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Dihydrogen Complexes as Homogeneous Reduction Catalysts

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I. Introduction

Complete cleavage of the rather strong H−H bond (103 kcal mol^{-1}) on metal surfaces or metal complexes has long been dogma in the mechanism of catalytic hydrogenation processes. Depending upon the catalytic system both homolytic and heterolytic cleavages had been proposed (eqs 1 and 2).[1]

(1)

$$M{-}Y + H_2 \longrightarrow M{-}H + H{-}Y \qquad (2)$$

The initial species formed upon approach of molecular hydrogen to the metal has been speculated upon for many years and was generally regarded to be only a transient. Thus, in 1959 Halpern speculated that the activation of hydrogen involved attack of the bonding electrons of the hydrogen molecule on a vacant metal d orbital.[2] Other researchers presented a different view: transfer of electrons from an occupied d orbital to the antibonding (σ^*) orbital of hydrogen.[3] In a sense both ideas were correct; it was Kubas who first obtained clear evidence for a stable dihydrogen complex, $W(\eta^2\text{-}H_2)(CO)_3(P^iPr_3)_2$.[4] Theoretical studies followed this discovery. Thus, orbital population analysis showed that the primary interaction is $H_2 \rightarrow M$ with a small amount of $M \rightarrow H_2$ σ^* back-bonding.[5]

Initially, the complex $W(\eta^2\text{-}H_2)(CO)_3(P^iPr_3)_2$ was viewed as an *arrested* intermediate along a reaction coordinate stabilized by sterically demanding phosphines. However, since the first report by Kubas et al. in 1984, numerous dihydrogen complexes have been synthesized. The spectroscopic characterization and some theoretical aspects on the nature and stabilization of the $M(\eta^2\text{-}H_2)$ bond of these complexes have been also the subject of intensive studies in recent years and various reviews of the field have appeared previously.[6−11] Thus, the known dihydrogen chemistry now indicates that some dihydrogen complexes are more than reactive intermediates and, therefore, must be considered to have an identity and chemistry of their own, including direct reactivity in homogeneous catalysis that will be the subject of this review.

Table 1 lists the known metal−dihydrogen complexes considered to be involved in homogeneous catalyst reduction reactions of alkenes, alkynes, and ketones.[12−41] Other reported homogeneous reactions include dimerization of alkynes,[42] dehydrogenation of alcohols[43] and alkenes,[44] as well as H/D isotopic exchange,[45−49] will be not considered in this paper. Furthermore the possible involvement of dihydrogen complexes in the action of hydrogenase and nitrogenase enzymes[50] has been also reported.

This review is classified according to metal and/or type of complexes and includes most relevant homogeneous dihydrogen compounds taking part in homogeneous reduction of unsaturated substrates by hydrogenation, hydrogen-transfer, and hydrosilylation reactions. Coverage of the literature is up to the middle of 1997. A comprehensive review by Jessop and Morris[9] on the reactivity of transition metal dihydrogen has previously highlighted catalysts and related reactions reported until 1991. According to Table 1 most of the dihydrogen complexes active as homogeneous catalysts in mild conditions are iridium, osmium, and ruthenium derivatives. Phosphine complexes of these metals are relatively rich in molecular dihydrogen chemistry. Some of them have provided interesting lights on the mechanism of catalytic reactions, and in particular on the role of the dihydrogen ligand in reduction processes.

II. Iridium– and Rhodium–Dihydrogen Complexes

A. Iridium–Dihydrogen Complexes

The largest number of observed reactions involving dihydrogen compounds proceed by loss of molecular hydrogen as a result of the weak binding of the

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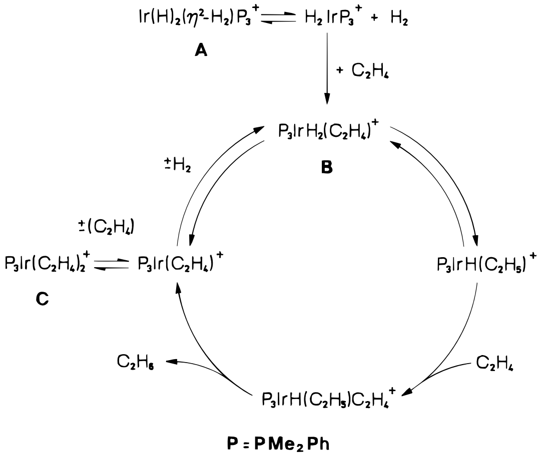
dihydrogen ligand to the metallic fragment. This good leaving ligand stabilizes unsaturated species in solution, without bothering the coordination of the substrate to the metallic center. The energies required for the dissociations of H_2 can be correlated with the structural features of the metal−dihydrogen moiety.[51] Several catalytic systems based upon this strategy have been reported, and some other catalysts, studied before 1984, would also contain the dihydrogen ligand. We have previously considered[52a] the possibility that dihydrogen intermediates of formula $[MH_2(\eta^2\text{-}H_2)_x(PR_3)_y]^+$ may be involved in catalytic hydrogenation by cationic iridium and rhodium precursors of formulas $[M(\text{diolefin})(PR_3)_y]^+$ (or $[Ir(\text{diolefin})L(PR_3)]^+$) extensively studied by Schrock and Osborn[53] and Crabtree.[54] These dihydrogen intermediates could be formed by substitution of S, usually a weak coordinating solvent, in the $[MH_2S_x(PR_3)_y]^+$ species generated from $[M(\text{diolefin})(PR_3)_y]^+$ complexes. Supporting this possibility for iridium, the complex $[IrH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]^+$ has been isolated, although the synthesis was made by protonation of $IrH_5(PCy_3)_2$; the addition of acetonitrile to this dihydrogen complex gives $[IrH_2(MeCN)_2(PCy_3)_2]^+$.[55] In the absence of coordinating solvents and molecular hydrogen, these iridium catalytic cations undergo an irreversible deactivation, as a result of the formation of the $[(PR_3)_2HIr(\mu\text{-}H)_3IrH(PR_3)_2]$ dimers.[55] Furthermore other bis(dihydrogen) complexes, such as the stable $RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$, have been reported.[56] The $[IrH_2S_2(PR_3)_2]^+$ complexes (S = $\eta^2\text{-}H_2$ or solvent) share some common characteristics with the $[IrH_2(\eta^2\text{-}H_2)(PMe_2Ph)_3]^+$ catalyst, in which an additional nondissociating phosphine is present, and in both systems the observation of hydride−olefin intermediates is allowed.

The role of the dihydrogen ligand in complex $[IrH_2(\eta^2\text{-}H_2)(PMe_2Ph)_3]^+$, prepared by protonation of $IrH_3(PMe_2Ph)_3$, is to allow access to ethylene, because it acts as a good leaving group. The catalytic cycle shown in Scheme 1 has been proposed for the ethylene hydrogenation at 25 °C and 1 atm. The complexes **A**−**C** have been detected or isolated.[13,14]

Scheme 1



An iridium−butyne complex of formula $[Ir(MeC_2Me)(PMe_2Ph)_3]BF_4$ has been isolated and structurally characterized,[15] by reacting $[IrH_2(\eta^2\text{-}H_2)(PMe_2Ph)_3]BF_4$ with 2-butyne; in this reaction a mixture of *cis*-2-butene and 1-butene is also detected. This butyne compound seems to be an intermediate in the selective hydrogenation of 2-butyne by the $[IrH_2(\eta^2\text{-}H_2)(PMe_2Ph)_3]^+$ cation at 25 °C and 1 atm. In this catalyst precursor the loss of the good leaving $\eta^2\text{-}H_2$ ligand gives the catalytically active unsaturated hydride species $[IrH_2(PMe_2Ph)_3]^+$, allowing ligands to access the reducible alkene or alkyne substrates.

Table 1. Dihydrogen Complexes Involved in Homogeneous Catalyst Reduction Reactions

complex	reaction	unsaturated substrate	ref(s)
$IrH_2Cl(\eta^2\text{-}H_2)(P^iPr_3)_2$	hydrogenation	benzylideneacetone	12
$[IrH_2(\eta^2\text{-}H_2)(PMe_2Ph)_3]^+$	hydrogenation	ethylene	13,14
$[IrH_2(\eta^2\text{-}H_2)(PMe_2Ph)_3]^+$	hydrogenation	2-butyne	15
$[FeH(\eta^2\text{-}H_2)(PP_3)]^+$ [a]	hydrogenation	alkynes	16−18
$[FeH(\eta^2\text{-}H_2)(PP_3)]^+$ [a]	hydrogen transfer	unsaturated ketones	19
$[FeH(\eta^2\text{-}H_2)(PP_3)]^+$ [a]	hydrogen transfer	cyclohexanone	19
$[RuH(\eta^2\text{-}H_2)(PP_3)]^+$ [a]	hydrogenation	phenylacetylene	20
$[RuH(\eta^2\text{-}H_2)(PP_3)]^+$ [a]	hydrogen transfer	unsaturated ketones	19,21
$[RuH(\eta^2\text{-}H_2)(PP_3)]^+$ [a]	hydrogen transfer	ketones, alkenes	19
$[OsH(\eta^2\text{-}H_2)(PP_3)]^+$ [a]	hydrogen transfer	unsaturated ketones	19
$[OsH(\eta^2\text{-}H_2)(PP_3)]^+$ [a]	hydrogen transfer	ketones, aldehydes	19
$[OsH(\eta^2\text{-}H_2)(PP_3)]^+$ [a]	hydrogen transfer	alkenes, alkynes	19
$OsHCl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$	hydrogenation	alkenes	22,23
$OsHCl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$	hydrogenation	phenylacetylene	23
$OsHCl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$	hydrogenation	benzylideneacetone	24
$OsHCl(\eta^2\text{-}H_2)(CO)(P^tBu_2Me)_2$	hydrogenation	styrene	23
$OsHCl(\eta^2\text{-}H_2)(CO)(P^tBu_2Me)_2$	hydrogenation	phenylacetylene	23
$OsHCl(\eta^2\text{-}H_2)(CO)(P^tBu_2Me)_2$	hydrogenation	benzylideneacetone	24
$Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$	hydrosilylation	phenylacetylene	25
$OsH_2(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$	hydrogen transfer	ketones	26
$OsH(C_2Ph)(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$	hydrogen transfer	phenylacetylene	27
$RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2$	hydrogenation	dimethyl fumarate	28
$RuH_2(\eta^2\text{-}H_2)(PPh_3)_3$	hydrogenation	ketones, arenes	29
$RuH_2(\eta^2\text{-}H_2)(PPh_3)_3$	hydrogen transfer	ketones	30
$[RuH(\eta^2\text{-}H_2)P_4]^+$ [b]	hydrogenation	alkynes	31
$[RuH(\eta^2\text{-}H_2)(binap)_2]^+$ [c]	hydrogenation	prochiral carboxylic ac.	32
$[Ru(HBpz_3)(\eta^2\text{-}H_2)(PPh_3)L]BF_4$ [d]	hydrogenation	alkenes	33
$RuH\{HB(3,5\text{-}Me_2pz)_3\}(\eta^2\text{-}H_2)_2$ [e]	hydrogenation	ketones	34
$RuH\{HB(3,5\text{-}Me_2pz)_3\}(\eta^2\text{-}H_2)_2$ [e]	hydrogen transfer	ketones	34
$(\eta^2\text{-}H_2)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)$ [f]	hydrogenation	alkenes	35,36
$(\eta^2\text{-}H_2)(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)$ [f]	hydrogen transfer	acetophenone	35
$(\eta^2\text{-}H_2)(P{-}N)Ru(\mu\text{-}Cl)_2(\mu\text{-}H)RuCl(PPh_3)_2$ [g]	hydrogenation	hexene	37
$(\eta^2\text{-}H_2)(PR_3)_2Ru(\mu\text{-}Cl)_2(\mu\text{-}H)RuCl(PR_3)_2$	hydrogenation	alkenes	38
$M(\eta^2\text{-}H_2)(NBD)(CO)_3$ [h]	hydrogenation [i]	norbornadiene	39,40
$[FeH(\eta^2\text{-}H_2)(P(OEt)_3)_4]^+$	hydrogenation	alkynes	41

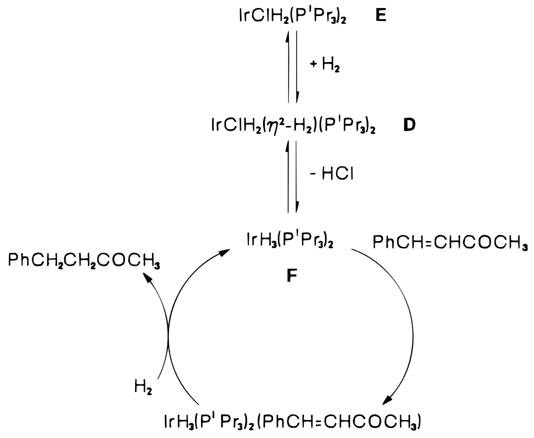
[a] $PP_3 = P(CH_2CH_2PPh_2)_3$. [b] $P = PPh(OEt)_2$, $P(OEt)_3$, $P(OMe)_3$. [c] binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl. [d] $HBpz_3$ = hydridotrispyrazolylborate; L = PPh_3, CH_3CN. [e] $HB(3,5\text{-}Me_2pz)_3$ = hydridotris(3,5-dimethyl)pyrazolylborate. [f] dppb = $Ph_2P(CH_2)_4PPh_2$. [g] $P{-}N = (\eta\text{-}C_5H_5)Fe(\eta\text{-}C_5H_3(CHMeNMe_2)P^iPr_2\text{-}1,2)$. [h] M = Cr, Mo. [i] Photocatalytic hydrogenation.

It was recognized at an early stage that another quite common property of dihydrogen complexes is that the coordinated dihydrogen ligand can act as a Brønsted acid.[9] This has prompted speculation that the dihydrogen compounds can be the key intermediates of the heterolytic hydrogen activation. Thus Crabtree[57] has proposed that the ruthenium complex $RuCl_2(PPh_3)_3$ could activate molecular hydrogen heterolytically via the dihydrogen complex $RuCl_2(\eta^2\text{-}H_2)(PPh_3)_3$. Recently we have found that the dihydrogen complex $IrH_2Cl(\eta^2\text{-}H_2)(P^iPr_3)_2$ (**D**) is an intermediate in heterolytic activation of dihydrogen.[12] Detailed kinetic studies suggest that this dihydrogen complex, initially reported by Jensen and co-workers,[58] is an intermediate in changing from $IrH_2Cl(P^iPr_3)_2$ (**E**) to $IrH_3(P^iPr_3)_2$ (**F**). Complex **E**, which unlike the catalytically inactive $IrH_2Cl(PPh_3)_3$ compound,[59] is coordinatively unsaturated, catalyzes the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one, in 2-propanol at 60 °C and 1 atm, via the trihydride complex **F** as shown in Scheme 2.

The kinetic studies appear to indicate that **E** should be considered the catalyst precursor and, under catalytic conditions, it is in equilibrium with the dihydrogen complex **D**, which subsequently loses HCl, as shown in eq 3:

$$IrH_2Cl(\eta^2\text{-}H_2)(P^iPr_3)_2 \rightarrow IrH_3(P^iPr_3)_2 + HCl \quad (3)$$

Scheme 2



Equation 3 and Scheme 2 indicate that the dihydrogen complex **D** is an intermediate in the heterolytical activation of hydrogen in changing from complex **E** to **F**. According to eq 3 the hydrogenation rate is inversely proportional to the concentration of added HCl.

In agreement with the above-mentioned heterolytic activation of dihydrogen, a neutron diffraction study on a single crystal of *cis*-$IrHCl_2(\eta^2\text{-}H_2)(P^iPr_3)_2$ reveals that one of the hydrogen atoms of the dihydrogen ligand interacts with the chloride of an adjacent molecule to give an infinite hydrogen-bonded polymer. Such hydrogen bonding is a vivid demonstration of the Brønsted acidity of the coordinated hydrogen molecule.[60a] A neutron diffraction study of the related $IrH_2I(\eta^2-H_2)(P^iPr_3)_2$ complex has been recently published.[60b] A total of 10 dihydrogen complexes have been determined to date by neutron diffraction.[61]

A possible dihydrogen−iridium(III) intermediate with a tripodal polyphosphine ligand could be involved in the solid−gas catalytic hydrogenation of ethylene at 60 °C by $[IrH_2\{MeC(CH_2PPh_2)_3\}(C_2H_4)]BPh_4$.[62]

B. Rhodium–Dihydrogen Complexes

Morokuma and co-workers[63] have studied in detail, with the ab initio MO method, the potential energy profile for the catalytic cycle of ethylene hydrogenation by the Wilkinson-type catalyst $RhCl(PH_3)_2$. The features of this profile fully support the Halpern mechanism for the Wilkinson-type catalysts.[64,65] Interestingly, the theoretical calculations agree with an oxidative addition by the intermediacy of $RhCl(\eta^2-H_2)(PH_3)_2$ species. In this intermediate the Rh−H bond lengths are 0.13 Å longer than those of the dihydride $RhClH_2(PH_3)_2$ complex, while the H−H distance is substantially longer than that of molecular hydrogen, suggesting a strong three-center interaction. Furthermore the optimized structure of the $Rh(\eta^2-H_2)$ fragment in $RhCl(\eta^2-H_2)(PH_3)_2$ is similar to that determined experimentally for the $W(\eta^2-H_2)$ fragment in $W(\eta^2-H_2)(CO)_3(P^iPr_3)_2$.[4] In agreement with the intermediacy of $M(\eta^2-H_2)$ species in the homolytic splitting of hydrogen, spectroscopic observations indicate that the solutions of some dihydrogen complexes contain a dihydride equilibrium fraction formed by oxidative addition.[4,6−10,66]

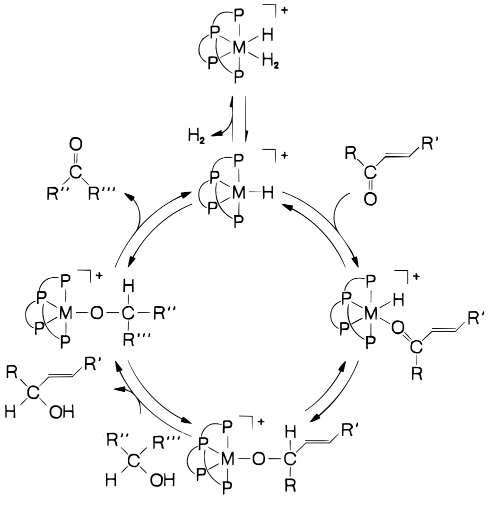
Homogeneous hydrogenation by rhodium complexes has played a key role in the fundamental understanding of catalytic reactions;[52,67,68] however, no evidence has been found for the participation of dihydrogen−rhodium complexes. A previous report[69] on the cationic dihydrogen complex, $[Rh(\eta^2-H_2)(PP_3)]^+$ ($PP_3 = P(CH_2CH_2PPh_2)_3$), active as hydrogenation catalyst, has been reinvestigated concluding that the complex must be considered as highly dynamic $[RhH_2(PP_3)]^+$ species.[70,71]

At first glance the above-mentioned catalytic reactions involving iridium and rhodium complexes can be considered as representative examples of three possible roles of metal-coordinated dihydrogen: it may consider as an intermediate on the way to homolytic or heterolytic activation of hydrogen, or may behave as a good leaving ligand that can provide a free coordination site for the incoming unsaturated substrate.

III. Hydride–η^2-Dihydrogen Complexes of Formulas $[MH(\eta^2-H_2)(PP_3)]^+$ (M = Fe, Ru, Os; $PP_3 = P(CH_2CH_2PPh_2)_3$)

The cationic complexes $[MH(\eta^2-H_2)(PP_3)]^+$ (M = Fe, Ru, Os; $PP_3 = P(CH_2CH_2PPh_2)_3$), extensively studied by Bianchini and co-workers[72,73] are nonclassical trihydrides displaying an identical octahedral structure where the metal is coordinated by the four phosphorus atoms, by a dihydrogen ligand and a terminal hydride ligand; they are active catalysts for hydrogen-transfer reactions, and provide the possibility of comparison among the three metal centers.[19,74] In these complexes the strength of the metal−dihydrogen bond increases in the order Ru < Fe < Os.[73] Irrespective of the metal center a common and classical catalysis cycle (Scheme 3) has been proposed for the reduction of unsaturated ketones from secondary alcohols.[19,74] The vacant coordination site for the incoming substrate is provided by dihydrogen unfastening from the catalyst precursors. Due to the different metal to dihydrogen bond strengths it is believed that for Ru the equilibrium is shifted toward $[RuH(PP_3)]^+$, whereas for Fe and Os, part of the metal is waiting as $[MH(\eta^2-H_2)(PP_3)]^+$.[19] The proposed cycle involves the classical four steps[52b,75] generally accepted for hydrogen-transfer reactions. In the osmium case an $Os(\eta^1$-O-ketone) intermediate has been observed and due to the remarkable steric hindrance of the metal centers in the $[MH(PP_3)]^+$ moiety the preservation of this η^1-O-bonding mode for the three complexes has been suggested.[19,72] Unsaturated ketones, such as benzylideneacetone are chemoselectively reduced to allylic alcohols by using the iron or ruthenium catalysts, at 60−80 °C, but the related osmium catalyst yields saturated ketones via isomerization of the allylic alcohols initially formed.[19] Some substrates deactivate the catalyst due to the formation of stable $[M(O_2CR)(PP_3)]^+$ (M = Fe, Ru) complexes.[19,21]

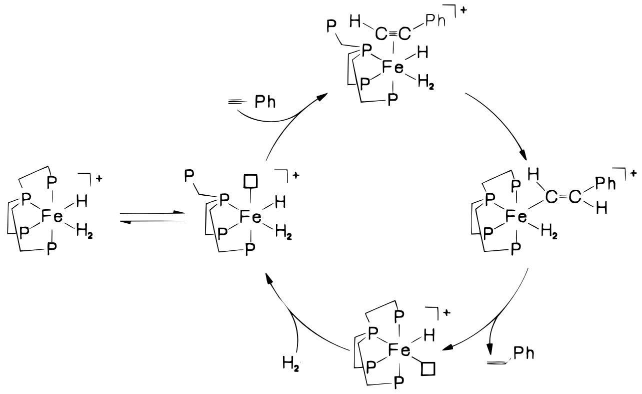
Scheme 3



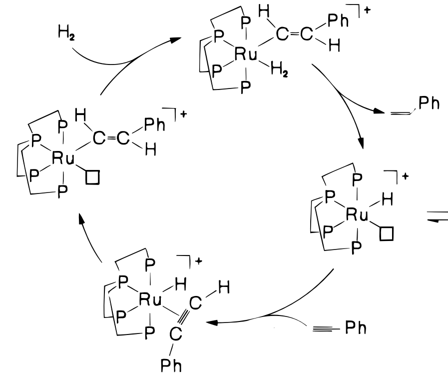
The important differences on metal−dihydrogen bond strengths are highlighted by the study of the selective hydrogenation of alkynes to alkenes by $[MH(\eta^2-H_2)(PP_3)]^+$ (M = Fe, Ru) complexes. In this context, it is interesting to mention that the iron complex is one of the most stable dihydrogen complexes reported in the literature.[9,18,73]

The reactions of the complex $[FeH(\eta^2-H_2)(PP_3)]^+$, under 1 atm of hydrogen, with alkynes are catalytic and produce only alkenes[16,18] except for $HC{\equiv}CSiMe_3$. In this case, the reductive dimerization of the alkyne

Scheme 4



Scheme 5

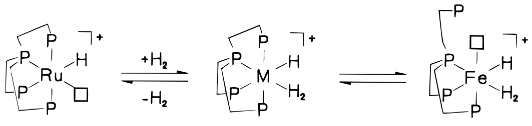


to 1,4-bis(trimethylsilyl)butadiene predominates over hydrogenation at high temperature.[16] No formation of alkanes was observed, even with very long reaction times;[18,76] the turnover numbers decrease by increasing the bulkiness of the alkyne substituent (e.g., PhC≡CH, 45 h^{-1}; ^{n}PrC≡CH, 37 h^{-1}, at 63 °C). Kinetic studies and other experimental data show that, under hydrogenation conditions (20−63 °C), the dihydrogen is so strongly bound to the iron center that the requested free coordination site is provided by the unfastening of one of the $-CH_2CH_2PPh_2$ arms of the PP_3 ligand rather than dihydrogen decoordination. The proposed mechanism is shown in Scheme 4.[18]

Particularly relevant is that the dihydrogen ligand does not leave the metal prior to alkyne coordination and that the reduction seems to occur via an intramolecular acid/base reaction involving dihydrogen and σ-vinyl ligands cis disposed. It seems possible that other hydrogenation reactions could involve protonation by η^2-H_2 intermediates of adjacent organyl ligands in a σ-bond metathesis or heterolytic cleavage reaction.

The related ruthenium derivative $[RuH(\eta^2\text{-}H_2)(PP_3)]^+$ also catalyzes the selective hydrogenation of phenylacetylene to styrene under mild conditions.[20] A kinetic study of the reaction suggests that the reaction mechanism essentially involves the usual cycle adopted by monohydride−metal hydrogenation catalysts (Scheme 5) although other more complex side intermediates also seem to contribute to the overall hydrogenation reaction. The weak dihydrogen coordination permits the stabilization of the formally unsaturated $[RuH(PP_3)]^+$ species in solution without affecting the coordination of the substrate to the metal center.

These observations on the hydrogenation reaction by $[MH(\eta^2\text{-}H_2)(PP_3)]^+$ complexes confirm that dihydrogen can play several roles in hydrogenation reactions. As shown in eq 4 for M = Ru the weakly bound dihydrogen provides a free coordination site at the metal for the incoming unsaturated substrate, while for M = Fe the strongly coordinated dihydrogen remains bound to the metal center in the course of the catalytic cycle and the free coordination site is provided by the unfastening of a phosphine arm of PP_3. Thus, for the iron complex the dihydrogen acts as a reagent capable of hydrogenating the substrate via an intramolecular acid/base reaction (Scheme 4). The different behavior is the consequence of the dissimilar metal−dihydrogen bond strengths, which increase in the order Ru < Fe.[77] Furthermore, inelastic neutron scattering experiments have provided experimental evidence for a larger $d\pi(M)-\sigma^*(H_2)$ back-donation for iron.[73] A similar trend has been observed for $[MH(\eta^2\text{-}H_2)(dppe)_2]BPh_4$ (M = Ru, Fe; dppe = $PPh_2CH_2CH_2PPh_2$) complexes.[61b]



(4)

IV. Osmium−Dihydrogen Complexes

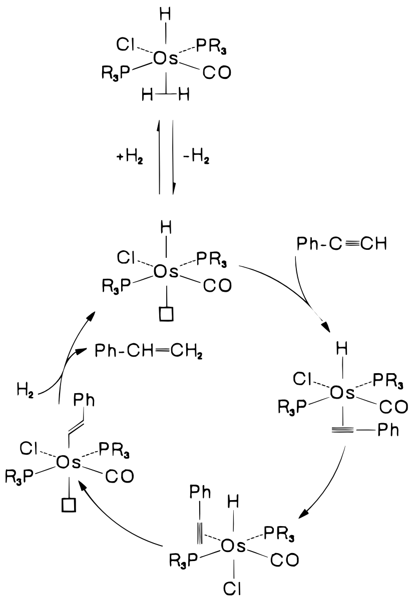
Several osmium−dihydrogen complexes with basic phosphines, such as P^iPr_3 or P^tBu_2Me, have been found to be involved in the reduction of unsaturated substrates. In particular, osmium−dihydrogen compounds, formed by reacting $OsHCl(CO)(PR_3)_2$ with hydrogen,[23] provide some insights on the mechanism of catalytic reactions, and will be treated separately. The catalytic activity of these $OsHCl(CO)(PR_3)_2$ complexes has been developed in the course of an extended cooperation between Zaragoza and Würzburg,[22,23,26,75,78] and we refer to them as the Zaragoza−Würzburg catalysts.

A. The Zaragoza−Würzburg Catalysts: $OsHCl(CO)(PR_3)_2$ ($PR_3 = P^iPr_3$, P^tBu_2Me)

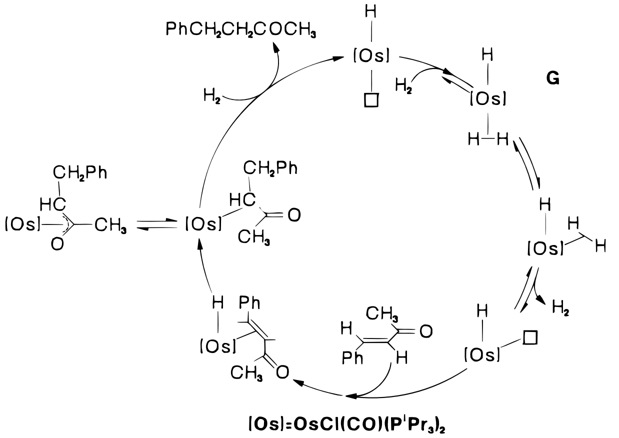
The complexes $OsHCl(CO)(PR_3)_2$ ($PR_3 = P^iPr_3$, P^tBu_2Me) are selective catalysts for the sequential hydrogenation of phenylacetylene in 2-propanol at 60 °C and 1 atm;[23] they react with phenylacetylene to give the five-coordinate alkenyl−osmium compounds $Os\{(E)\text{-}CH{=}CHPh\}Cl(CO)(PR_3)_2$ ($PR_3 = P^iPr_3$, P^tBu_2Me) almost quantitatively, that subsequently react with hydrogen to produce styrene, ethylbenzene, and the dihydrogen complexes $OsHCl(\eta^2\text{-}H_2)(CO)(PR_3)_2$. These reactions constitute a catalytic cycle for the reduction of alkynes to alkenes, with selectivities close to 100%. A kinetic investigation of these reactions indicates that the rate of formation of styrene is determined by the rate of reaction of alkenyl compounds with hydrogen, in agreement with the cycle shown in Scheme 6.

In contrast to the hydrogenation of phenylacetylene, the reduction of benzylideneacetone in the

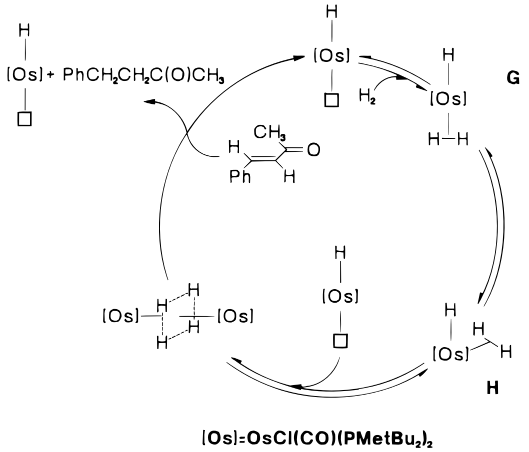
Scheme 6



Scheme 7



Scheme 8



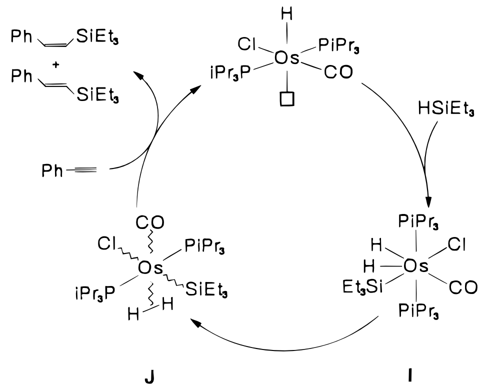
presence of $OsHCl(CO)(P^iPr_3)_2$ is first-order with respect to the concentration of catalyst and substrate and independent of the pressure of hydrogen in the 0.7−1.3 atm range. The mechanism deduced for this reaction based on the kinetic data and on spectroscopic observations is shown in Scheme 7. As the insertion of the benzylideneacetone substrate in the Os−H bond of $OsHCl(CO)(P^iPr_3)_2$ is not favored due most probably to the trans disposition of the hydride ligand and the coordination vacancy, the formation of *trans*-(hydride,dihydrogen)-$OsHCl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (**G**) following isomerization to *cis*-(hydride,dihydrogen)-$OsHCl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (**H**) and subsequent hydrogen dissociation produces a rearrangement of the catalyst ligands to give a new monohydride isomer that contains the hydride ligand and the coordination vacancy in a cis disposition. Then, coordination of the benzylideneacetone substrate and its subsequent insertion in the Os−H bond must lead to an alkyl intermediate that by reaction with molecular hydrogen gives 4-phenylbutan-2-one and regenerates the catalyst. Recent experimental and theoretical studies show that the *trans*-(hydride, dihydrogen)-$OsHCl(\eta^2\text{-}H_2)(CO)(PR_3)_2$ species are the most stable products among all possible hydride−dihydrogen or trihydride species, while the *cis*-(hydride,dihydrogen)-$OsHCl(\eta^2\text{-}H_2)(CO)(PH_3)_2$ complex occupies, according to ab initio calculations, a local minimum in the potential hypersurface with a relative energy of 13.8 kcal mol^{-1}.[79]

On the other hand, the kinetic investigation of the hydrogenation of benzylideneacetone by $OsHCl(CO)(P^tBu_2Me)_2$ shows that the reaction is second-order with respect to the catalyst and first-order with respect to hydrogen (0.8−1.5 atm range) and benzylideneacetone.[24] Scheme 8 shows a tentative catalytic cycle in agreement with these kinetic data and which contains, in equilibrium, the species spectroscopically detected in the reaction of $OsHCl(CO)(P^tBu_2Me)_2$ with molecular hydrogen. Under catalytic conditions (60 °C, 1 atm) this monohydride is in a dynamic equilibrium with the *trans*-(hydride, dihydrogen) complex **G** that isomerizes to *cis*-(hydride,dihydrogen) compound **H**. The subsequent reaction of complex **H** with the monohydride $OsHCl(CO)(P^tBu_2Me)_2$ could lead to a binuclear intermediate which, by reaction with benzylideneacetone gives the saturated ketone and regenerates the catalyst. On the basis of theoretical work by Burdett and Pourian[80] the binuclear intermediate is proposed to contain a planar tetragon of cyclically bound hydrogen atoms. This proposal should be considered in the wider context of the possible existence of polyhydride complexes best described as containing H_n ligands.[80]

It is interesting to remark that slight modifications on the electronic properties and on the steric requirements of the catalyst ligands, as well as on the characteristics of the substrates, can completely change the direction of the equilibria and therefore, the contribution of a particular species, in these cases nonclassical hydrogen intermediates, to the overall catalytic process.

Interestingly $OsHCl(CO)(P^iPr_3)_2$ is also a very active and selective catalyst for the addition of triethylsilane to phenylacetylene at 60 °C, to yield *trans*- and *cis*-$PhHC{=}CH(SiEt_3)$.[25] The reaction of $OsHCl(CO)(P^iPr_3)_2$ with triethylsilane is the rate-determining step. The catalytic reaction proceeds (Scheme 9) via a silyl−dihydrogen intermediate of formula $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$ (**J**) and its dihydride tautomer, $Os(SiEt_3)ClH_2(CO)(P^iPr_3)_2$ (**I**). In the isolable silyl−dihydrogen $Os(SiEt_3)Cl(\eta^2\text{-}$

Scheme 9

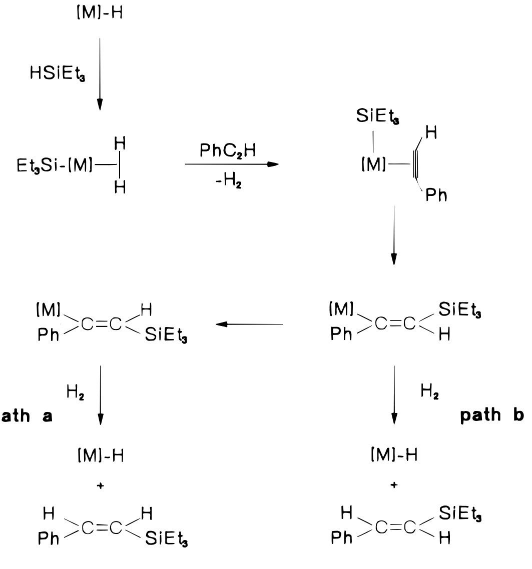


H_2)(CO)(P^iPr_3)$_2$ intermediate, Os($SiEt_3$)(η^2-H_2) bonding is preferred over that of OsH(η^2-$HSiEt_3$). A recent theoretical study by Maseras and Lledós[81a] shows that the η^2 coordination of the H−$SiEt_3$ ligand to the OsHCl(CO)(PH_3)$_2$ fragment is stronger than that of the dihydrogen ligand to the Os($SiEt_3$)Cl(CO)(PH_3)$_2$ fragment by about 15 kcal/mol, a value that compensates almost exactly the superior strength of the H−H bond with respect to the H−$SiEt_3$ bond. Therefore both coordination bonds could be found. Thus, Luo and Crabtree[81b] have reported a MH(η^2-$HSiEt_3$) bonding mode for the complex [IrH_2(η^2-$HSiEt_3$)(PPh_3)$_2$]$^+$. Very recently, Kubas and coworkers have reported detailed comparisons of H−H versus Si−H σ-bond coordination and activation on various 16e metal centers.[82]

The hydrogenation and hydrosilylation mechanisms using OsHCl(CO)(P^iPr_3)$_2$ as catalyst shows significant differences (Schemes 6 and 9). Thus, although the very stable Os{(*E*)-CH═CHPh}Cl(CO)(P^iPr_3)$_2$ is the only complex observed under catalytic conditions in both cases, the hydrosilylation catalysis proceeds by initial reaction of $HSiEt_3$ with OsHCl(CO)(P^iPr_3)$_2$. The formation of *cis*-PhHC═CH($SiEt_3$) seems to occur by isomerization of a vinyl intermediate (Scheme 10) formed by displacement of the coordinated dihydrogen ligand and subsequent insertion of phenylacetylene into the Os−$SiEt_3$ bond of Os($SiEt_3$)Cl(η^2-H_2)(CO)(P^iPr_3)$_2$. The related RuHCl(CO)(P^iPr_3)$_2$ complex is also an active catalyst and extremely selective for the hydrosilylation of phenylacetylene, with exclusive formation of *cis*-PhHC═CH($SiEt_3$), most probably through a similar mechanism.[83]

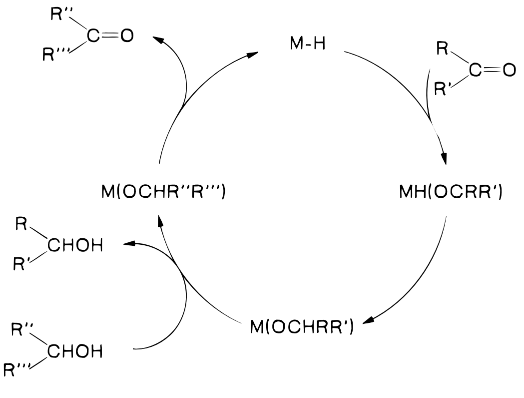
The OsHCl(CO)(P^iPr_3)$_2$ complex is a modest catalyst for the hydrogen transfer from 2-propanol to unsaturated substrates, such as styrene, ketones, and unsaturated ketones at 83 °C. However the addition of $NaBH_4$ leads to an important increase of activity.[75,78] Under hydrogen-transfer conditions the catalyst precursor OsH_4(CO)(P^iPr_3)$_2$, that should be considered as the dihydrogen compound OsH_2(η^2-H_2)(CO)(P^iPr_3)$_2$,[84] is formed. It affords OsH_2(CO)(P^iPr_3)$_2$[26] that acts as the catalyst. The experimental evidence indicates that the hydrogen transfer from 2-propanol to ketones follows the catalytic cycle shown in Scheme 11.[26]

Scheme 10



[M]=MCl(CO)(PiPr3)2; M=Ru, Os

Scheme 11



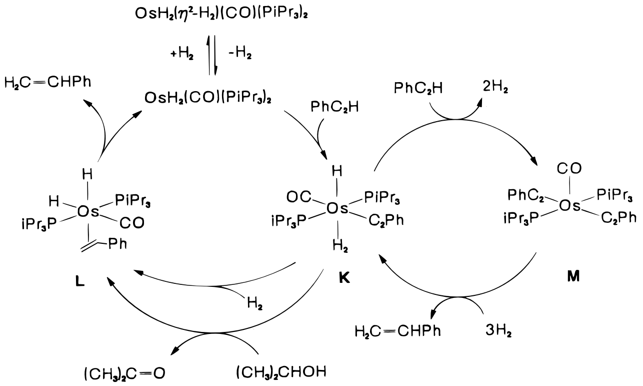
[M-H]=[OsXH(CO)(PiPr3)2]; (X=Cl, H)

B. Other Osmium–Dihydrogen Complexes

The alkynyl−dihydrogen complex, OsH(C_2Ph)(η^2-H_2)(CO)(P^iPr_3)$_2$ (Scheme 12), is an intermediate in the reduction of phenylacetylene to styrene, by hydrogen transfer from 2-propanol.[27] This alkynyl−dihydrogen osmium complex can be isolated by reaction of phenylacetylene with the catalyst precursor OsH_2(η^2-H_2)(CO)(P^iPr_3)$_2$; its activation involves the loss of one dihydrogen ligand per molecule of complex to give the OsH_2(CO)(P^iPr_3)$_2$ catalyst. In this way the formation of OsH(C_2Ph)(η^2-H_2)(CO)(P^iPr_3)$_2$ (**K**) could be rationalized as the result of the reaction of a terminal alkyne to the unsaturated dihydride complex, OsH_2(CO)(P^iPr_3)$_2$, via the initial protonation of the dihydride complex by the acidic phenylacetylene to give the previously reported[85] cationic dihydrogen intermediate [OsH(η^2-H_2)(CO)(P^iPr_3)$_2$]$^+$, and subsequent coordination of PhC≡C$^-$.

It is interesting to mention that under argon a 2-propanol solution of the dihydrogen complex **K** leads to the styrene complex OsH_2(η^2-CH_2═CHPh)(CO)(P^iPr_3)$_2$ (**L**). A simplified catalytic cycle that seems to be operating under hydrogenation and hydrogen-transfer conditions is shown in Scheme

Scheme 12



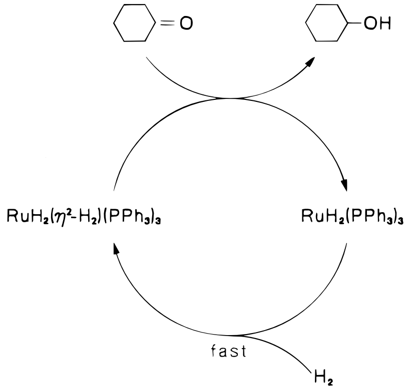
12.[27] A lateral reaction that reduces the reaction rate is the transformation of the OsH(C$_2$Ph)(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ intermediate into the bis(alkynyl) complex Os(C$_2$Ph)$_2$(CO)(P^{i}Pr$_3$)$_2$ (**M**).[86] Complex **M** is an active catalyst for the addition of triethylsilane to phenylacetylene at 60 °C, leading to the formation of *cis*- and *trans*-PhCH=CH(SiEt$_3$) as well as the dehydrogenative silylation product PhC≡C(SiEt$_3$).[87]

The osmium(IV) OsH$_2$Cl$_2$(PR$_3$)$_2$ (PR$_3$ = P^{i}Pr$_3$, P^{t}Bu$_2$Me) complexes are active catalysts for hydrogenation of olefins (60 °C, 1 atm), and in the presence of NaBH$_4$, catalyze the hydrogen transfer from 2-propanol to ketones at 83 °C; under these conditions the OsH$_6$(PR$_3$)$_2$ compounds, which more likely are nonclassical hydride complexes are formed, affording in a subsequent step the unsaturated catalytically active "OsH$_4$(PR$_3$)$_2$" species.[88] In addition, it should be mentioned the easy formation of osmium(II)−dihydrogen complexes containing the Os(η^2-H$_2$)(P^{i}Pr$_3$)$_2$ moiety by simple addition of a variety of neutral and anionic ligands to the osmium(IV) compound, OsH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$.[89,90] Morris and co-workers have recently reported some osmium complexes having elongated dihydrogen ligands, arrested along the pathway to oxidative addition.[11,91] It has been suggested that dihydrogen−vinylidene species of osmium(II) are key intermediates in the synthesis of hydride−carbyne complexes of osmium(II) by reaction of OsH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$ with terminal alkynes.[92]

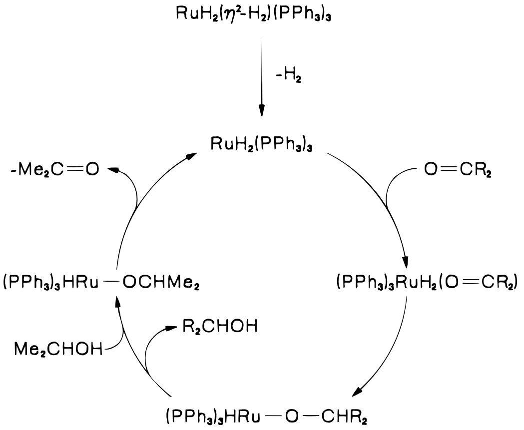
A neutron diffraction study on the active hydrogenation catalyst [OsH$_5$(PMe$_2$Ph)$_3$]BF$_4$, initially formulated as a dihydrogen complex,[93] shows that it is a cationic pentahydride with relatively short H/H separations.[94]

The above-mentioned observations support the increasing evidence that for group 8 metals not only ruthenium but also osmium forms a large variety of dihydrogen and hydride complexes with phosphine ligands which are good catalysts for the reduction of unsaturated organic substrates.[95]

Scheme 13



Scheme 14



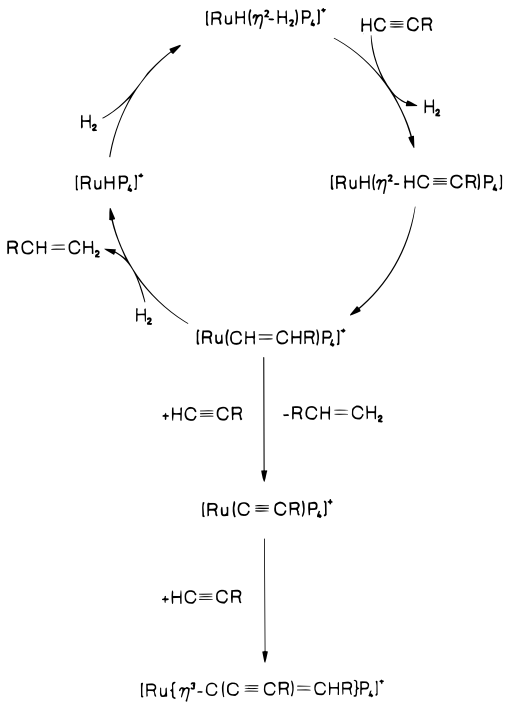
V. Ruthenium Dihydrogen Complexes

The bis(dihydrogen) complex RuH$_2$(η^2-H$_2$)$_2$(PCy$_3$)$_2$ is an active catalyst for the hydrogenation of dimethyl fumarate, an alkene with electron-withdrawing substituents; after hydrogenation this complex is the major organometallic compound along with the hydride−dihydrogen complex RuH(η^2-H$_2$)(η^2-O$_2$CCH$_2$CH$_2$CO$_2$CH$_3$)(PCy$_3$)$_2$.[28] In contrast the reaction with ethylene leads to the reduction to ethane, by dehydrogenation of the cyclohexyl group, and concurrent formation of RuH((η^3-C$_6$H$_8$)PCy$_2$)(C$_2$H$_4$)(PCy$_3$) which contains a cyclohexenyl ring. This compound is the only species observed after the highly selective dehydrogenative silylation of ethylene[96] promoted by RuH$_2$(η^2-H$_2$)$_2$(PCy$_3$)$_2$. It has been recently reported that one or two dihydrogen ligands from the RuH$_2$(η^2-H$_2$)$_2$(PCy$_3$)$_2$ complex can be substituted leading to complexes where one or two H−Si bonds are η^2-coordinated to the metal.[97]

The dihydride−dihydrogen complex RuH$_2$(η^2-H$_2$)(PPh$_3$)$_3$, initially formulated as RuH$_4$(PPh$_3$)$_3$, catalyzes the hydrogenation of cyclohexanone.[29] Detailed kinetic studies show that the rate-determining step is the reaction of the coordinatively saturated RuH$_2$(η^2-H$_2$)(PPh$_3$)$_3$ species with cyclohexanone (Scheme 13). Arene substrates such as 9-methylanthracene are also effectively hydrogenated. The catalytic cycle seems to be analogous for unactivated ketones and arene substrates, and some key intermediates have been isolated. This complex is also an effective catalyst for the reduction of cyclic ketones by hydrogen transfer from 2-propanol at room temperature.[30] The dihydrogen ligand in RuH$_2$(η^2-H$_2$)(PPh$_3$)$_3$ seems to act as a good leaving group, both under reduction by molecular hydrogen (Scheme 13) and under hydrogen-transfer conditions (Scheme 14).

Complexes [RuH(η^2-H$_2$)P$_4$]$^+$ (P = PPh(OEt)$_2$, P(OEt)$_3$, P(OMe)$_3$) are active catalysts for the selective hydrogenation of alkynes to alkenes. The reaction

Scheme 15

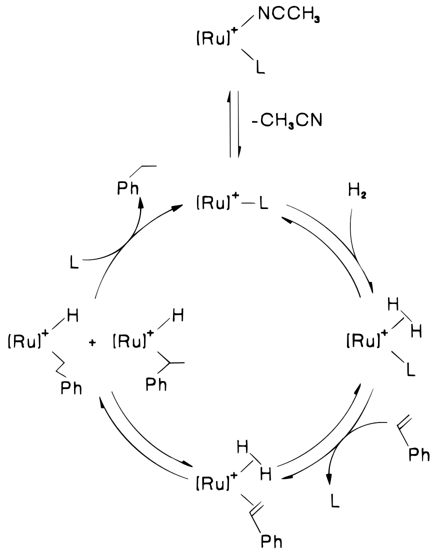


is initially fast, but the formation of butenylnyl derivatives of formulas $[Ru(\eta^3\text{-}RC{\equiv}CC{=}CHR)P_4]^+$ causes the deactivation of the catalyst. The reaction path shown in Scheme 15 has been proposed on the basis of experimental observations.[31]

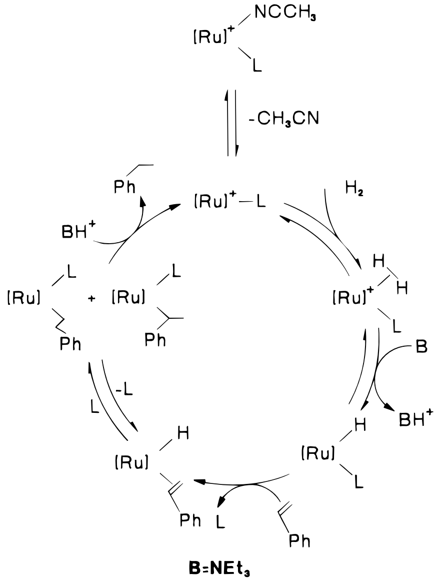
Two chiral dihydrogen complexes of formula $[RuH(\eta^2\text{-}H_2)(L{-}L)_2]PF_6$ (L−L = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (binap),[32] or 1,2-bis((2*R*,5*R*)-2,5-dimethylphospholano)benzene (Me-duphos)[98]) have been reported. The complexes are readily formed in the presence of hydrogen from the efficient asymmetric hydrogenation $[RuH(L{-}L)_2]PF_6$ catalysts. The structure of *trans*-$[RuH(\eta^2\text{-}H_2)(\text{Me-duphos})_2]PF_6$ has been determined by X-ray; the η^2-H_2 ligand is trans to the hydride ligand and located in a chiral pocket defined by the Me-duphos ligands.[98] The catalytically active species in these systems is thought to be formed by losing one of the chiral diphosphine ligands.[32b,99] Very recently some related thermolabile complexes containing diphosphines with large natural bite angles of formula $[RuH(\eta^2\text{-}H_2)(\text{diphosphine})_2]^+$ have been reported.[100]

Dihydrogen complexes of formulas $[Ru(HBpz_3)(\eta^2\text{-}H_2)(PPh_3)L]BF_4$ (L = PPh_3, CH_3CN) are likely involved in hydrogenation of olefins catalyzed by $[Ru(HBpz_3)(PPh_3)_x(CH_3CN)_{3-x}]BF_4$ (x = 1 or 2) in anhydrous tetrahydrofuran under 40 atm of hydrogen according to Scheme 16.[33] Enhanced catalytic activities were observed in the presence of triethylamine or water. The proposed mechanism involves protolysis of Ru-alkyls with $HNEt_3^+$ or H_3O^+, in such a way that olefins are reduced through a stepwise H^-/H^+ transfer process (Scheme 17). It is interesting to mention that deuterium was incorporated into the catalytic hydrogenation products when D_2O was present. The enhanced catalytic activity in the presence of water, and incorporation of deuterium in the hydrogenation products, were explained with mechanisms involving dihydrogen complexes.[33] The related complexes $RuH\{HB(3,5\text{-}Me_2pz)_3\}(\eta^2\text{-}H_2)_2$ and $RuH\{HB(3,5\text{-}Me_2pz)_3\}(COD)$ are also good catalysts for the reduction of unactivated ketones by molecular hydrogen or by hydrogen transfer from 2-propanol in basic media. These reactions occur in mild conditions (50−80 °C, 3 atm of H_2) with good turnover numbers (~50 h^{-1} under H_2, 400 h^{-1} in hydrogen transfer conditions).[34]

Scheme 16



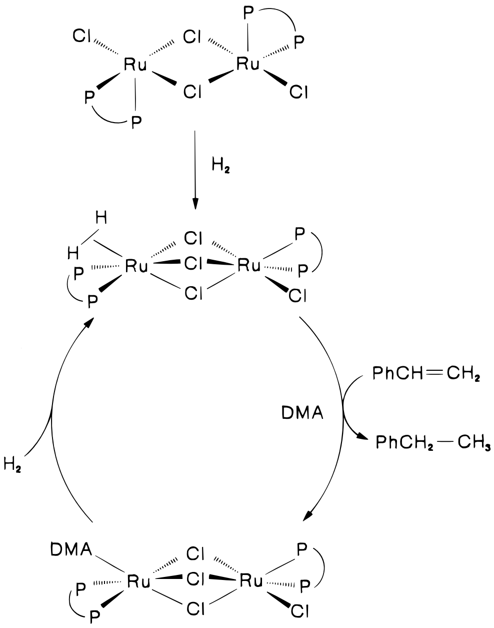
Scheme 17



The catalytic hydrogenation activity of the *cis*-$[Ru(6,6'\text{-dichloro-}2,2'\text{-bipyridine})(OH_2)_2](CF_3SO_3)_2$ at 105 °C and 40 atm of hydrogen is greatly enhanced by addition of small amounts of water. On the basis of labeling experiments it has been suggested that a dihydrogen−ruthenium complex intermediate is heterolytically cleaved by water to form an active metal hydride complex.[101] This water soluble complex was found to be an effective catalyst for the hydrogenation of organic carbonyl compounds and olefins in biphasic aqueous/organic systems.[102]

James and co-workers[35−38] have reported a number of dinuclear ruthenium dihydrogen complexes that

Scheme 18



are active as reduction catalysts. The (η^2-H_2)(dppb)Ru(μ-Cl)$_3$RuCl(dppb) complex, obtained by addition of dihydrogen to [RuCl(dppb)(μ-Cl)]$_2$ is an effective catalyst for hydrogenation under hydrogen and for transfer hydrogenation from 2-propanol.[35,36] A detailed kinetic study of the hydrogenation of styrene in *N*,*N*-dimethylacetamide (DMA) suggests a catalytic cycle as shown in Scheme 18. Only dinuclear species are detected and thus, dinuclear η^2-H_2 species seems to be involved in the catalytic process. The experimental observations are interpreted in terms of a basic hydride route in which the dinuclear dihydrogen complex (η^2-H_2)(dppb)Ru(μ-Cl)$_3$-RuCl(dppb) (dppb = $Ph_2P(CH_2)_4PPh_2$) transfers in two steps both hydrogens to the alkene.[36]

Other related dinuclear dihydrogen ruthenium complexes containing the (η^2-H_2)Ru(μ-Cl)$_2$(μ-H)Ru moiety, of formulas (η^2-H_2)(P−N)Ru(μ-Cl)$_2$(μ-H)RuCl-(PPh_3)$_2$[37] (P−N = (η-C_5H_5)Fe(η-C_5H_3(CHMeNMe$_2$)-P^{i}Pr$_2$-1,2)) or (η^2-H_2)(PR_3)$_2$Ru(μ-Cl)$_2$(μ-H)RuCl(PR_3)$_2$[38] have been found to be active catalysts for the hydrogenation of alkenes.

Mezzeti et al.[103] have reported that the dihydrogen complex RuCl$_2$(η^2-H_2)(biphemp) (biphemp = (*S*)-2,2′-bis(diphenylphosphino)-6,6′-dimethylbiphenyl) could be an intermediate in the enantioselective hydrogenation of 2,4-diketones by RuCl$_2$(PPh_3)(biphemp), facilitating the transfer of a proton from the acidic dihydrogen ligand to a carbonyl oxygen atom, followed by hydride attack. A dinuclear complex of formula (η^2-H_2)(biphemp)Ru(μ-Cl)$_3$RuCl(biphemp) was also detected, but its formation appears to be nonfavorable for the hydrogenation reaction.

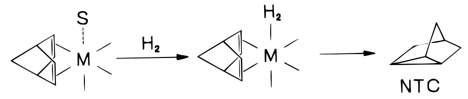
Interestingly, Hembre et al. have reported that some dihydrogen ruthenium complexes are hydrogenase reactivity models.[104] In particular, the cationic complex [Ru(C_5Me_5)(η^2-H_2)($PPh_2CH_2PPh_2$)]$^+$ is a well-characterized compound, illustrating the cooperative roles of a dihydrogen complex and a transition metal hydride as a functional model of hydrogenase enzymes.

VI. Non-platinum Group Metal Dihydrogen Complexes

Most of the dihydrogen complexes active as homogeneous reduction catalysts are platinum group metal derivatives. In addition some iron and group 6 metal complexes have been found to be involved in homogeneous catalytic reductions.

Poliakoff and co-workers have reported that dihydrogen complexes are key intermediates on the photocatalytic hydrogenation of norbornadiene by group 6 metal carbonyls.[39,40] The dihydrogen complexes were generated by the photolysis of M(NBD)-(CO)$_3$ (NBD = 2,5-norbornadiene; M = Cr, Mo) complexes with molecular hydrogen. The proposed mechanism implies that the intramolecular transfer of H_2 (or D_2) to the diolefin in *mer*-M(η^2-H_2)(NBD)-(CO)$_3$ leads to formation of norbornene (eq 5), but in *fac*-M(η^2-H_2)(NBD)(CO)$_3$ leads to nortricyclene (eq 6).

(5)



(6)

Two hydride dihydrogen iron complexes have been reported to hydrogenate 1-alkynes to alkenes. Both complexes, [FeH(η^2-H_2)(P(OEt)$_3$)$_4$]$^+$ [41] and [FeH(η^2-H_2)(PP_3)]$^+$ [18] are cationic and contain four-coordinated phosphorus atoms. The catalytic mechanism for the latter complex has been discussed above (Scheme 4) and proceeds through the unfastening of a phosphine arm of the PP_3 ligand due to the strong bonding of the dihydrogen ligand.

VII. Conclusions

In the preceding pages, we have offered a comprehensive up-to-date review of dihydrogen compounds in hydrogenation, hydrogen transfer and hydrosilylation reactions. A quick glance of the proposed cycles suggests that under catalytic conditions the dihydrogen intermediates can be formed either by coordination of molecular hydrogen to an unsaturated metallic fragment[9] or by addition of $HSiR_3$ molecules to unsaturated monohydride compounds.[25] Although experimental evidence for the formation of dihydrogen intermediates by coordination of unsaturated organic substrates to unsaturated dihydride complexes, still have not been found, the recent synthesis of new dihydrogen complexes by coordination of nucleophilic ligands to the complex OsH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$[90] suggests that this transformation could also occur under catalytic conditions. The formation of catalytic dihydrogen intermediates by protonation of hydride compounds would be also anticipated, in particular for reactions involving terminal alkynes or weakly protic HX molecules. In this context it should be mentioned that this reaction pathway is a general method for the stoichiometric preparation of dihydrogen complexes.[9]

The examination of the proposed catalytic cycles also indicates that the dihydrogen intermediates can play different roles in these types of reactions. Some of them are proposed as intermediates for the homolytic activation of hydrogen. In agreement with this, spectroscopic observations indicate that the solutions of some reported dihydrogen complexes contain a dihydride equilibrium fraction,[6−10] which is formed by oxidative addition of the dihydrogen ligand. The Morokuma theoretical studies[63] also show that the oxidative addition of molecular hydrogen to the $RhCl(PH_3)_2$ fragment also involves a strong three-center interaction. Schemes 2 and 4 also illustrate that the heterolytic hydrogen activation involves dihydrogen intermediates.[12,18] In general, this activation appears to be favored by the presence as ancillary ligands of both acceptor molecules, trans disposed to the dihydrogen ligand, and ligands with a lone pair coordinated cis to dihydrogen. It is noteworthy that dihydrogen complexes can be tuned for the efficient heterolytic activation of dihydrogen and the acidity of some dihydrogen complexes are greater than the related dihydride compounds.[9,105] There is a need for a better knowledge of the heterolityc splitting of dihydrogen.

The dihydrogen ligand of some compounds can be easily substituted by unsaturated organic molecules; in this way, it stabilizes unsaturated catalysts without bothering the coordination of the substrate, the complex $[IrH_2(\eta^2\text{-}H_2)(PMe_2Ph))_3)]^+$ is a good example of this.[14] In contrast, in the related $[FeH(\eta^2\text{-}H_2)(PP_3)]^+$ complex, the dihydrogen ligand is so strongly bonded that favor the decoordination of other ligands, while as reagent can hydrogenate the substrate.[18]

The hydrogenation cycles shown in Schemes 6−8 illustrate three fascinating roles, which produce the catalytic activation of the nonactive precursor of formulas $OsHCl(CO)(PR_3)_2$ ($PR_3 = P^iPr_3$, P^tBu_2Me) as a result of dihydrogen coordination.[23,24] The hydrosilylation of phenylacetylene in the presence of $OsHCl(CO)(P^iPr_3)_2$ is a consequence of the formation of $Os(SiEt_3)Cl(CO)(P^iPr_3)_2$ via $Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(P^iPr_3)_2$.[25]

Despite the apparent simplicity of the dihydrogen ligand much more research must be carried out for better understanding of the role of the dihydrogen complexes in homogeneous catalytic reactions. Numerous dihydrogen complexes have been reported. However the ancillary ligands contained by them are very similar. This problem is a result of the limited number of useful synthetic routes described for their preparation. New developments in catalytic reactivity of dihydrogen complexes will most probably require new types of compounds with new ligands. Further work needs to be done to find alternative reaction pathways which lead to new types of dihydrogen compounds that could be implicated as intermediates in homogeneous catalytic processes. There is also a need for mechanistic reinvestigation of known systems on the basis of spectroscopic techniques, such as high-pressure NMR, and kinetic studies.

VIII. Acknowledgments

We gratefully acknowledge the efforts of a group of talented individuals responsible for the studies developed in Zaragoza and summarized herein: Cristina Bohanna, Ana López, Natividad Ruiz, Eduardo Sola, and Cristina Valero. It is also a pleasure to acknowledge Professor Helmut Werner at Würzburg University for stimulating discussions and collaborations. The generous research award from the Humboldt Foundation to one of us (L.A.O.) for making possible a stay in Würzburg University, where a significant part of this review was written is gratefully acknowledged. The author's own work mentioned in this review was financially supported by DGICYT (Spain) and the European Commission.

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