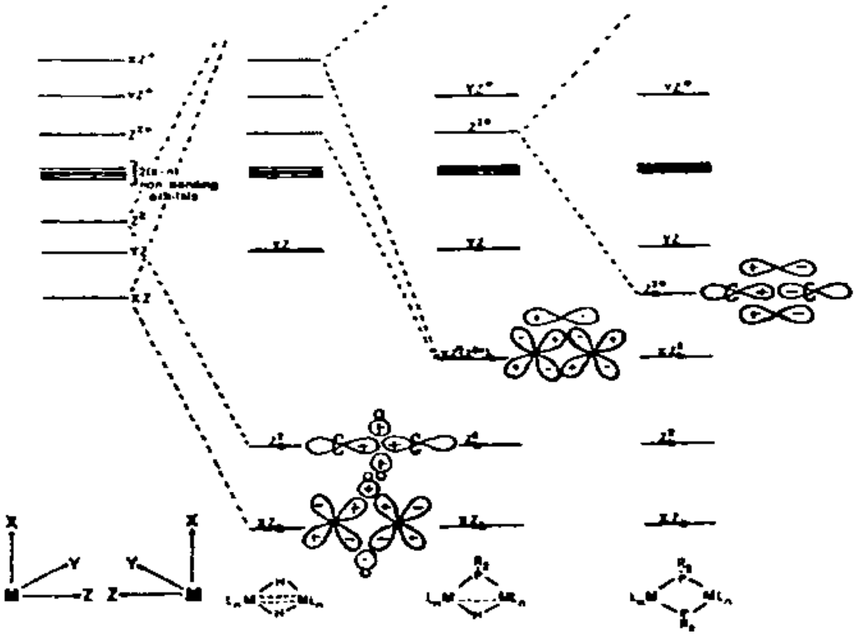


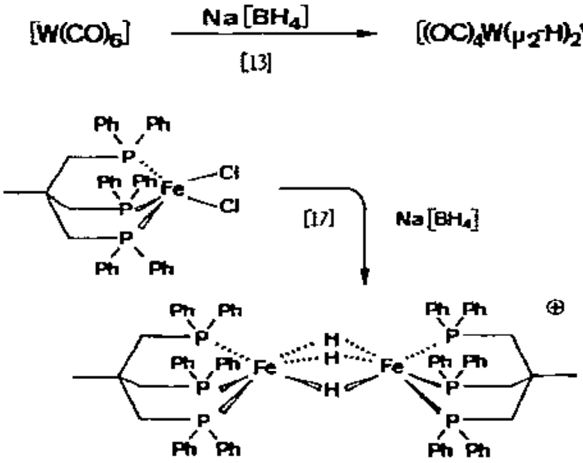
Fig. 8. Bridging unit orbital interaction in $[L_nMH_2ML_n]$ complexes.

(ii) Di- and trihydrido-bridged complexes

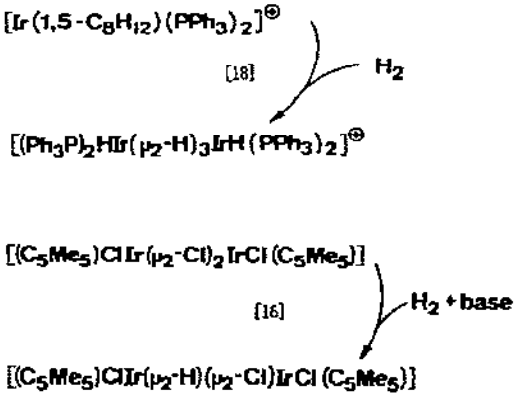
These are generally discussed using an MO model [23]. Frequently bridge formation is described as resulting from the interaction of a multiply bonded M–M unit with "protons" and, for this purpose, the terminology "protonated double bonds" has been used [24]. A schematic representation of some of the orbital interactions postulated for this type of unit [23] is shown in Fig. 8.

C. PREPARATIVE STUDIES

Examination of literature data on bimetallic, hydrido-bridged complexes shows that, until very recently, all the compounds of this type had been obtained unintentionally. Furthermore, it is significant that most of them



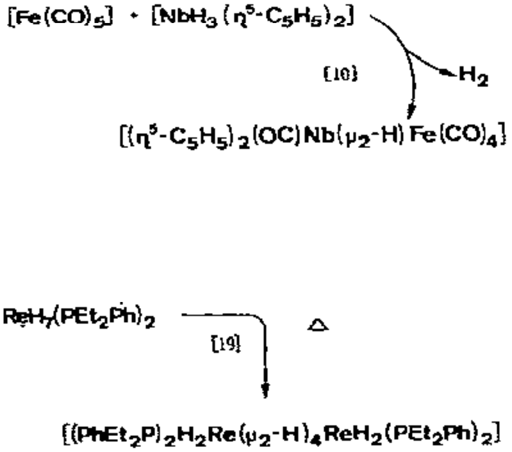
Scheme 1



Scheme 2

were obtained while attempting to prepare mononuclear hydrido complexes.

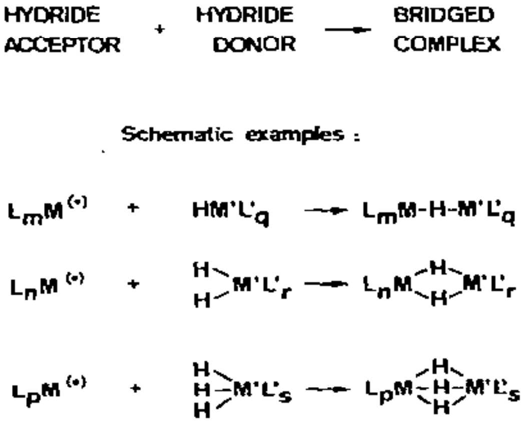
Some examples of binuclear compounds obtained using Main Group hydride reagents are shown in Scheme 1. Other examples of hydrido-bridged compounds, obtained by the action of molecular hydrogen on appropriate substrates, are shown in Scheme 2. Finally, hydrogen elimination reactions from mononuclear hydrides can also produce hydrido-bridged species as shown by the examples presented in Scheme 3.



Scheme 3

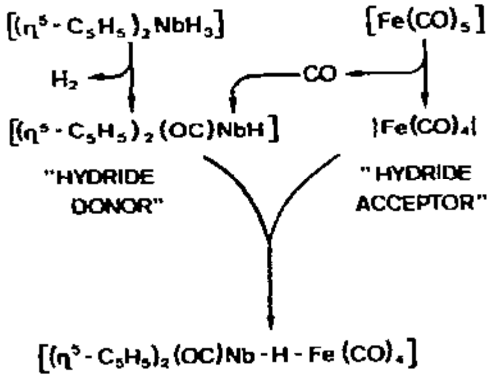
D. "DONOR–ACCEPTOR" SCHEME

The formation of the hydrido-bridged complexes mentioned earlier can be rationalized on the basis of a formal scheme in which a mononuclear hydrido complex acts as a "ligand", binding through one or more of its



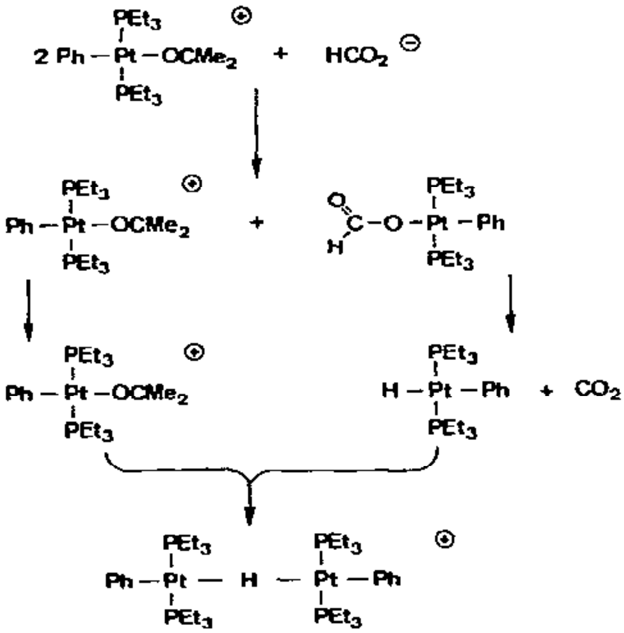
Scheme 4

hydrogen atoms to a coordinatively unsaturated complex, which acts as an "acceptor", resulting in the formation of one or more two-electron, three-centre M–H–M bonds as depicted in Scheme 4. Thus, the formation of $[(\eta^5\text{-}C_5H_5)_2(CO)Nb(\mu_2\text{-}H)Fe(CO)_4]$ can be formally described as shown in Scheme 5.



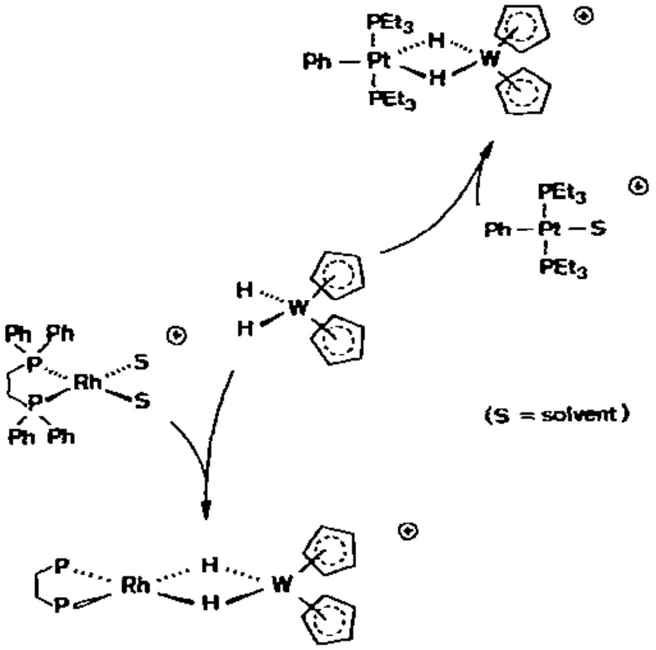
Scheme 5

This simple scheme can be used to devise innumerable binuclear species. Examples of the planned synthesis of hydrido-bridged complexes, taken from the work of the author and co-workers, are shown in Scheme 6 [25] for a mono-hydrido species, while typical preparations of some di- and trihy-



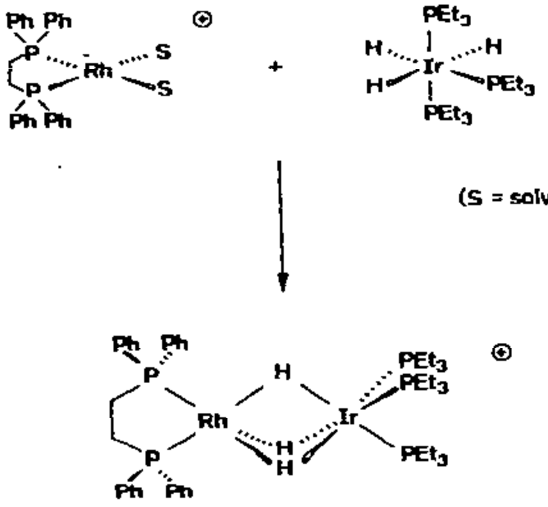
Scheme 6

drido-bridged complexes are shown in Schemes 7 [26] and 8 [27], respectively.



(S = solvent)

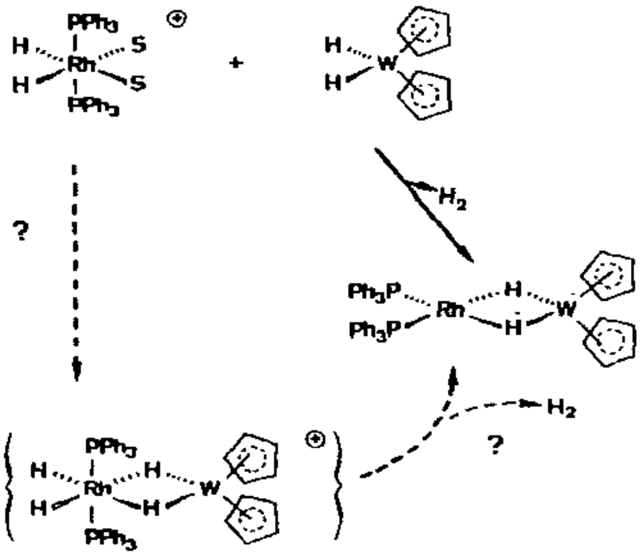
Scheme 7



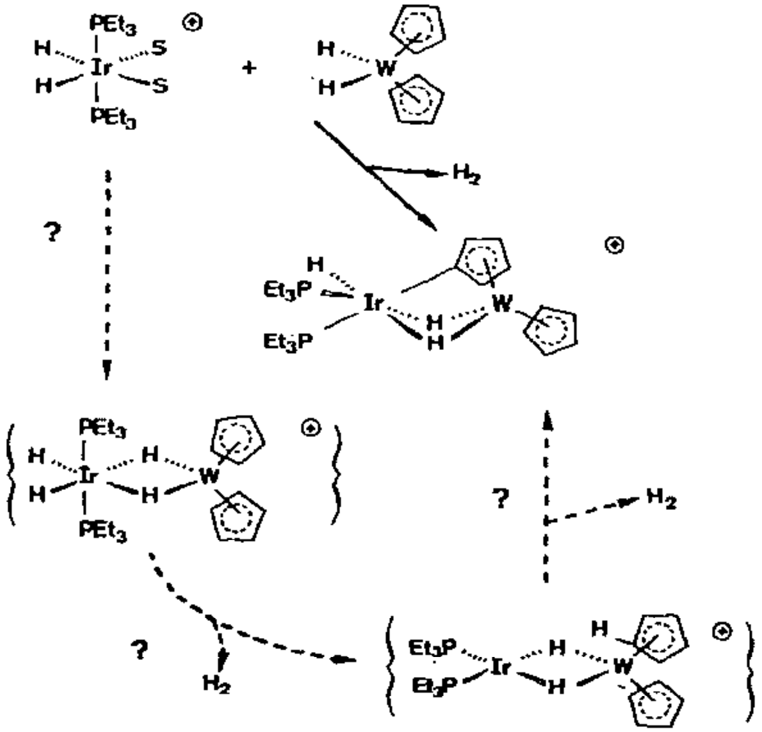
(S = solvent)

Scheme 8

Although the "donor–acceptor" interaction outlined above can generally be invoked to rationalize the nature of the initial product formed, quite often this primary "complex" undergoes a subsequent reaction which may or may not result in the formation of a hydrido-bridged species. Two examples of this type of behaviour are shown in Schemes 9 [28] and 10 [26]. The

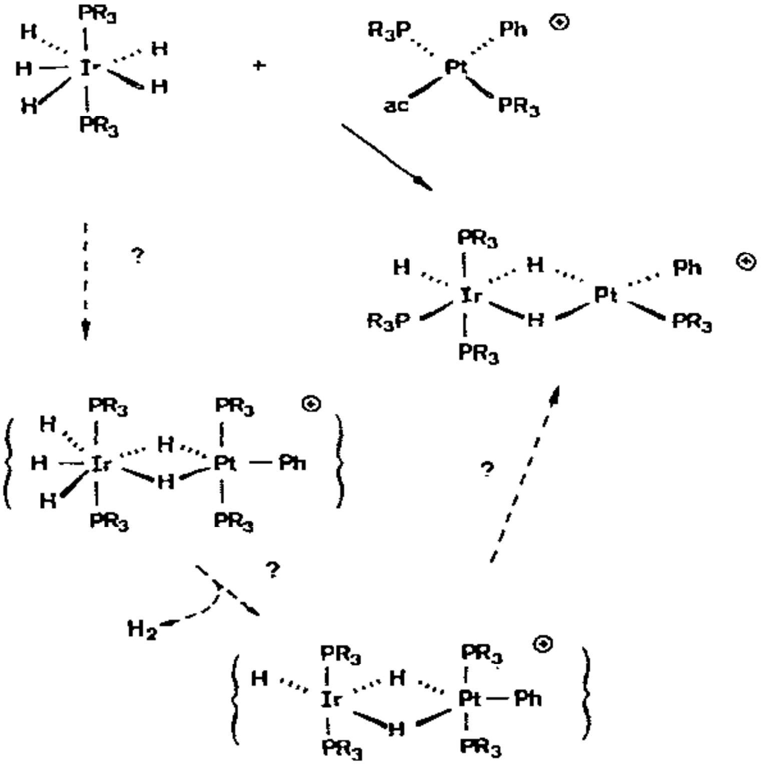


Scheme 9



Scheme 10

elimination of molecular hydrogen from a bi- or polyhydrido complex of the type shown on the above schemes is a frequently occurring reaction, e.g. it is a typical reaction of $[IrH_5(PR_3)_2]$. In this case, the coordinatively unsaturated iridium(III) species, resulting from the loss of H_2, abstracts a ligand from another molecule of complex present in solution, producing a coordinatively saturated iridium(III) trihydrido complex and another coordinatively unsaturated species. The two then combine to form the hydrido-bridged complex. An example is shown in Scheme 11 [29].

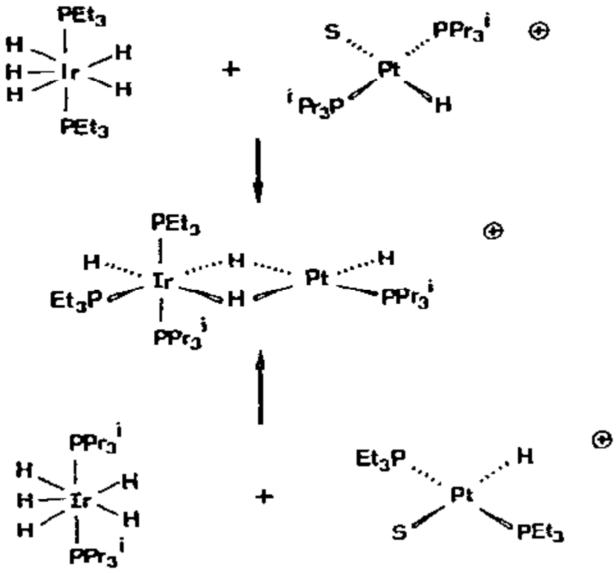


Scheme 11

E. REACTION PATHWAYS AND DYNAMIC BEHAVIOUR IN SOLUTION

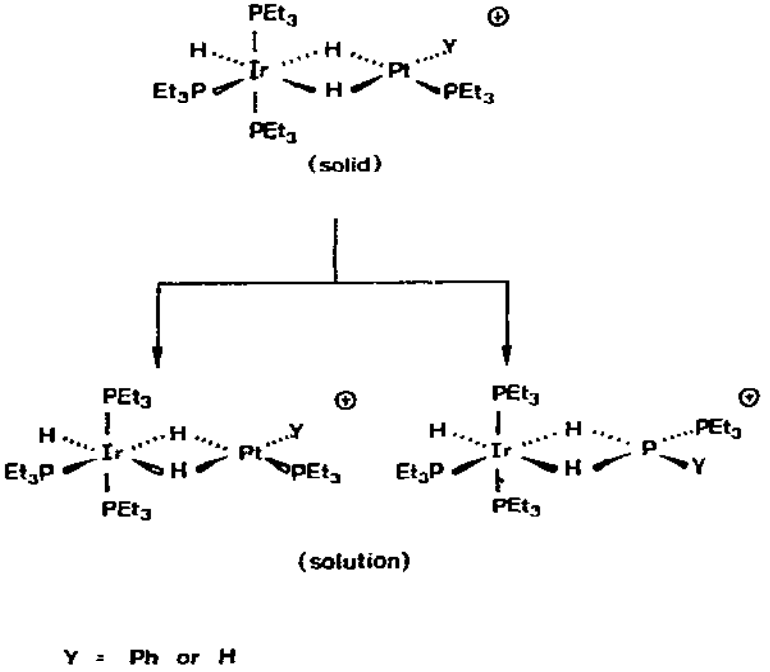
Reaction pathways for the formation of hydrido-bridged complexes of the type discussed are likely to be quite complex. An indication of this is provided by the frequent phosphine site-exchange observed during product formation. An example of this exchange, as observed in complexes of the type $[(PR_3)_3HIr(\mu_2\text{-}H)_2PtR'(PR_3)_2]^+$, is shown in Scheme 12 [30].

Furthermore, compounds of this type show interesting dynamic behaviour in solution:



Scheme 12

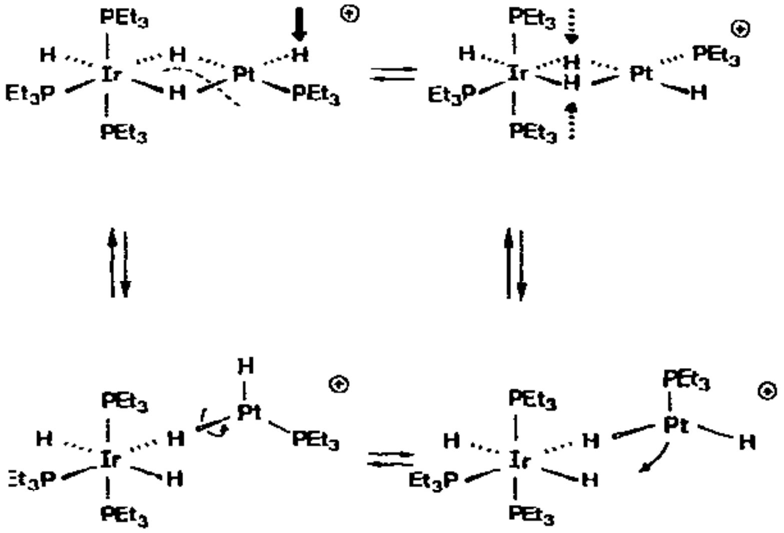
(1) The complex $[(PEt_3)_3HIr(\mu_2\text{-}H)_2PtPh(PEt_3)]^+$ in the solid state has the cisoid phosphine arrangement shown in Scheme 13. This structure is



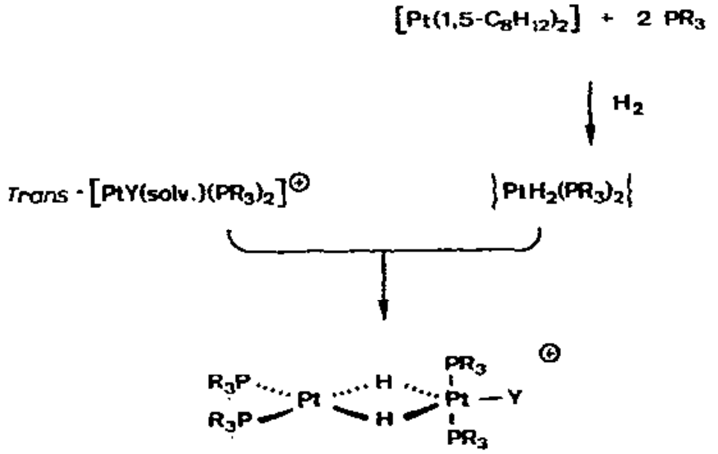
Scheme 13

maintained in solution when the solid is dissolved in a solvent which has been pre-cooled to −60°. On warming up the solution isomerization takes place and a mixture of the cisoid and transoid forms is obtained.

(2) The complex $[(PEt_3)_3HIr(\mu_2\text{-}H)_2PtH(PEt_3)]$ is also present in an isomeric mixture of cisoid and transoid forms in solution (see Scheme 13).



Scheme 14



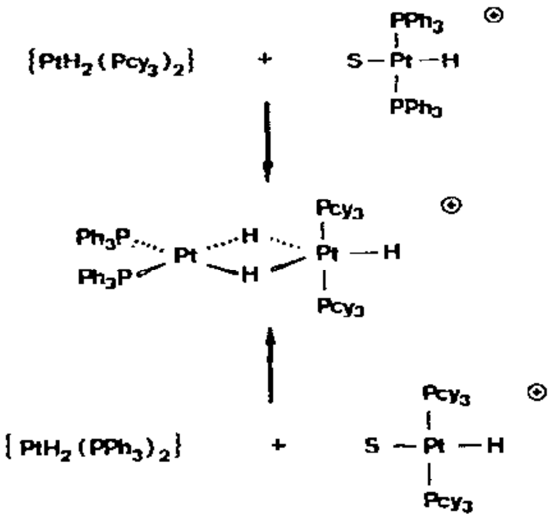
(R = Et, Y = H or Ph; R = Ph or cy, Y = H)

Scheme 15

(3) The compound $[(PPr^i_3)(PEt_3)HIr(\mu_2\text{-}H)_2PtH(PPr^i_3)]^+$, however, is present only in its cisoid form in solution.

(4) Spin-saturation experiments [31] show that compound $[(PEt_3)_3HIr(\mu_2\text{-}H)_2PtH(PEt_3)]^+$ undergoes a dynamic process in solution which exchanges the two bridging hydride ligands and can be described as shown in Scheme 14. As can be seen, this process isomerizes the cisoid into the transoid form and thus provides a basis for the description of the isomerization pathway.

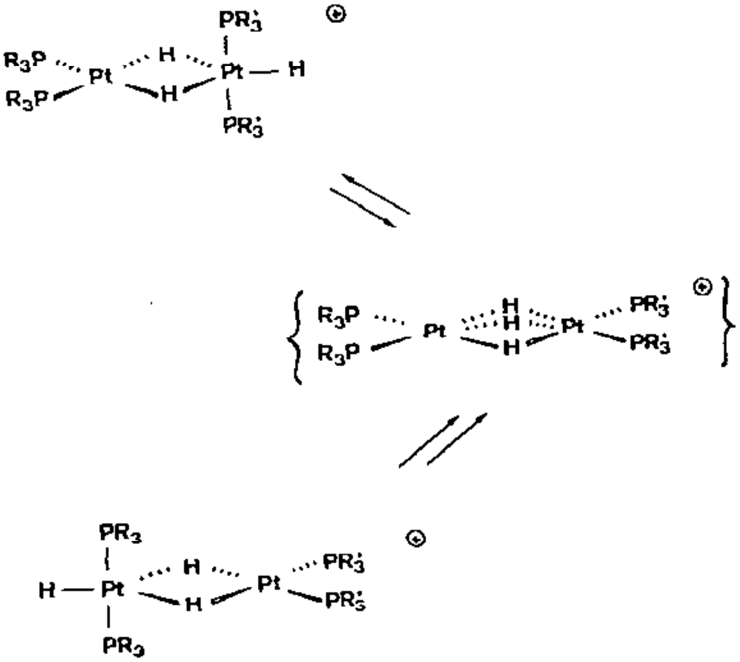
Phosphine site-exchange has also been observed during the reaction shown in Scheme 15 which gives dihydrido-bridged complexes containing one four-coordinate and one five-coordinate platinum atom [32]. When this reaction is carried out using different phosphines on the two reactants the bulkier phosphine is found on the square planar platinum atom irrespective of whether it was originally bound on the cationic species or the di-hydride. An example of this type of phosphine exchange is shown in Scheme 16 [33].



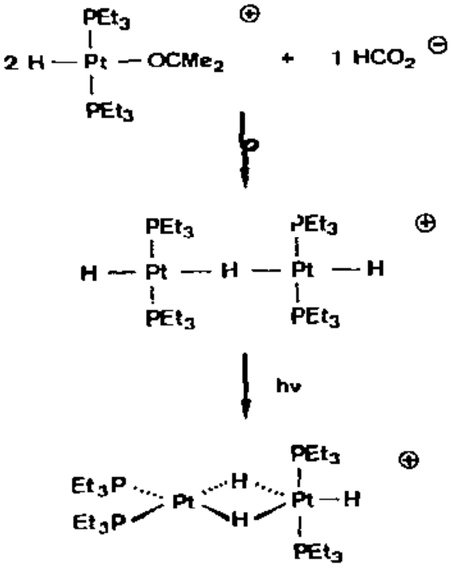
Scheme 16

This process can be rationalized by assuming that, during the formation reaction, a trihydrido-bridged intermediate of the type $[(PR_3)_2P(\mu_2\text{-}H)_2PtH(PR_3)_2]^+$ is formed (see Scheme 17). Compounds of this type have been described by T.H. Tulip et al. [34] who also report the crystal structure of $[Pt_2H_3({}^tBu_2PCH_2CH_2CH_2PBu^t_2)_2]^+$.

Finally, it has been observed [35] that compounds of the type $[(PR_3)_2HPt(\mu_2\text{-}H)PtH(PR_3)_2]^+$ can be obtained by a reaction analogous to that shown in Scheme 6 but that these complexes rearrange in solution to their dihydrido-bridged structural isomers $[(PR_3)_2Pt(\mu_2\text{-}H)_2PtH(PR_3)_2]^+$ as shown in Scheme 18.



Scheme 17



Scheme 18

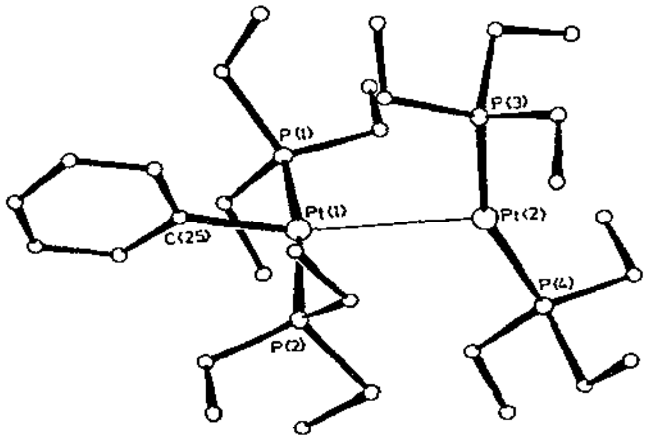


Fig. 9. The molecular structure of $[(Et_3P)_2(Ph)Pt(\mu_2\text{-}H)PtH(PEt_3)_2]^+$. Bond lengths (Å): Pt1–Pt2 3.09, Pt1–P1 2.29, Pt1–P2 2.31, Pt1–C25 2.02, Pt2–P3 2.26, Pt2–P4 2.30. Interbond angles (°): P1–Pt1–Pt2 93.7, P1–Pt1–P2 169.4, P1–Pt1–C25 87.8, P2–Pt1–Pt2 93.0, P2–Pt1–C25 87.9, C25–Pt1–Pt2 164.3, Pt1–Pt2–P3 91.1, Pt1–Pt2–P4 112.0, P3–Pt2–P4 156.8. Torsion angles (°): P1–Pt1–Pt2–P3 87.4, P1–Pt1–Pt2–P4 −90.4, P2–Pt1–Pt2–P3 −100.6, P2–Pt1–Pt2–P4 81.6.

F. X-RAY CRYSTAL STRUCTURES

The molecular structures of several of the hydrido-bridged complexes prepared in the author's laboratories have been determined.

The most prominent feature of the structure of $[(PEt_3)_2HPt(\mu_2\text{-}H)PtPh(PEt_3)_2]^+$ [36] (see Fig. 9) is the bent arrangement of the Pt(2)–Pt(1)–C(25) atoms from which it can be deduced that the Pt(1)–H–Pt(2) atoms are not collinear. As the Pt(2)–Pt(1)–C(25) bond angle is ca. 164°, it is also deduced that, in this compound, the extent of metal–metal interaction is slight and the bridged structure can be described as "open".

The coordination geometry of $[(PEt_3)_2Pt(\mu_2\text{-}H)_2PtPh(PEt_3)_2]^+$ [33] is shown in Fig. 10. The positions of the heavy atoms clearly indicate that, in the solid state, the $Pt(\mu_2\text{-}H)_2Pt$ bridge is not symmetrical although there do not appear to be packing interactions which could impose distortions, in the crystal lattice, on an otherwise symmetrical bridge. Although such asymmetric interactions have not been reported for potentially symmetrical bridging units, it is tempting to speculate that, at the static limit, distorted bridging arrangements may be of general occurrence and that their detection has been prevented by either disorder in the crystal lattice or by low activation energy for rearrangement in the solid state.

An unsymmetrical bridging unit has also been found in $[(PEt_3)_3HIr(\mu_2\text{-}$

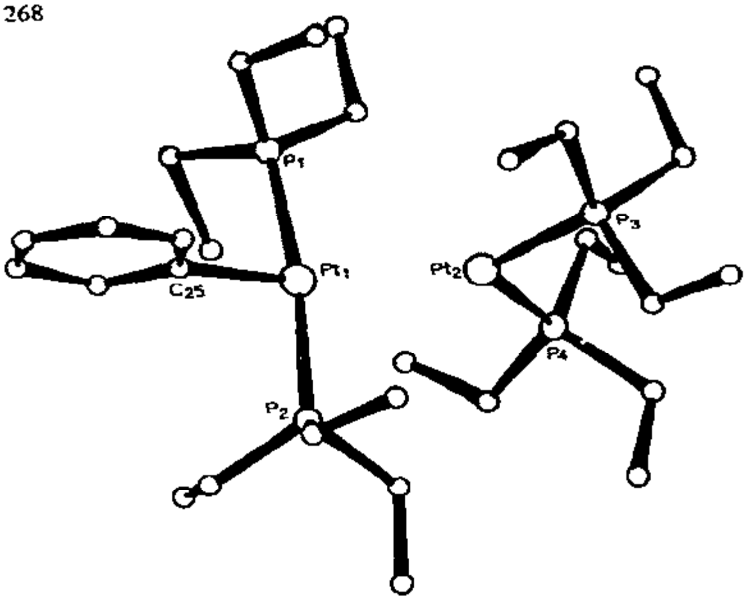


Fig. 10. The molecular structure of [(Et$_3$P)$_2$Pt(μ_2-H)Pt(Ph)(PEt$_3$)$_2$]$^{\ominus}$. Pt(1)–Pt(2) 2.819(1), Pt(1)–P(1) 2.297(5), Pt(1)–P(2) 2.293(4), Pt(1)–C(25) 2.070(15), Pt(2)–P(3) 2.257(4), Pt(2)–P(4) 2.314(5), P(1)–Pt(1)–Pt(2) 93.2(1), P(1)–Pt(1)–P(2) 171.5(2), P(1)–Pt(1)–C(25) 87.5(4), P(2)–Pt(1)–Pt(2) 93.8(1), P(2)–Pt(1)–C(25) 87.9(4), C(25)–Pt(1)–Pt(2) 158.3(4), Pt(1)–Pt(2)–P(3) 132.9(1), Pt(1)–Pt(2)–P(4) 124.5(1), P(3)–Pt(2)–P(4) 102.5(1).

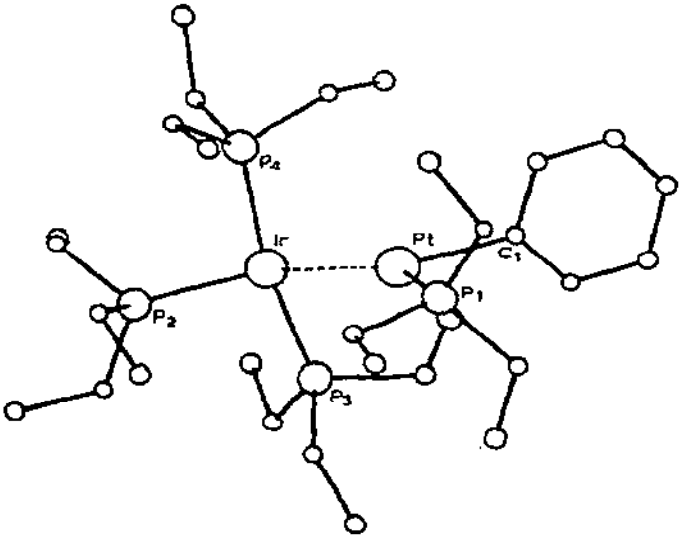


Fig. 11. The molecular structure of [(Et$_3$P)$_3$HIr(μ_2-H)$_2$PtPh(PEt$_3$)]$^{\oplus}$. Bond lengths (Å): Pt···Ir 2.687(2), Pt–C 2.08(2), Pt–P1 2.213(6), Ir–P2 2.323(5), Ir–P3 2.354(6), Ir–P4 2.341(6). Bond angles (°): Pt–Ir–P2 138.2(1), Pt–Ir–P3 86.6, Pt–Ir–P4 91.2(1), Ir–Pt–C1 133.0(3), Ir–Pt–P1 140.7(1), P2–Ir–P3 96.6, P2–Ir–P4 94.5(2), P3–Ir–P4 165.7(1). Torsion angles (°, av. error ca. 1°): P1–Pt–Ir–P2 −2, P1–Pt–Ir–P3 94, P1–Pt–Ir–P4 −100, P2–Ir–Pt–C1 −178, P3–Ir–Pt–C1 −82, P4–Ir–Pt–C1 84.

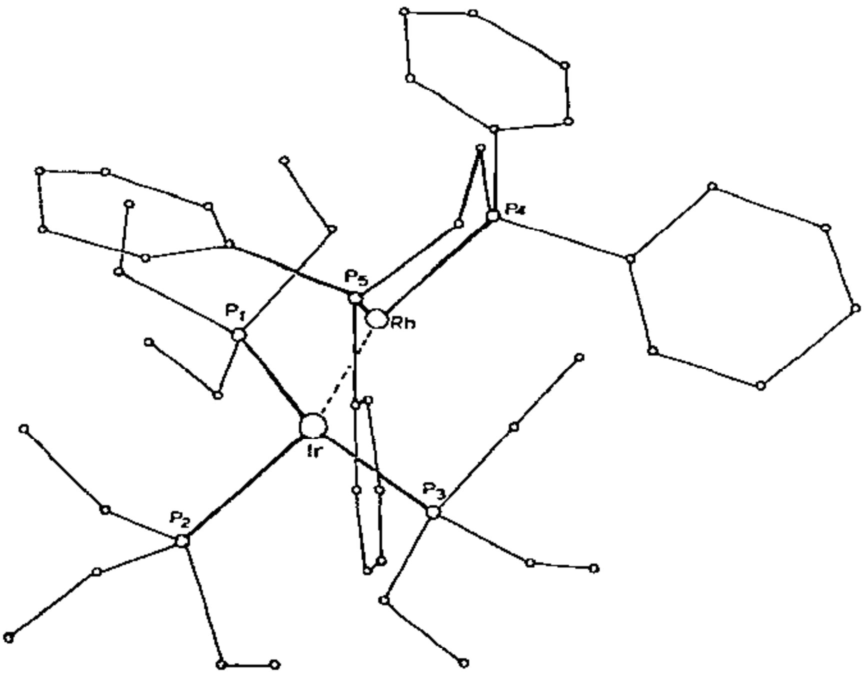


Fig. 12. The molecular structure of $[(Et_3P)_3Ir(\mu_2\text{-}H)_3Rh(Ph_2PCH_2CH_2PPh_2)]^{\oplus}$. Bond lengths (Å): Ir···Rh 2.636(2), Ir–P1 2.352(4), Ir–P2 2.299(6), Ir–P3 2.334(4), Rh–P4 2.151(6), Rh–P5 2.194(6). Bond angles (°): P1–Ir–P2 101.4(2), P2–Ir–P3 100.5(2), P1–Ir–P3 98.6(1), Rh–Ir–P1 111.6(1), Rh–Ir–P2 122.0, Rh–Ir–P3 118.9(1), P4–Rh–P5 83.2(2). Torsion angles (°) (av. errors ca. 0.6°): P2–Ir–Rh–P4 −178.8, P2–Ir–Rh–P5 1.6, P1–Ir–Rh–P4 61.2, P3–Ir–Rh–P5 127.9.

$H)_2PtPh(PEt_3)]^+$ (see Fig. 11). In this case the asymmetry must be due, to a great extent, to the difference in *trans* influence of the two donor atoms bonded to the platinum atom [37].

The X-ray crystal structure of the trihydrido-bridged complex $[(Ph_2PCH_2CH_2PPh_2)Rh(\mu_2\text{-}H)_3Ir(PEt_3)_3][BF_4]$ [27] has also been determined and is shown schematically in Fig. 12. Also in this compound one finds a dissymmetric bridging unit which is not required either by the nature of the ligands present or by apparent packing in the crystal.

Finally, mention should be made of the molecular structure of $[(Et_3P)_2Rh(\mu_2\text{-}H)(\mu_2\text{-}Cl)IrH_2(PEt_3)_2]$ [38]. The bridging unit in this complex is also quite distorted but, given the nature of the donor atoms, it is not possible to state whether metal–metal bonding makes a significant contribution to the distortion. The relative positions of the heavy atoms are shown in Fig. 13.

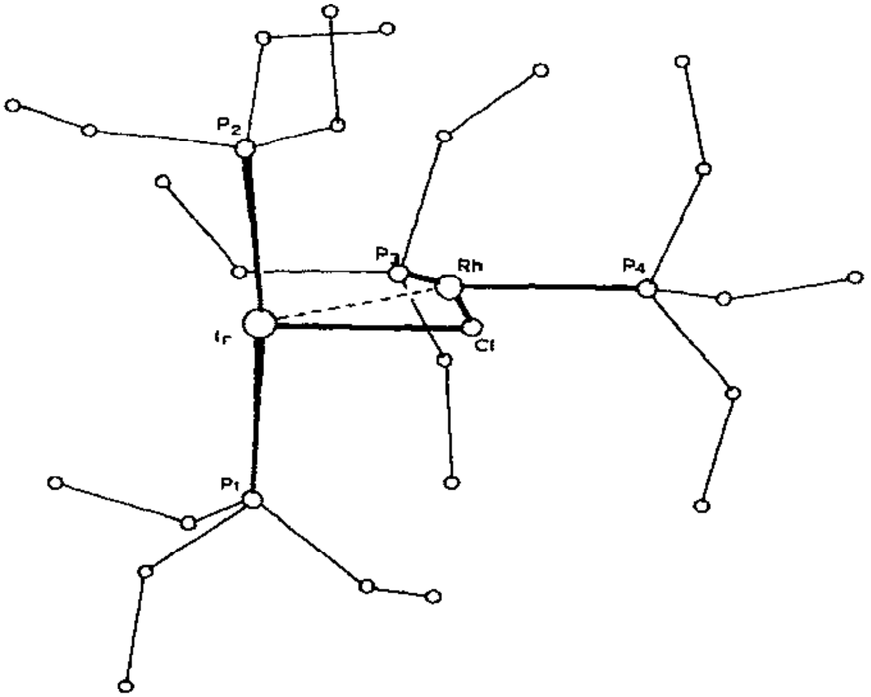
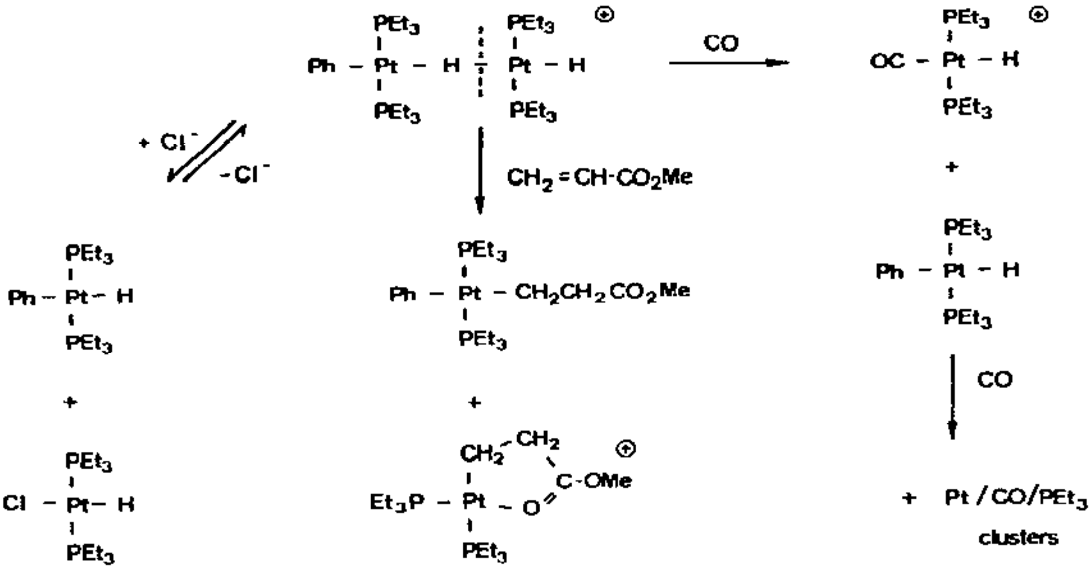


Fig. 13. The molecular structure of $[(Et_3P)_2Rh(\mu_2\text{-}H)(\mu_2\text{-}Cl)IrH_2(PEt_3)_2]^{\oplus}$. Bond lengths (Å): Rh–Ir 2.899(1); Ir–Cl 2.494(3); Rh–Cl 2.427(3); Ir–P(1) 2.263(4); Ir–P(2) 2.272(4); Rh–P(3) 2.199(3); Rh–P(4) 2.245(3); ⟨P–C⟩ av. value 1.85(2). Bond angles (°): Ir–Cl–Rh 72.2(1); Rh–Ir–P(1) 91.7(1); Rh–Ir–P(2) 101.8(1); P(1)–Ir–P(2) 166.4(2); Ir–Rh–P(3) 117.0(1); Ir–Rh–P(4) 145.1(1); P(3)–Rh–P(4) 97.9(1). Torsion angles (°, av. error ca. 0.5°): P(1)–Ir–Rh–P(4) 96.4; P(2)–Ir–Rh–P(4) −85.3; Cl–Ir–Rh–P(3) 178.9; Cl–Ir–Rh–P(4) 1.0. Average displacement of Cl and Ir from LSQ plane defined by Rh, P(3) and P(4) <0.04 Å.

Summing up, one finds that many of the $M(\mu_2\text{-}H)_nM'$-units are distorted in the solid state. However, NMR studies show that, in solution, all the bridging hydride ligands are "equivalent".

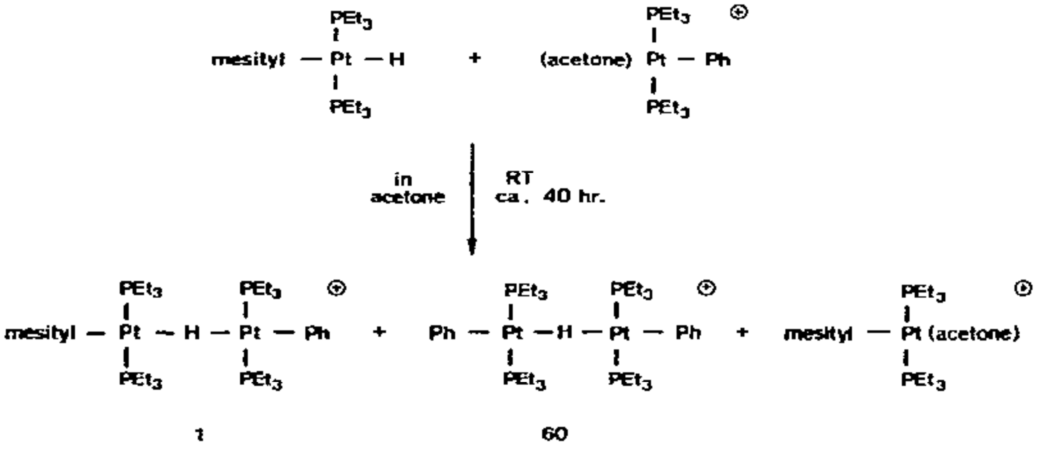
G. REACTIVITY

The "donor–acceptor" scheme outlined earlier can also be used to describe some of the reactions of hydrido-bridged complexes. Thus, in the simplest cases, the addition of a ligand L to a hydrido-bridged complex leads to the primary formation of an adduct between the hydride "acceptor" and L with liberation of the hydride donor. The species thus formed may undergo subsequent reactions with formation of species which are not hydridic. This reactivity pattern can be illustrated using the cation $[(PEt_3)_2(Ph)Pt(\mu_2\text{-}H)PtH(PEt_3)_2]^+$ [36]. As shown in Scheme 19, the reaction of this cation with chloride is reversible but those with CO and $CH_2{=}CHCO_2Me$ are irreversible because of subsequent reactions of one or both of the primary species formed [39].



Scheme 19

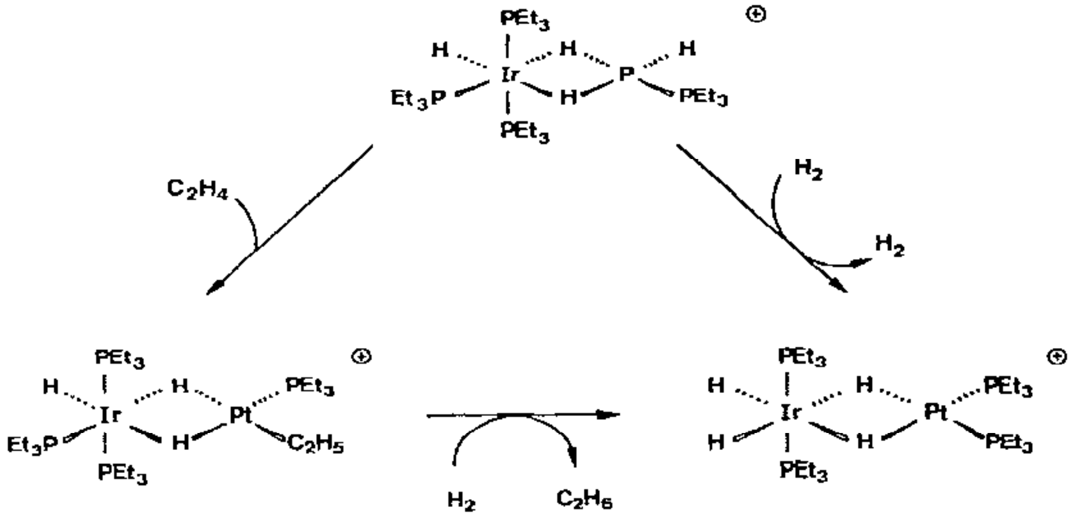
Hydride exchange reactions have also been observed and provide information about the relative stabilities of different hydrido-bridged species. The



Scheme 20

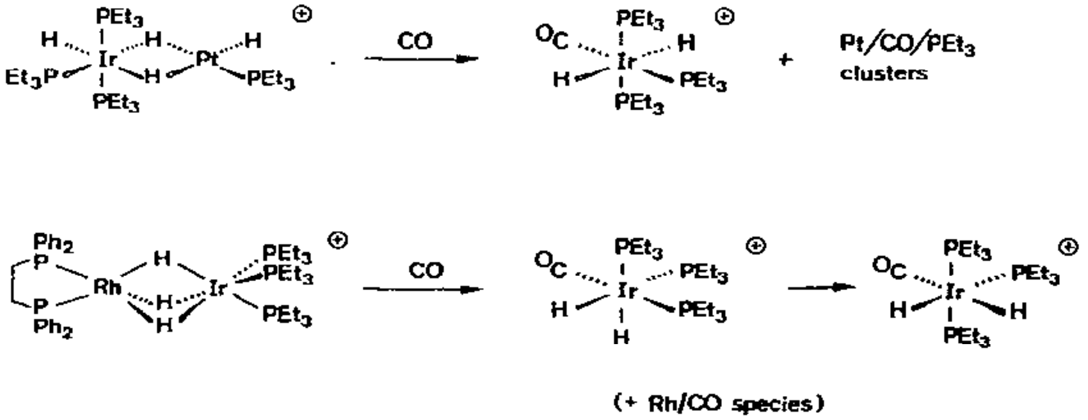
reaction shown in Scheme 20 [25] indicates that the symmetrical phenyl-substituted compound is favoured over the mixed phenyl–mesityl species.

Some hydrido-bridged species undergo the "alkene insertion" reaction [5] without cleavage of the binuclear unit. A reaction of this type is shown in Scheme 21 [30]. The resulting ethyl derivative reacts with H_2 to give ethane and another bimetallic hydride $[(PEt_3)_2H_2Ir(\mu_2\text{-}H)_2Pt(PEt_3)_2]^+$. It is interesting to note that this compound is also obtained by the direct reaction of $[(PEt_3)_3HIr(\mu_2\text{-}H)_2PtH(PEt_3)]^+$ with H_2, i.e. this complex activates H_2 as confirmed by experiments using D_2. These two cations, however, show only moderate activity towards catalytic alkene hydrogenation [30].



Scheme 21

Different types of heteronuclear hydrido-bridged complexes can steer substitution reactions as shown in Scheme 22 [30,27]. Although the mecha-



Scheme 22

nisms of these reactions are obviously complex, their potential for selective synthesis in coordination chemistry deserves further study.

Finally, mention should be made of relative reactivity trends in complexes with varying numbers of bridging hydride ligands.

Maitlis and co-workers [16] have established that in complexes of the type $\{Rh_2(C_5Me_2)_2H_nCl_{4-n}\}$ ($n = 0$ to 3) the catalytic activity decreases with an increase in number of bridging hydride ligands. Furthermore, Crabtree et al. [18] find that $[(PPh_3)_2HIr(\mu_2\text{-}H)_3IrH(PPh_3)_2]^+$ is produced when $[Ir(1,5\text{-}C_8H_2)(PPh_3)_2]^+$ loses its catalytic activity towards alkene hydrogenation. Thus, it would seem that poly-hydrido-bridged complexes are an unpromising set of compounds from the point of view of applications in homogeneous catalysis. This, however, is not the case as shown by the recent studies of Muetterties and co-workers who report [40] that species such as $[\{P(OR)_3\}_2Rh(\mu_2\text{-}H)_2Rh\{P(OR)_3\}_2]$ are very active hydrogenation catalysts.

H. CONCLUSIONS

It is now apparent that a wide variety of mononuclear hydrido complexes can form bi- or polymetallic species with bridging hydride ligands. Many of these complexes are quite inert and are responsible for the de-activation of catalytic systems. It is, however, also becoming apparent that some of them show marked catalytic activity which, in principle, could be finely "tuned" because of the presence of more than one metal centre. Thus further studies of bi- or polymetallic hydrido-bridged species are likely to improve our understanding of the nature of the dative bond and to make significant contributions to synthetic organic chemistry.

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