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Review

Some ruthenium hydride, dihydrogen, and dihydrogen-bonded complexes in catalytic reactions

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Contents

Abstract

The transfer of the hydrogen atoms from the η^2-H_2 ligand to the *cis*-disposed olefin ligand in a ruthenium olefin–dihydrogen complex is discussed. It is realized that H_2O and NEt_3 exhibit promoting effects in the catalytic hydrogenation of olefins with a couple of hydro(trispyrazolyl)borate (Tp)-supported ruthenium complexes. A reaction mechanism that accounts for the promoting effect has been proposed. A Tp-supported ruthenium solvento hydride complex $TpRu(PPh_3)(CH_3CN)H$ was found to react with H_2 and R_3SiH to form the fluxional dihydrogen–hydride, and η^2-silane–hydride complexes, respectively. Although no stable and isolable σ-complex was formed with CH_4, the solvento hydride complex was found to be active in catalyzing H/D reactions of CH_4 with some deuterated common organic solvents. In the catalytic CO_2 hydrogenation reactions in THF/H_2O or alcohol, the complex $TpRu(PPh_3)(CH_3CN)H$ generates the metal-ligand bifunctional catalyst $TpRu(PPh_3)(ROH)H$ (R = H or alkyl) which transfers the hydride and a proton from ROH to the CO_2 molecule in a concerted manner, without coordination of the latter to the metal center. Aminocyclopentadienyl ruthenium complexes, which exhibit intramolecular Ru–H$\cdots$H–N dihydrogen-bonding interactions were synthesized and characterized. These complexes provide good models for the study of heterolytic cleavage of η^2-H_2 ligand and its reverse-protonation of metal hydride to form dihydrogen complex. An indenyl ruthenium hydride complex was synthesized and found to be good catalyst for nitrile hydration reactions to give amides; these reactions nicely demonstrate the principle of utilizing dihydrogen bond to promote catalytic reactions.

Keywords: Hydride; Dihydrogen complexes; Dihydrogen bond; Ruthenium; Heterolytic cleavage; Catalysis

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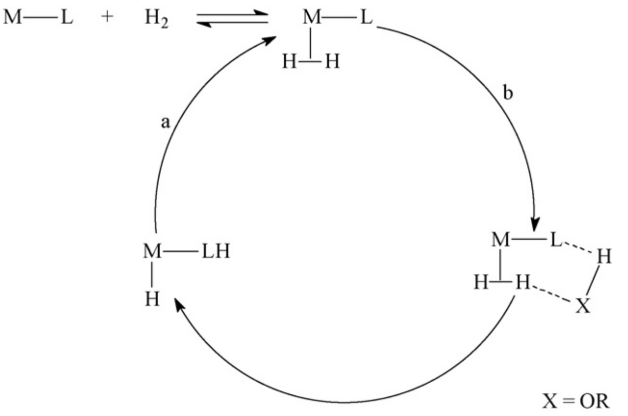
1. Introduction

Transition metal hydrides are an important class of complexes involved in numerous stoichiometric and catalytic processes. For example, in the catalytic hydrogenation of unsaturated organic functions with transition metal complexes, reaction mechanisms involving oxidative addition of H_2 to the metal center to form metal dihydrides are well established [1]. However, nonclassical dihydrogen species instead of the classical dihydrides have been proposed as intermediates in some catalytic hydrogenation reactions [2]; examples are known where the hydrogen atoms of the η^2-coordinated dihydrogen are catalytically transferred to the products via heterolytic cleavage of H–H [3]. In the reactions of hydrogenases, the metal hydrides derived from heterolytic cleavage of H_2 are among the key intermediates [4]. Heterolytic H_2 cleavage, which is relevant to activation of dihydrogen by hydrogenases, with bimetallic complexes has been reported [5].

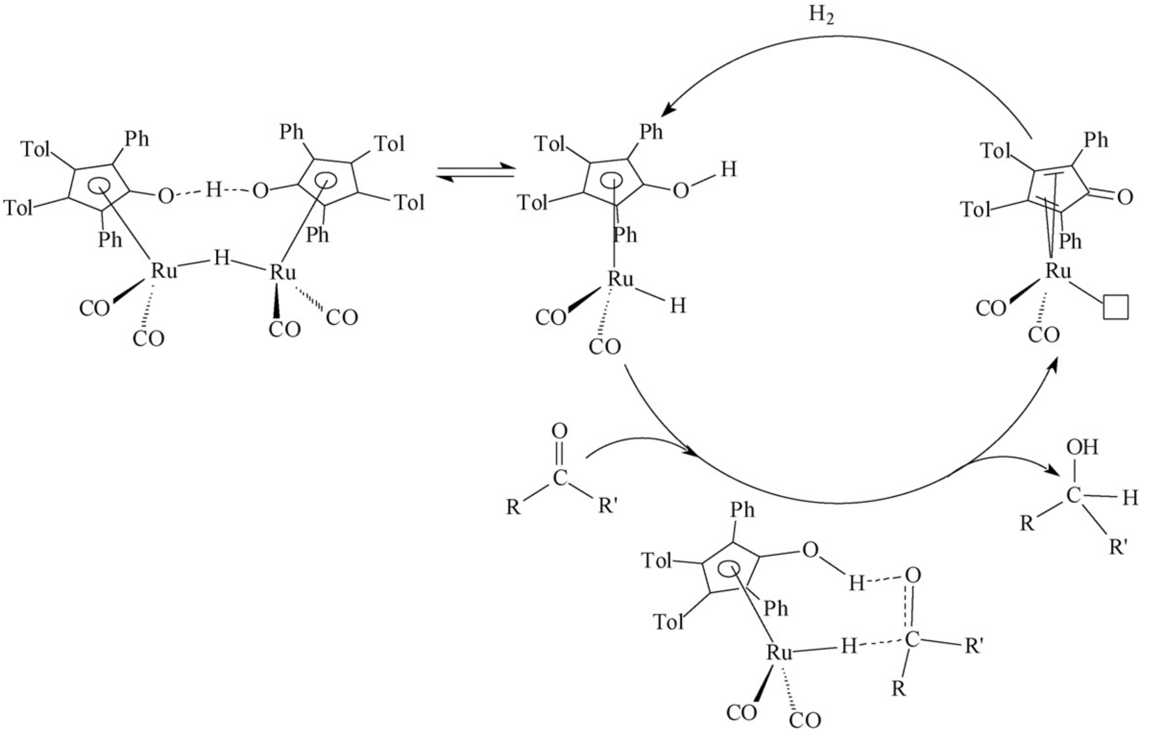
Metal-ligand bifunctional hydrogenation catalysis is an important recent development, especially in the enantioselective reduction of ketones and unsaturated ketones [6]. In the catalytic reactions, the heterolytic splitting of dihydrogen to generate the protonated ligand and metal hydride is a crucial step (Scheme 1). The heterolytic H_2 splitting is sometimes promoted by a proton relay group such as an alcohol (b route in Scheme 1).

The first metal-ligand bifunctional catalyst, a hydroxycyclopentadienyl diruthenium bridging hydride, was reported by Shvo in the mid-1980 [7]. Casey et al. later provided experimental evidence suggesting a concerted hydrogen transfer mechanism for the reduction of carbonyls with the tolyl derivative of the Shvo's hydroxycyclopentadienyl-ruthenium systems (Scheme 2) [8]. The reduction of imines with the Shvo's system is, however, more complex; the reduction mechanism has been found to be dependent on the electronic nature of the imine [9]. Similar concerted hydrogen transfer mechanisms for carbonyl compound reduction with ruthenium-diamine-diphosphines have been proposed by Noyori [6b,10]. Metal/NH_2 bifunctional catalysts similar to Noyori's systems have also been developed by Morris [11].

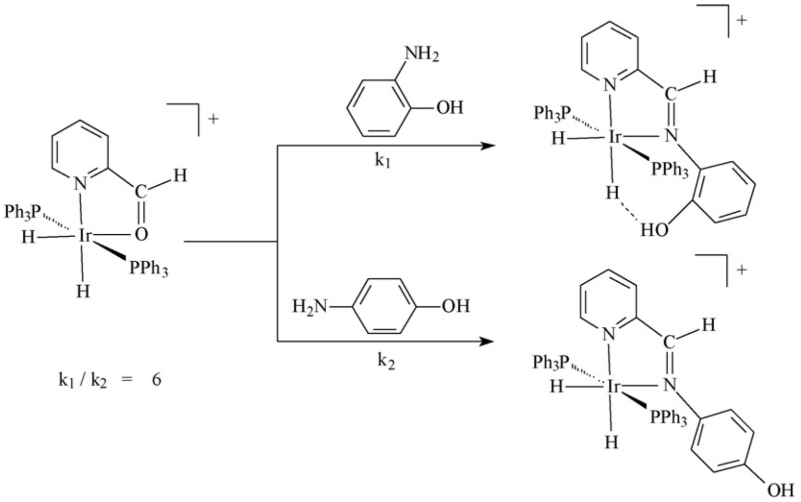


Scheme 1.

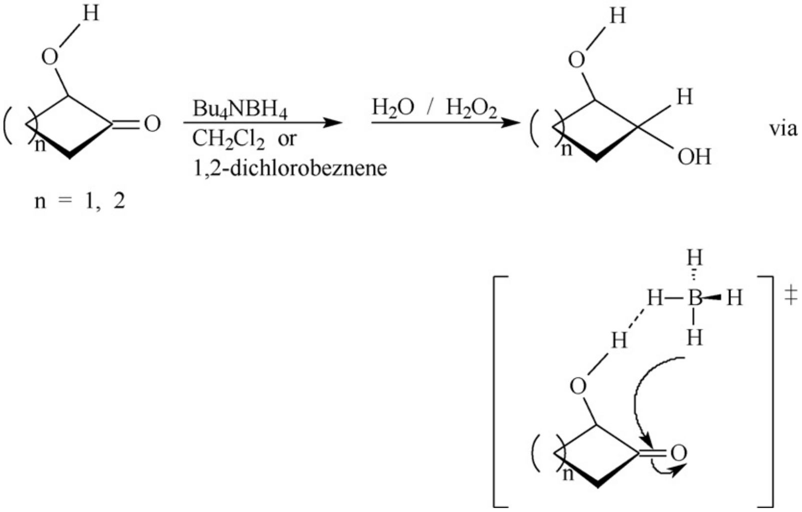
It is probably true that heterolytic cleavage of the η^2-H_2 ligand and its reverse-formation of η^2-dihydrogen species proceed via an intermediate containing the M–H···H–X dihydrogen bond; in fact, numerous complexes and systems containing intramolecular and intermolecular M–H···H–X dihydrogen-bonding interaction have been identified in the last decade [12]. This hydride-proton interaction of the dihydrogen bond might



Scheme 2.



Scheme 3.



Scheme 4.

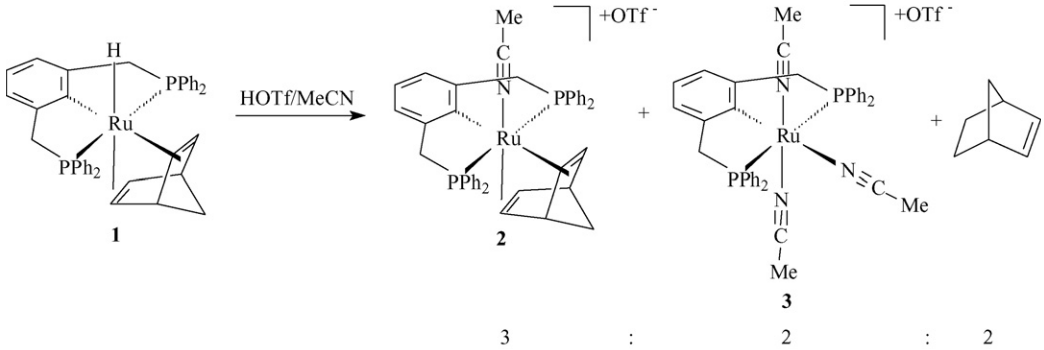
significantly contribute to the stabilization of organometallic structures of mononuclear complexes and cluster hydride derivatives. More interestingly, dihydrogen bonds might sometimes play important roles in controlling reactivity and regio selectivity of chemical reactions [13]. For example, when the iridium complex $[IrH_2(\eta^2\text{-}C_5H_4NCHO\text{-}N,O)(PPh_3)_2]^+$ reacts with an equimolar mixture of 2-aminophenol and 4-aminophenol, the aldehyde function of the pyridinecarboxaldehyde ligand undergoes selective imination in favor of the former; the intramolecular Ir–H···H–O dihydrogen bonding stabilize the 2-aminophenol-derived product and probably also the transition state leading to it (Scheme 3) [13e]. Jackson et al. have unequivocally demonstrated control by dihydrogen bonding of the diastereoselective borohydride reduction of α-hydroxoketones to give trans-diols (Scheme 4); the reduction reaction with tetrabutylammonium borohydride in non-hydrogen-bonding solvents such as CH_2Cl_2 and 1,2-dichlorobenzene are accelerated about 150 times relative to the reduction of the unsubstituted cycloalkanones. These effects are, however, greatly reduced in the presence of competing hydrogen-bonding alcohols or anions such as F^-, Cl^-, and Br^- [14].

In this review, we will summarize some of our work on the synthesis, characterization, and reactivity of ruthenium dihydrogen complexes. We will also review our study of the reactivity and catalytic activity of some ruthenium hydride complexes which either function as metal-ligand bifunctional catalyst or exhibit dihydrogen-bonding interactions with proton donors; these interactions, in some cases, play important roles in mediating catalytic reactions.

2. Hydrogen transfer in the dihydrogen(norbornadiene)-ruthenium complex

In the classical olefin hydrogenation reactions catalyzed by transition-metal complexes not containing M–H bonds, activation of H_2 by the metal fragment leads to the formation of the metal dihydride, which transfer the two hydrogen atoms to the olefin within the coordination sphere of the metal [15]. For metal fragments that react with H_2 to form non-classical dihydrogen species rather than the metal dihydrides, catalytic olefin hydrogenation reactions with these metal fragments probably proceed via the intermediacy of dihydrogen-olefin complexes. Catalytic hydrogenation reactions involving dihydrogen-olefin-metal intermediates have been reported. For example, in the photocatalytic hydrogenation of norbornadiene (NBD) by the metal carbonyls $[M(CO)_6]$ (M = Cr, Mo, W), it is suggested that the dihydrogen(olefin) complexes *mer*-$[(NBD)M(CO)_3(H_2)]$ and fac-$[(NBD)M(CO)_3(H_2)]$ are intermediates in the reaction; intramolecular transfer of H_2 to the diene in the former leads to the formation of norbornene and in the latter leads to nortricyclene. The norbornene–dihydrogen complexes were identified by fast time-resolved IR spectroscopy [16]. Poliakoff et al. also studied the mechanism of the catalytic hydrogenation of dimethylfumarate (DF) with $[Fe(CO)_4(\eta^2\text{-DF})]$ using polyethylene matrix, by use of FTIR spectroscopy. They were able to identify the dihydrogen-olefin intermediate $[Fe(CO)_3(\eta^2\text{-DF})(\eta^2\text{-}H_2)]$ [17].

Our work on the protonation reaction of [Ru(PCP)H(NBD)] (**1**) (PCP = 2,6-$(PPh_2(CH_2)_2C_6H_3)$ provides an example of studying the transfer of hydrogen atoms from a η^2-H_2 ligand to the neighboring olefinic ligand. Protonation of **1** with HOTf in the presence of acetonitrile gives [Ru(PCP)(NBD)(MeCN)]OTf (**2**) and $[Ru(PCP)(MeCN)_3]$OTf (**3**) along with norbornene in a 3:2:2 ratio (Eq. (1)). Protonation of **1** forms the dihydrogen complex $[Ru(PCP)(NBD)(\eta^2\text{-}H_2)]$OTf (**4**), displacement of the dihydrogen ligand in **4** yields **2**. Apparently, **4** also undergoes a hydrogen-transfer reaction in the presence of MeCN to give norbornene and **3**. The ratio of the products of the reaction indicates that the η^2-H_2 ligand in **4** is not displaced instantaneously by MeCN.



(1)

Density functional calculations at the B3LYP level of theory were performed to gain insight into the favorable pathway for the hydrogen-transfer reaction, using the model compound $[Ru\{2,6\text{-}(H_2PCH_2)_2C_6H_3\}(NBD)(H_2)]^+$. Fig. 1 shows the reaction pathway for the hydrogen-transfer reaction; the relative free energies and reaction energies (in parentheses) are also shown. The reaction proceeds through a stepwise pathway in which the first step is the transfer of one hydrogen atom of the coordinated H_2 ligand to NBD to form a pentagonal–bipyramidal intermediate via the transition state **TS1** which corresponds to a dihydrido species in which one of the hydrides is 1.645 Å from the receiving carbon of NBD; the energy barrier of this step is 19.08 kcal/mol. Transfer of the hydride ligand to the partially reduced organic moiety through the second transition state

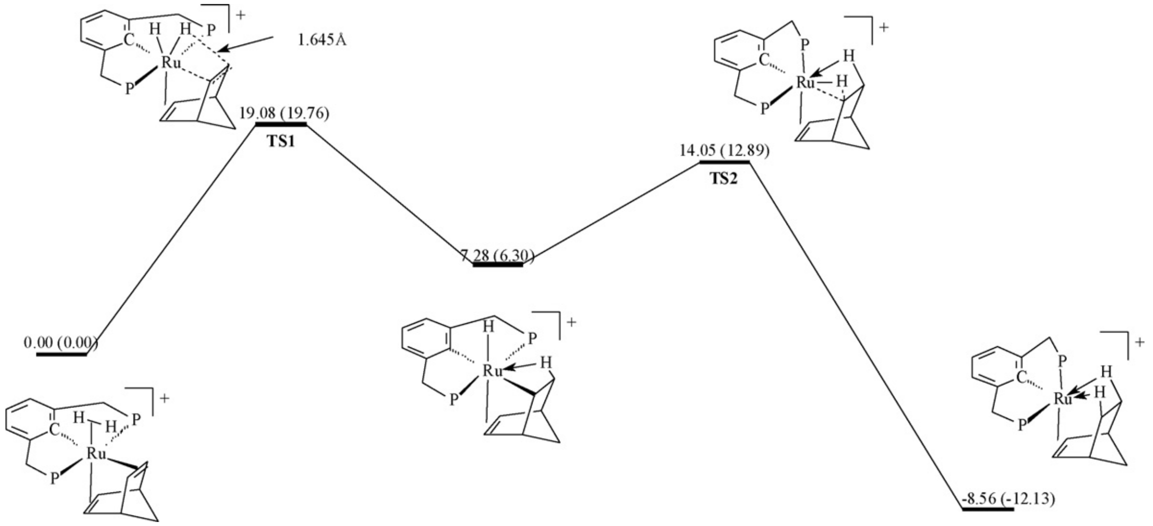


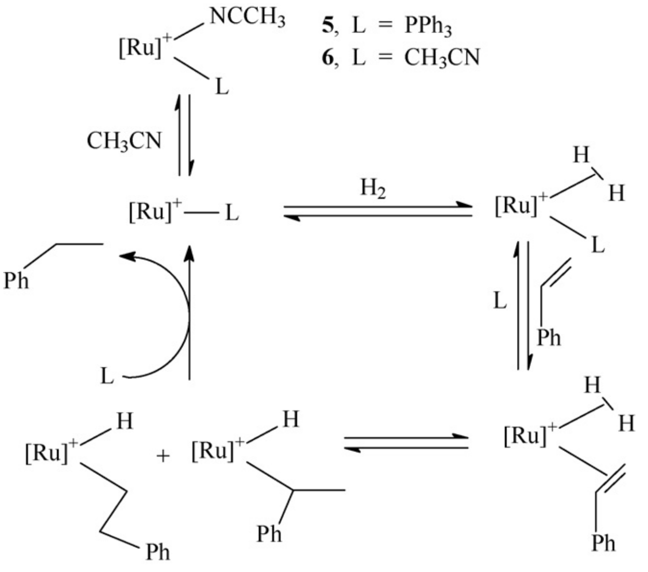
Fig. 1. Schematic illustration of the reaction pathways of $[Ru(2,6\text{-}(PH_2CH_2)_2C_6H_3)(NBD)(H_2)]^+$, with calculated relative free energies (kcal/mol) and reaction energies (kcal/mol) (in parentheses); figure was reproduced from Ref. [18], with permission of the copyright holders.

TS2, which has a lower barrier of 6.77 kcal/mol, form the NBE complex [18].

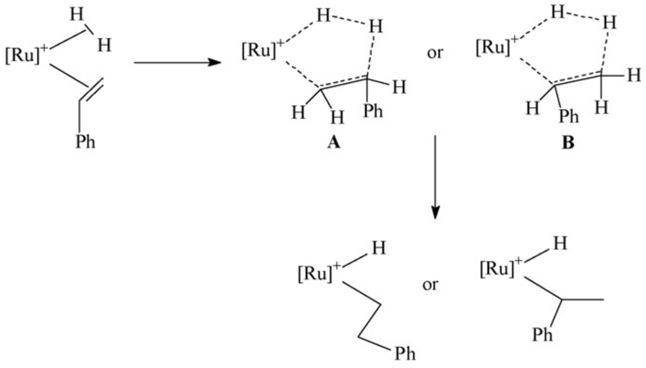
3. Tp-ruthenium dihydrogen and hydride complexes

3.1. Tp-ruthenium dihydrogen complexes in the catalytic hydrogenation of olefins in anhydrous THF

To gain more insight into the roles of dihydrogen complexes in catalysis, we studied the catalytic hydrogenation of alkenes with the hydro(trispyrazolyl)borato (Tp)-ruthenium complexes, $TpRu(PPh_3)(L)(CH_3CN)$ (**5**, L = PPh_3; **6**, L = CH_3CN) [19]. The dihydrogen complex $[TpRu(PPh_3)(L)(H_2)]BF_4$ (**7**, L = PPh_3; **8**, L = CH_3CN) could be readily synthesized by protonation of the hydride precursors with $HBF_4{\cdot}OEt_2$. Moreover, a high-pressure ^{1}H NMR study showed that **7** and **8** could also be generated by reacting **5** and **6** with pressurized H_2, respectively. Complexes **5** and **6** were found to be active catalysts for the hydrogenation of alkenes in anhydrous THF. In view of the fact that the $TpRu(PPh_3)L^+$ moiety supports the η^2-dihydrogen ligand rather than the dihydride, a mechanism different from the common Wilkinson catalyst-type dihydride mechanism was suggested for the hydrogenation reactions in anhydrous THF with **5** and **6** (Scheme 5). The dihydrogen–olefin complex rather than the dihydride–olefin species is proposed to be an intermediate in the catalytic cycle. That the former is preferred is based on the fact that the olefinic fragment $TpRu(PPh_3)(olefin)^+$ is less electron-rich than the $TpRu(PPh_3)(L)^+$ fragments which had been shown to form dihydrogen complexes instead of dihydride. The conversion of the dihydrogen–olefin complex to the alkyl-hydride species has been discussed in the previous section on the hydrogen transfer in dihydrogen(norbornadiene)–ruthenium complex. On the other hand, five-membered ring species **A** and **B** might be proposed to be the transition structures for the conversion of the dihydrogen–olefin intermediate to the alkyl-hydride species (Scheme 6). This step is reminiscent of the formation of five-membered metallacycles via oxidative coupling reactions involving η^2-olefin/η^2-olefin, η^2-olefin/η^2-alkyne, and η^2-alkyne/η^2-alkyne [20]. Similar mechanisms involving oxidative coupling of η^2-H_2 and η^2-olefin ligands have also been proposed and supported by DFT calculations for the iridium-catalyzed asymmetric hydrogenation of arylalkenes and dienes [21].

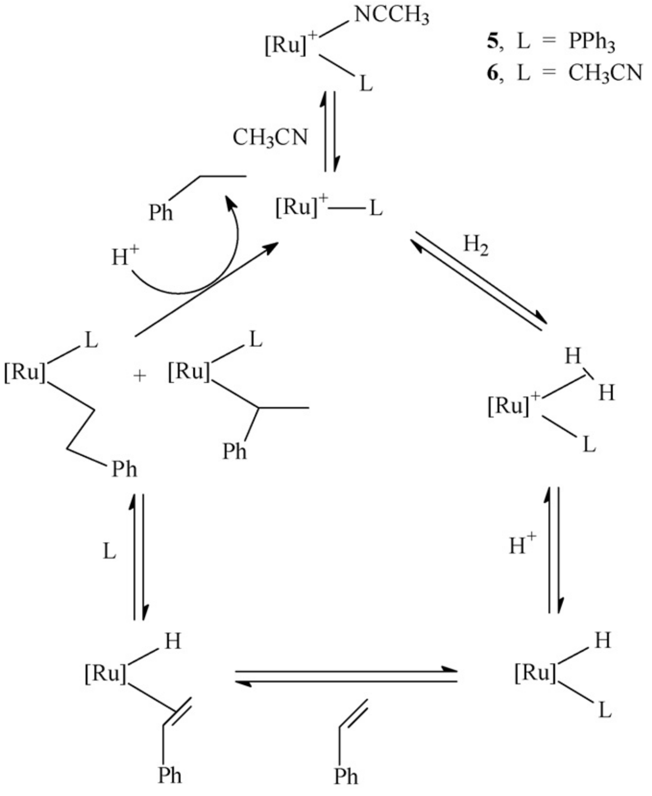


Scheme 5.

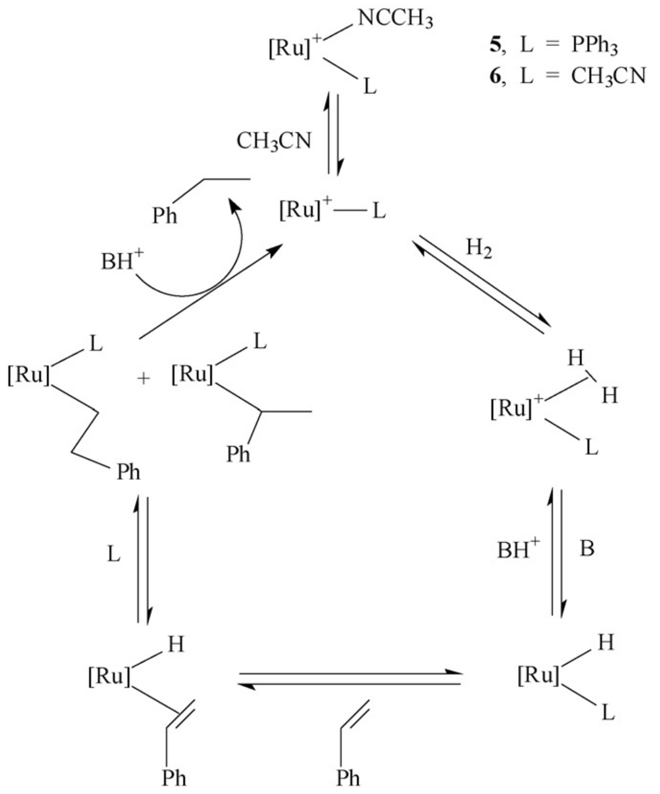


Scheme 6.

Scheme 7 shows an alternative catalytic pathway for the hydrogenation reaction; it might also help to provide rationalization for the promoting effect of base in the hydrogenation reaction that we are going to present in the next section (Section 3.2). In Scheme 7, the dihydrogen ligand, instead of protonating the olefin to form the alkyl-hydride species, undergoes deprotonation; olefin then inserts into the Ru–H, and the product is generated by protonation of the Ru–alkyl.



Scheme 7.



Scheme 8.

Other dihydrogen complexes have been shown to be active catalysts for hydrogenation of unsaturated organic functions; these complexes, however, contain M–H bonds. The catalytic reactions probably do not involve the intermediacy of dihydrogen–olefin complexes [2].

3.2. *Promoting effect of base (H_2O or NEt_3) in the catalytic hydrogenation reactions*

Interestingly, enhanced catalytic activities in the **5**- and **6**-catalyzed hydrogenation reactions were observed in the presence of water or triethylamine. (Using styrene as example; for **5**, catalytic activities are enhanced 2.8 and 2.4 times in the presence of H_2O and NEt_3, respectively; for **6**, 3.2 and 2.6 times, respectively) When D_2O was added, deuterium was incorporated into the products. A proposed mechanism, involving heterolytic cleavage of the η^2-dihydrogen ligand by the base (water or NEt_3), for the catalytic hydrogenation reaction in the presence of water or triethylamine is depicted in Scheme 8. The catalytic cycle proceeds with olefin insertion into Ru–H bond and is completed by protolysis of the Ru–alkyl with H_3O^+ or $HNEt_3^+$. The promoting effect of the base might be attributed to its enhancing the deprotonation of the η^2-H_2 ligand.

3.3. *Reaction of $TpRu(PPh_3)(CH_3CN)H$ with H_2*

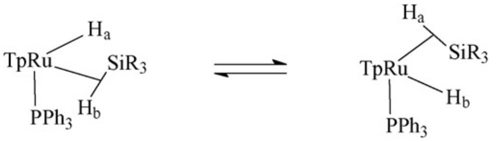
The hydride precursor, $TpRu(PPh_3)(CH_3CN)H$ (**9**), of the dihydrogen complex **8** is a versatile complex exhibiting interesting reactivities and catalytic activities. It reacts with H_2 under pressure to give the dihydrogen-hydride complex $TpRu(PPh_3)(H_2)H$ (**10**), whose ^1H NMR spectrum shows only one hydride signal, which integrates for 3H and does not decoalesce down to −110 °C. The presence of dihydrogen ligand in **10** is confirmed by the small T_1 (min) value (34 ms at 210 K and 400 MHz) for the hydride signal and the $J(HD)$ value of 29.7 Hz of the HD isotopomers $TpRu(PPh_3)H_xD_{3-x}$. Rapid fluxionality between the hydride and dihydrogen ligands therefore exists in **10** [22].

3.4. *Reactions of $TpRu(PPh_3)(CH_3CN)H$ with primary alcohols*

Reaction of **9** with primary alcohols RCH_2OH lead to decarbonylation of the latter and the formation of $TpRu(PPh_3)(CO)R$; a mechanism involving the alcohol-hydride, η^2-aldehyde and η^2-dihydrogen intermediates, all of which are observable by H NMR spectroscopy at the early stage of the reaction, has been proposed for the decarbonylation reactions (Scheme 9). During the reaction, free aldehyde is, however, not detected [21]. Incorporation of the R group of RCH_2OH into the final metal complex is unusual, as the R group is usually not retained on the metal in most of the known decarbonylation reactions with transition metal complexes [23].

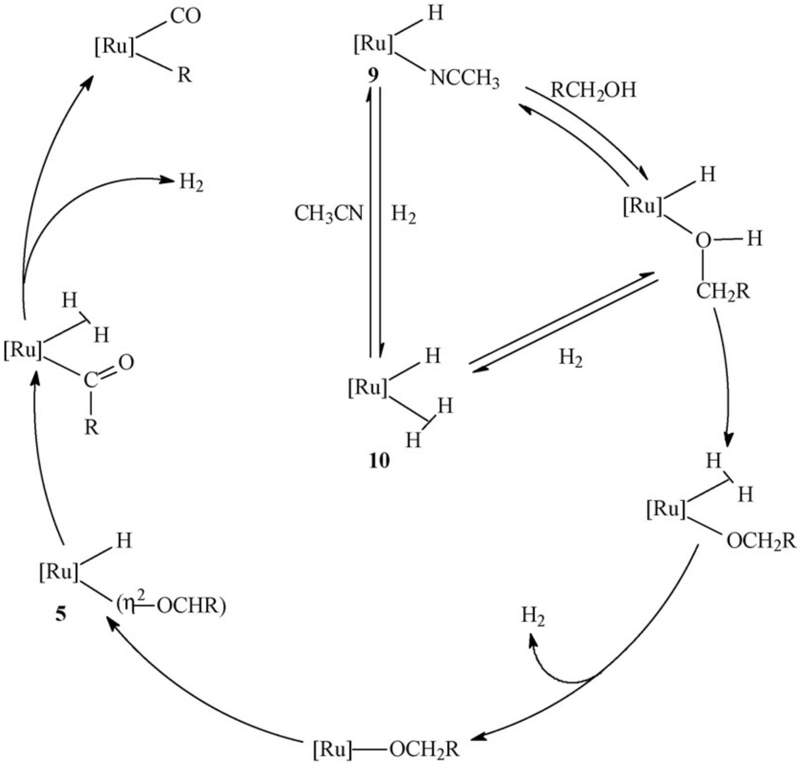
3.5. *Reactions of $TpRu(PPh_3)(CH_3CN)H$ with silanes*

The reactions of **9** with silanes $HSiR_3$ (R_3 = Et_3, $(EtO)_3$, Ph_3, HEt_2, HPh_2, and H_2Ph) yield the η^2-silane complexes $TpRu(PPh_3)(\eta^2\text{-H–SiR}_3)H$ (**11**), the formulations of which are inferred from NMR spectroscopy. The chemical equivalence of the two hydrogen atoms in the complexes down to −100 °C is attributed to rapid fluxionality between the two tautomers (Eq. (2)) [24].



(2)

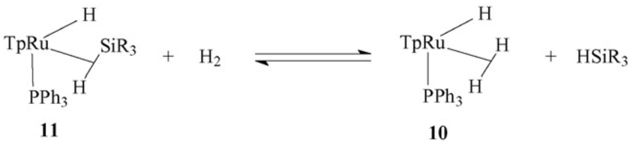
Molecular orbital calculations at the B3LYP level of theory have been performed to investigate the stereochemistry and the interconversion processes of various structural isomers for $TpRu(PPh_3)(\eta^2\text{-H–SiR}_3)H$. The results further support the existence of the η^2-silane hydride formulation for these complexes. Crabtree reported the synthesis of a similar η^2-silane hydride complex $[IrH_2(\eta^2\text{-H–SiEt}_3)_2(PPh_3)_2]SbF_6$ by addition of excess Et_3SiH to $[IrH_2(CH_3OH)_2(PPh_3)_2]SbF_6$ in CD_2Cl_2 at −80 °C; the complex was stable only at low temperature and extremely sensitive to nucleophiles [25]. On the other hand, it was reported that reaction of $OsHCl(CO)(P^iPr_3)_2$ with Et_3SiH gave the silyl η^2-dihydrogen complex $OsCl(SiEt_3)(H_2)(CO)(P^iPr_3)_2$, which was considered as an intermediate in the hydrosilylation of phenylacetylene catalyzed by $OsHCl(CO)(P^iPr_3)_2$ [26].



$[Ru] = [TpRu(PPh_3)]^+$
$R = H, Me, Et, Pr, Ph, C_6H_4CH_3, C_6H_4Cl$

Scheme 9.

The η^2-silane complexes **11** react reversibly with H_2 to generate the dihydrogen–hydride complex **10** (Eq. (3)).



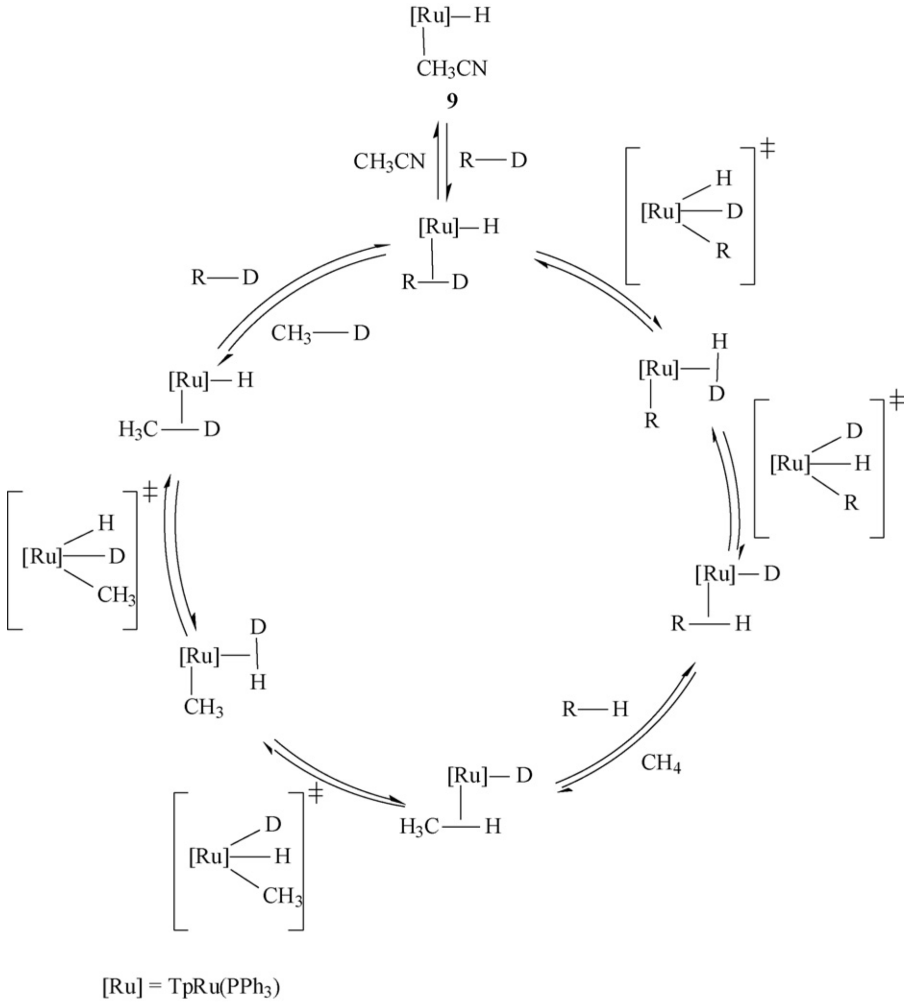
(3)

3.6. $TpRu(PPh_3)(CH_3CN)H$-catalyzed H/D exchange between CH_4 and R–D

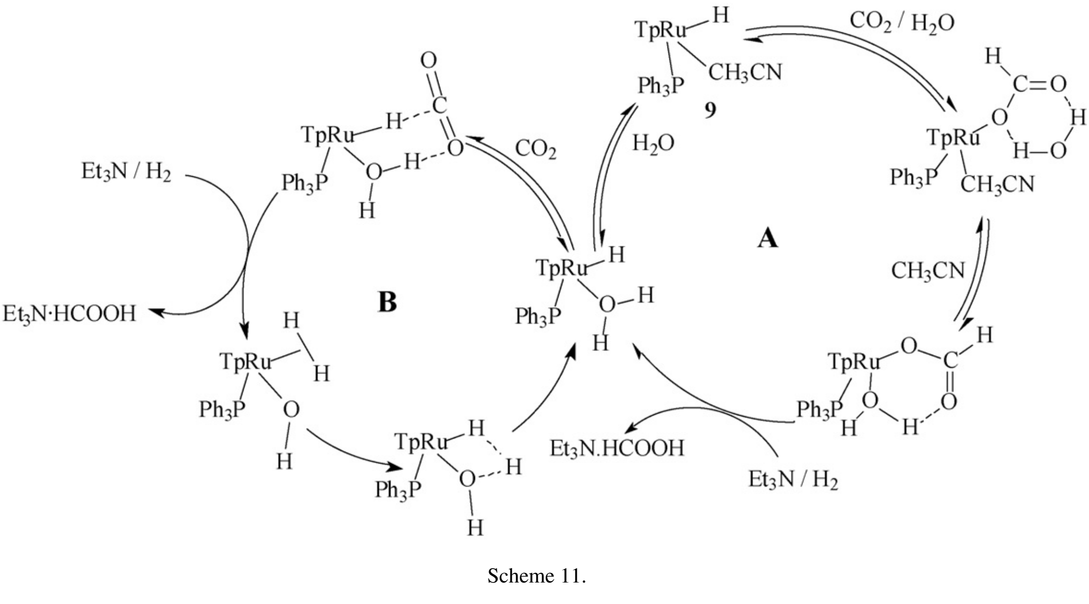
Unlike its reactions with H_2 and $HSiR_3$, which give the isolable η^2-dihydrogen and η^2-silane complexes, respectively, the reaction of **9** with CH_4 did not yield any isolable or NMR-detectable σ-methane complex. It was, however, found by NMR and mass spectroscopy that **9** was able to catalyze H/D exchange between CH_4 (8 atm) and deuterated organic compounds (R–D) such as benzene-d_6, THF-d_8, diethylether-d_{10}, and 1,4-dioxane-d_8 at 100 °C. Density functional theory calculations lead to the idea that the σ-complexes $TpRu(PPh_3)(\eta^2\text{-}D\text{–}R)H$ and $TpRu(PPh_3)(\eta^2\text{-}H\text{–}CH_3)D$ are the intermediates in the proposed H/D exchange mechanism (Scheme 10). During the exchange process, reversible transformations of the two σ-complexes to their corresponding η^2-HD tautomers, $TpRu(PPh_3)(\eta^2\text{-HD})R$ and $TpRu(PPh_3)(\eta^2\text{-HD})(CH_3)$, respectively, are the crucial steps [27]. The seven-coordinated species, $TpRu(PPh_3)(R)(H)(D)$ and $TpRu(PPh_3)(CH_3)(H)(D)$, derived from oxidation addition of R–D and CH_3–H to the metal center, are transition states, but not intermediates. This seems to be in accord with the fact that the Tp ligand generally enforces an octahedral geometry about the metal [28].

3.7. Promoting effect of water in $TpRu(PPh_3)(CH_3CN)H$-catalyzed CO_2 hydrogenation

Study of catalytic hydrogenation of CO_2 to formic acid with solvento hydride complex **9** in THF reveals a large promotion effect of water in the catalysis. Accelerating effects of small amounts of added water in catalytic hydrogenation of CO_2 to formic acid have been observed in other systems [29]. It has been speculated that the water promoting effect might be a result of hydrogen-bonding interaction between a water molecule and the oxygen atom of CO_2 which enhances the electrophilicity at carbon and facilitates its insertion into the metal–hydride bond. Our in-situ NMR study showed that under catalytic conditions, CO_2 readily inserts into the Ru–H to give metal formates, which are stabilized by intra- and intermolecular hydrogen bonding with the water molecules. In the light of the Halpern axiom that observations of “likely” intermediates in catalytic cycles generally signal, in fact, a nonproductive, sluggish loop of the pathway [30], one would reasonably expect that the production



Scheme 10.

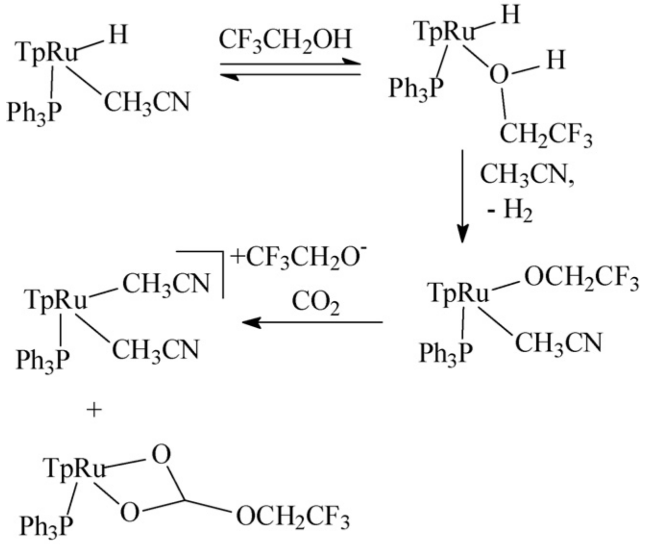


Scheme 11.

of formic acid via the formate intermediates is slow (cycle **A** of Scheme 11). With the support of theoretical study, a productive catalytic cycle, which takes into account the promoting effect of water, was proposed (cycle **B** of Scheme 11). The key species in the cycle is the aquo hydride species TpRu(PPh_3)(H_2O)H, which is generated, in very small amount, by the ligand displacement reaction of **9** with H_2O. The aquo hydride complex is a metal-ligand bifunctional catalyst; it transfers the hydride and a proton of the H_2O ligand to CO_2 to yield formic acid in a concerted manner, and itself being converted to a transient hydroxo species, which then reacts with H_2 to regenerate TpRu(PPh_3)(H_2O)H via a σ-metathesis process [31]. Such concerted transfer of a hydride from the metal and a proton from a ligand to the substrate is similar to that observed for the asymmetric hydrogenation of ketones with the hydridodiamine complexes [10,11]. In a recent study of ruthenium-catalyzed hydrogenation of α,β-unsaturated aldehyde, the regioselective reduction of the carbonyl function is explained in terms of a water-assisted mechanism, in which a ruthenium aquo dihydride can perform the regioselective hydrogenation of the substrate in one step. The hydride of the metal and a proton of the water ligand are transferred, respectively, to the carbon and the oxygen atoms of the carbonyl function in a concerted manner, via a six-centered transition state, leading to the coordinated alcohol and an OH ligand; the alcohol is then displaced by H_2, which undergoes σ-metathesis with the OH group to regenerate the metal aquo dihydride [32]. This mechanism is very similar to that depicted in Scheme 11.

3.8. *TpRu(PPh$_3$)(CH$_3$CN)H-catalyzed CO$_2$ hydrogenation in alcohols*

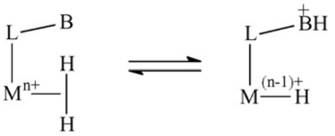
Similar to water, alcohols also exhibit a promoting effect in the **9**-catalyzed CO_2 hydrogenation reactions. It is believed that the active species in the catalysis is the analogous alcohol-hydride complex TpRu(PPh_3)(ROH)H; the reaction proceeds via a reaction sequence similar to that shown in Scheme 11. Trifluoroethanol (CF_3CH_2OH) shows much larger promoting effect than methanol and other non-acidic alcohols; it is probably due to the enhanced electrophilicity of the carbon atom of CO_2 resulting from the strong interaction between the proton of the highly acidic alcohol in TpRu(PPh_3)(CF_3CH_2OH)H and an oxygen atom of CO_2. The electrophilic carbon atom of CO_2 could in turn abstract the hydride from Ru–H in a more facile manner. In methanol and other non-acidic alcohols, CO_2 inserts into Ru–H to form the stable metal formate intermediate, which is stabilized by the hydrogen-bonding interaction between the formato ligand and an alcohol molecule; similar to the formato complexes observed in the THF/H_2O catalysis, the metal formate in the alcohol medium is also not within the productive catalytic cycle. In the case of the acidic CF_3CH_2OH, the observable intermediates are [TpRu(PPh_3)(CH_3CN)$_2$]$^+$ $CF_3CH_2O^-$ and the alkyl carbonate complex TpRu(PPh_3)(η^2-$O_2COCH_2CF_3$), which are formed by the reaction of CO_2 with the alkoxide species, TpRu(PPh_3)(CH_3CN)(OCH_2CF_3), generated by a very facile reaction between TpRu(PPh_3)(CH_3CN)H and CF_3CH_2OH (Scheme 12) [33].



Scheme 12.

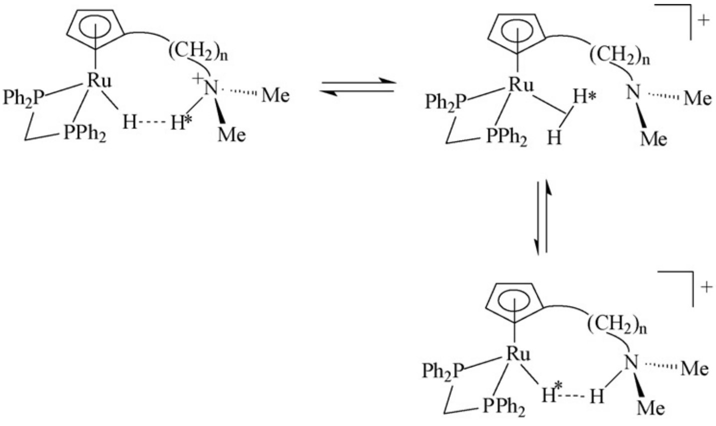
4. Synthesis, characterizations, and reactivities of intramolecularly dihydrogen-bonded ruthenium complexes

One of the features of dihydrogen complexes is the activation of the H_2 ligand with respect to heterolysis. Intermolecular heterolytic cleavage of η^2-H_2 can be achieved by a variety of bases. We have proposed a mechanism that includes heterolytic splitting of η^2-H_2 in a Tp-ruthenium dihydrogen species as a crucial step to account for the enhanced catalytic activity of the complex in olefin hydrogenation reactions in the presence of a base, H_2O or NEt_3 (see Scheme 8). Reversible heterolytic splitting of the η^2-D_2 ligand by H_2O has been proposed to be an important step in H/D exchange between H_2O and D_2 in a solution of [W(CO)$_3$(P^{i}Pr$_3$)$_2$(D_2)] [34].



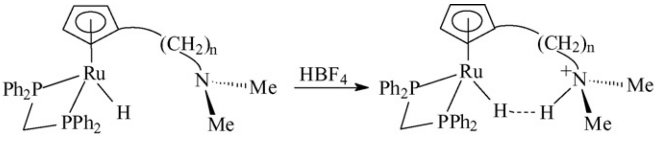
(4)

Intramolecular heterolytic cleavage of dihydrogen ligand results from its deprotonation by the basic site of a coligand. This reaction and its reverse (Eq. (4)) have been postulated to explain the H/D exchange reactions in [IrH(H_2O)(bq)(PCy_3)$_2$]$^+$ (bq = 7,8-benzoquinolinato) [35], [Ir(H)$_2$(HS(CH$_2$)$_3$SH(PCy_3)$_2$]$^+$ [36], and [IrHX(NH_3)$_2$(PEt_3)$_2$]$^{+,2+}$ (X = Cl$^-$, NH_3, PEt_3) [37]. Intramolecular proton transfer from bound H_2 to neighboring organic group could be important in catalytic reactions. Moreover, complexes containing intramolecular M–H···H–X dihydrogen-bonding interaction are regarded as intermediates in the intramolecular heterolytic splitting of dihydrogen. To gain insight into the process of intramolecular heterolytic splitting of H_2 ligand and intramolecular protonation of metal hydride, we designed a metal hydride complex which contains an aminocyclopentadienyl ligand (L–B in Eq. (4)). Addition of one equiv of HBF_4 to (η^5-C_5H_4(CH$_2$)$_n$NMe$_2$)Ru(dppm)H (**11**, n = 2; **12**,



Scheme 13.

$n = 3$) gave $[(\eta^5\text{-}C_5H_4(CH_2)_nNMe_2H)Ru(dppm)H]BF_4$ (**11H**$^+$, $n = 2$; **12H**$^+$, $n = 3$) in which the amino side arms were protonated (Eq. (5)).



11, n = 2
12, n = 3

11H$^+$, n=2
12H$^+$, n=3

(5)

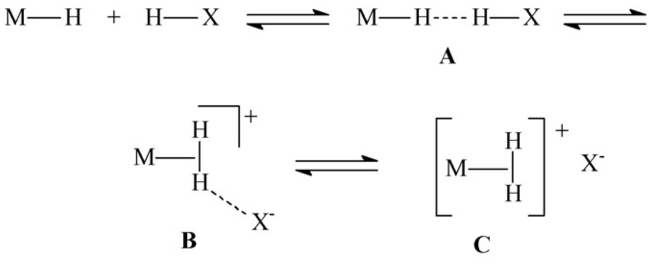
Relaxation time T_1 measurements indicated the existence of intramolecular Ru–H···H–N dihydrogen-bonding interactions in these complexes. A spin saturation transfer experiment was carried out with **12H**$^+$; irradiation of the hydride signal led to an approximately 80% decrease of the intensity of the N–H signal, this phenomenon can be interpreted as resulting from a rapid exchange process between the metal hydride and the N-bonded proton via a η^2-H_2 complex intermediate (Scheme 13). The exchange process was corroborated by facile deuteration of the hydride ligand by D_2O; the N–H first underwent H/D exchange with D_2O to form the N–D function, which then H/D-exchanged with Ru–H [38]. In contrast, the complex $[IrH(\eta^1\text{-}SC_5H_4NH)(\eta^2\text{-}SC_5H_4)(PPh_3)_2]$ BF_4, in which Ir–H···H–N interaction has been ascertained, does not show Ir–H/N–H exchange, probably due the weakness of the dihydrogen-bonding interaction [39].

Addition of 1 equiv. of HBF_4 to **11H**$^+$ and **12H**$^+$ led to the formation of dihydrogen complexes $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H)Ru(dppm)(H_2)](BF_4)_2$ (**13**) and $[(\eta^5\text{-}C_5H_4(CH_2)_3NMe_2H)Ru(dppm)(H_2)](BF_4)_2$ (**14**), respectively. The generation of the dihydrogen complexes reveals the fact that the stronger acid HBF_4 is able to fully protonate Ru–H to form the η^2-H_2 ligand, while the weaker acid–the ammonium ion NH^+ only forms dihydrogen bond with the hydride. The interaction of metal hydride with a proton donor H–X can be visualized as shown in Scheme 14. The far right is the free ion pair (dihydrogen complex), while **B** is the hydrogen-bonded ion pair and **A** is the dihydrogen-bonded species; whether **A**, **B**, or **C** would predominate is very dependent on the proton donor strength of H–X [40]. We have also demonstrated that the M–H···H–X dihydrogen bond strength is critically dependent on the donating ability of the proton donor in our study of protonation of the cationic ruthenium hydride complex $[tpmRu(PPh_3)_2H]BF_4$ (tpm = tris(pyrazolyl)methane) with aqueous HBF_4 at variable temperatures. Decrease of the dihydrogen bond (Ru–H···$H(H_2O)_n$) strength with temperature can be attributed to the decline of acidity that results from the formation of larger $H^+(H_2O)_n$ clusters at lower temperatures; steric hindrance of these large clusters also contribute to the weakening of the dihydrogen-bonding interactions [41].

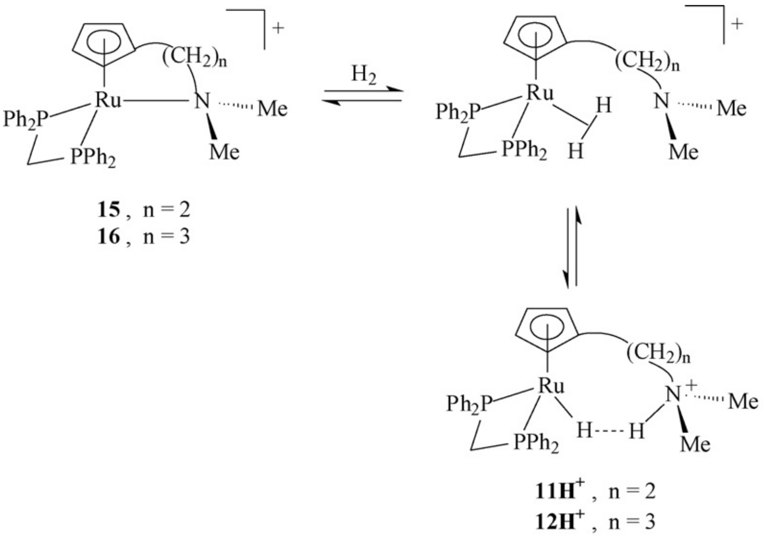
The dihydrogen-bonded species **11H**$^+$ and **12H**$^+$ can be generated by exposure of the amine-bonded complexes $[(\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_nNMe_2)Ru(dppm)]BF_4$ (**15**, $n = 2$; **16**, $n = 3$) to H_2 (60 atm) at 60 °C for 30 min. **11H**$^+$ and **12H**$^+$ lose H_2 to regenerate **15** and **16**, respectively, on prolonged standing. The dihydrogen-bonded and the amine-bonded complexes probably interconvert via the dihydrogen complex intermediate (Scheme 15).

Sabo-Etienne et al., however, reported that in the triphenylphosphine analogue of **11H**$^+$, the exchange process between the hydride and the ammonium proton involves a dihydride intermediate [42].

Complex **15** or **16** was found to be able to catalyze CO_2 hydrogenation to formic acid, although in low yields. The crucial step in the catalysis is proposed to be the heterolytic cleavage of H_2 to generate **11H**$^+$ or **12H**$^+$. Theoretical investigation indicated that hydrogen bonding of the amine proton in **11H**$^+$ or **12H**$^+$ to the



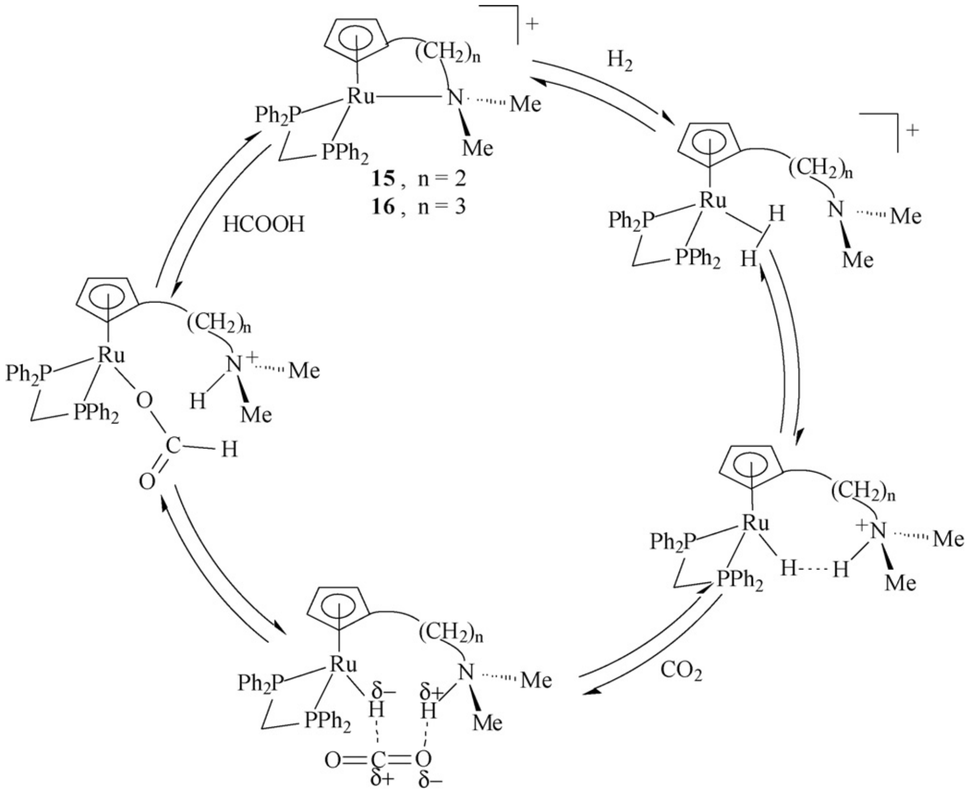
Scheme 14.



Scheme 15.

oxygen atom of an incoming CO_2 enhances the electrophilicity at the carbon of the molecule, enabling it to abstract the hydride from the metal to form the transient metal-formate intermediate [43]. Not unexpectedly, **15** and **16** catalyzes the decomposition of formic acid too (Scheme 16).

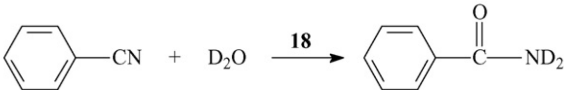
Not only is the M–H···H–X dihydrogen bond strength affected by the acidity of H–X, it is also expected to be dependent on the hydridicity of M–H. Continuing our study of dihydrogen bonding in aminocyclopentadienyl ruthenium hydride complexes, we have studied the influence of decreased basicity of the metal center on the strength of the M–H···H–X dihydrogen bond. We have demonstrated that in $[(\eta^5\text{-}C_5H_4(CH_2)_2NMe_2H^+)Ru(P(OPh)_3)_2H$ (**17**), which contains the less donating phosphite ligands, the stable conformation of the complex in solution is one in which no Ru–H···H–N dihydrogen bonding interaction is present between the hydride and the ammonium proton. We attribute the lack of interaction to reduced hydridicity of the hydride ligand in **17** [44].



Scheme 16.

5. Dihydrogen bond-promoted catalytic hydration of nitriles

Although it is well-established that dihydrogen bonds can be utilized to control reactivity and selectivity of chemical reactions, well-recognized cases of dihydrogen bonds playing an essential role in promoting catalytic reaction are still rare. In the course of studying C–H bond activation by the indenylruthenium hydride ($(\eta^5\text{-}C_9H_7)Ru(dppm)H$ (**18**), the complex was found to be able to catalyze H/D exchange between D_2O and some aromatic solvents such as benzene, toluene, chlorobenzene, and xylene. However, in the case of benzonitrile, H/D exchange was not observed; the organic compound was instead hydrated to give the deuterated benzamide (Eq. (6)). Catalytic hydration of nitriles to amides with transition metal complexes is well known [45], the **18**-catalyzed hydration reaction, however, is interesting in the mechanistic aspect [46].

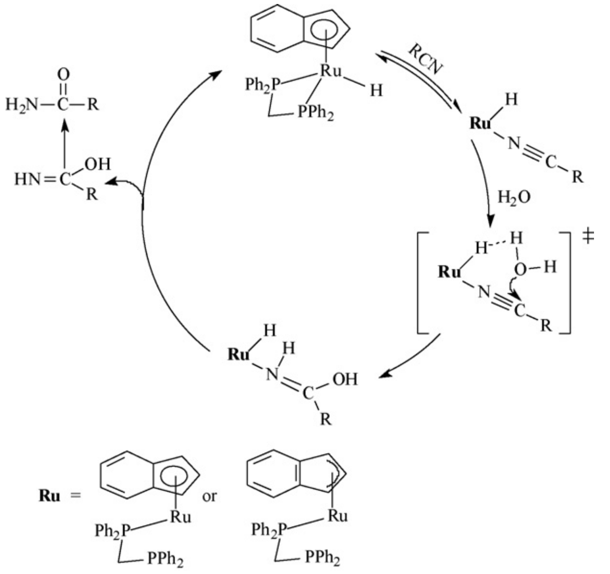


(6)

The chloro analogue $(\eta^5\text{-}C_9H_7)Ru(dppm)Cl$ (**19**) was also examined for the catalytic nitrile hydration reaction, and surprisingly, it was found to be inactive. If the crucial step of the hydration reaction is the nucleophilic attack of H_2O at the carbon of the bound nitrile, complex **19**, which contains a more electronegative chloro group, would render the nitrile carbon more susceptible to water attack. One may argue that **18** could react with water to form the hydroxo complex $(\eta^5\text{-}C_9H_7)Ru(dppm)OH$, which is the real active species. This hypothesis, however, seems unlikely, because in a NMR-monitored **18**-catalyzed acetonitrile hydration reaction, it was observed that the complex remained unchanged throughout the experiment; furthermore, independent experiment showed that after heating at 80 °C a THF-d_8 solution of **18** containing 20 equiv. of H_2O for 4 days, the complex remained intact. Therefore, the fact that **18** but not **19**, is active for catalytic nitrile hydration seems to imply that the hydride ligand of the former might play an important role in the reaction.

A mechanism that accounts for the catalytic activity of **18** in nitrile hydration is depicted in Scheme 17. We suggest that the **18**-catalyzed hydration is a dihydrogen bond-promoted reaction; the dihydrogen-bonding interaction between the metal hydride and the incoming H_2O molecule might be crucial in lowering the activation energy of the C–O bond formation step of the hydration reaction. That the chloro complex is not active is probably attributable to the fact that the chloro ligand is not as capable as the hydride of **18** in playing an active role.

To study the feasibility of the proposed reaction mechanism for the catalytic hydration reactions with **18**, theoretical calculations at the B3LYP level of density function theory to study a more detailed catalytic pathway for acetonitrile hydration with model catalyst $(\eta^5\text{-}C_9H_7)Ru(H_2PCH_2PH_2)H$ (**20**), in which the phenyl groups of the dppm ligand are replaced by H atoms, have been carried out. The calculations indicate that the catalytic process is initiated by the dissociation of one arm of the bidentate ligand instead of the $\eta^5 \rightarrow \eta^3$ ring slippage, which is a well-known phenomenon for η^5-indenyl transition-metal complexes [47], and followed by CH_3CN coordination. Fig. 2 shows the possible reaction pathway, together with calculated energies (kcal/mol, in parentheses) for species involved in the reaction.



Scheme 17.

The acetonitrile-coordinated species **20C** is weakly dihydrogen-bonded to a H_2O molecule, having an H···H distance of 2.123 Å, and is in equilibrium with the hydride complex **20**. From **20C**, the reaction can proceed via two possible pathways, a concerted one (path 2 of Fig. 2) and a stepwise one (path 1 of Fig. 2); the former is found to have a substantially higher barrier than the latter. For the stepwise pathway, the reaction overcomes a barrier of 38 kcal/mol through **TS-20CD**, which is the rate-determining step, forming a four-legged piano-stool *cis*-dihydride intermediate **20D**. This relatively high barrier is responsible for the harsh experimental conditions (120 °C, 72 h) of the catalytic hydration reactions. After the limiting barrier is surmounted, the reaction proceeds easily with a proton transfer to form complex **20E**. The dissociation of the hydrated nitrile (HN = C(OH)Me) requires only 11.6 kcal/mol, making the catalytic cycle feasible. It is noted that dihydrogen-bonding interaction exists from **20C** to the transition state **TS-20CD** in the rate-determining step. The strong H(water)···H(hydride) (1.071 Å) interaction makes **TS-20CD** an early transition state and lowers the reaction barrier. In contrast, the corresponding transition state **TS-21CD** for the chloro system $(\eta^5\text{-}C_9H_7)Ru(H_2PCH_2PH_2)Cl$ (**21**) (Fig. 3) does not contain this type of interaction (H(water)···Cl = 2.582 Å) and is a late transition state having a structure closer to the four-legged piano-stool hydride intermediate **21D**. Therefore, the rate-determining step of the chloro system has a much higher reaction barrier of 45.8 kcal/mol.

The catalytic hydration of nitriles with **18** provides a clear example demonstrating the principle of promoting a catalytic reaction by use of M–H···H–X dihydrogen-bonding interaction;

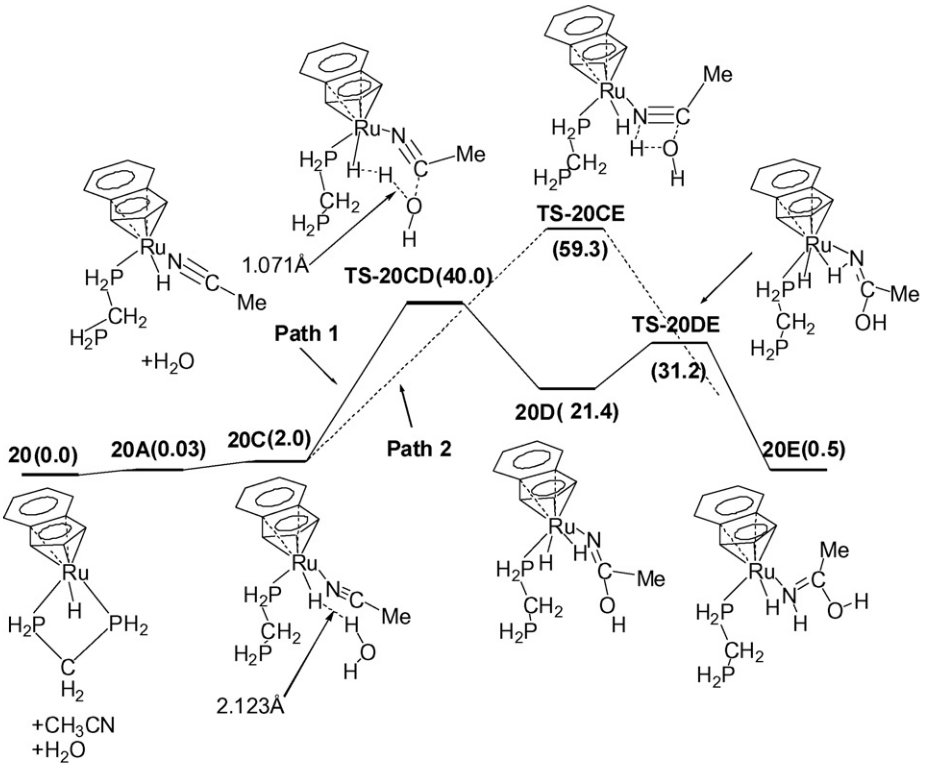


Fig. 2. Schematic illustration of the mechanism for complex **20** together with calculated free energies (kcal/mol) for species involved in the reactions; figure was reproduced from Ref. [46], with permission of the copyright holders.

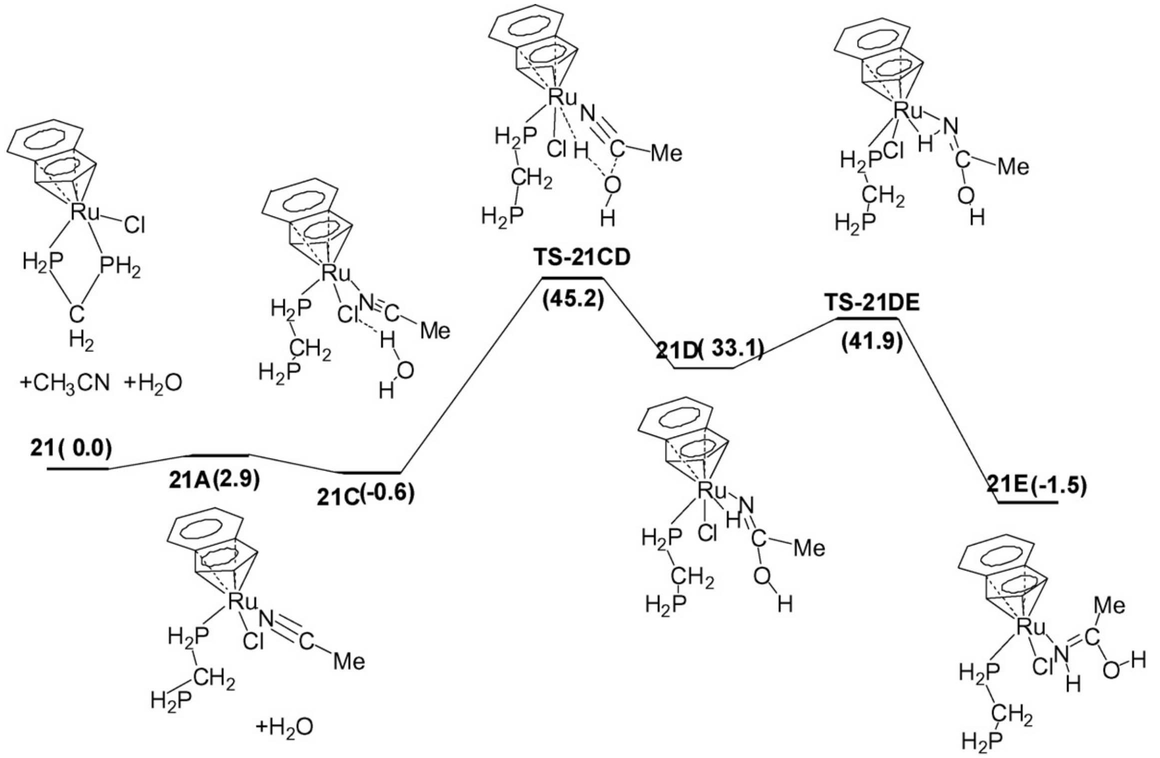


Fig. 3. Schematic illustration of the mechanism for complex **21** together with calculated free energies (kcal/mol) for species involved in the reactions; figure was reproduced from Ref. [46], with permission of the copyright holders.

such a promoting effect might be common to other transition-hydride complexes also.

6. Summary

In this review, we have summed up some of our work on Tp-ruthenium dihydrogen complexes including the possible roles of these complexes in the catalytic hydrogenation of olefins. We have given an explanation for the enhancement effect of bases such as H_2O and NEt_3 in the catalysis in terms of heterolytic cleavage of the η^2-H_2 ligand by the base to give the metal hydride, and product-generating by protonation of the metal alkyl by the conjugated acid of the base. We have synthesized the aminocyclopentadienyl ruthenium complexes containing intramolecular Ru–H···H–N dihydrogen bonds; these complexes provide good model systems for the study of activation of the dihydrogen ligand with respect of heterolysis and its reverse, i.e., formation of η^2-H_2 ligand via protonation of metal hydride with HX. Dihydrogen-bonded complexes are considered intermediates in these processes. We have, via our study of the mechanistic aspects of the catalytic hydration of nitriles with an indenyl ruthenium hydride, provided a novel example demonstrating the principle of utilizing the M–H···H–X dihydrogen bond to promote a catalytic reaction. We believe that although well-recognized instances of catalytic reactions promoted or mediated by dihydrogen bonds are still rare, many of these reactions might have gone unnoticed. Also included in this review is the realization that transition metal hydrides, in the presence of water, might be able to generate an aquo–hydride species; these species could act as metal-ligand bifunctional catalyst, transferring a hydride and a proton to a substrate, whose coordination to the metal center is not required, in a concerted manner. It is therefore important to take into consideration the possibility of an in-situ generated aquo-hydride species playing a role in catalytic hydration reactions or catalysis with transition metal hydrides in aqueous medium. We have shown that alcohol-hydride complexes, which might be generated in catalytic reactions with metal hydrides in alcoholic media, can also act as metal-ligand bifunctional catalysts. All the studies that we discuss in this review are interrelated, and the major ingredient that links them together is the heterolytic cleavage of the dihydrogen ligand.

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