# Proton Transfer to Hydride Ligands with Formation of Dihydrogen Complexes: A Physicochemical View

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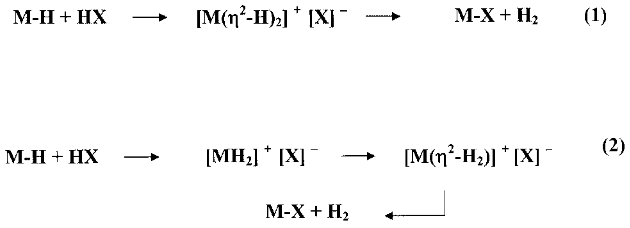
Protonation of hydridic hydrogens has attracted increasing interest from chemists over the past decade. This review, focusing on key physicochemical data, describes general rules governing proton transfer to hydride ligands and discusses kinetic schemes for the protonation as a process starting from dihydrogen-bonded adducts and H-bonded contact ion pairs and ending in dihydrogen complexes as solvent-separated ion pairs or free ions. It has been shown that the particulars of proton transfer to hydride ligands and to conventional organic bases are similar. The difference between them is apparent in the contact ion pair formation step.

## 1. Introduction

Proton transfer to hydridic hydrogens with $H_2$ elimination, which has attracted great interest from chemists, plays a key role in various chemical and biochemical processes[1] occurring in solution and the solid state.[2] In the case of transition metal hydrides this reaction gives dihydrogen complexes[3] which can initiate, for example, catalytic ionic hydrogenation of unsaturated compounds.[4] The elucidation of the mechanism of proton transfer to hydride ligands has been a main goal from the beginning of the interest in the chemistry of dihydrogen complexes. Important aspects of acid-base reactivity, protonation and hydrogen bonding of transition metal hydride systems have already been the subject of several reviews.[5a–5d] Nevertheless, it seems to the author that a reader who is not familiar with transition metal hydride chemistry in particular, still needs a general physicochemical view on this important topic. This approach does not go into the details of hydride chemistry but provides (i) analysis of key results (earlier and recent) from the studies of the spectroscopic, kinetic and thermodynamic parameters which vary with the nature of the metal hydrides, acids and solvents used (ii) a description of the energy profile of proton transfer occurring via a chain of H-bonded intermediates and transition states (iii) a discussion of the driving force in each step of the overall process and also (iv) a comparison of the mechanism of proton transfer to hydride ligands with that operating in proton transfer to conventional organic bases.



Scheme 1

Dihydrogen complexes can be generated through direct proton attack on hydride ligands or an initial protonation of the metal centre[3] (Scheme 1) leading to classical hydrides $[MH_2]^+$ which then convert to dihydrogen complexes

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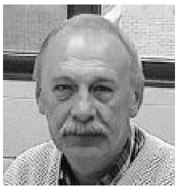

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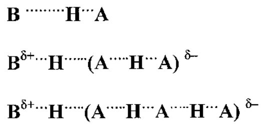


Scheme 2

$[M(\eta^2\text{-}H_2)]^+$ as the thermodynamic products of the reaction. Since protonation of hydride sites is kinetically preferable,[6] the second pathway (rather rare and resulting from a unique combination of steric and electronic features of the initial hydrides) has not been considered in this paper. For the same reason, we have not discussed H-bonded species H–M···H–X as intermediates in proton transfer to metal centres.[7a,7b] Finally, we have also not discussed $H_2$ elimination from dihydrogen complexes, the species being considered stable under the experimental conditions.

## 2. Reaction Intermediates: Spectroscopic (IR, NMR) and DFT Studies

Strong hydrogen bonds dominate in the protonation of usual organic bases.[8] For example, proton transfer from acetic acid, (H-A), to pyridine, (B), occurs via the H-bonded complexes in Scheme 2 which can be directly observed by $^1$H and $^{15}$N NMR spectroscopy in $CDClF_2/CDF_3$ at low temperatures.[8a] It is known now that the hydrogen bond strength increases with a partial proton transfer. For this reason, if the proton overcomes an energy barrier due only to its motion, this barrier must be very small.[8a] In full agreement with this statement, protonation of common organic bases is a very fast process. According to recent DFT calculations, a similar situation takes place for transition metal hydrides in the gas phase. When a strong acid, $H_3O^+$, is placed near a hydride molecule, for example $[CpRuH(CO)(PH_3)]$[9] or $[Cp_2NbH_3]$,[10] the proton is transferred directly to the negatively charged hydride ligand *without* an energy barrier. However such a single-step process is not realistic in solvents with a relatively small polarity such as THF, toluene and $CH_2Cl_2$ which are usually used for the protonation of transition metal hydrides. Under these conditions, even strong acids (HCl, HBr, $CF_3COOH$ or $CF_3SO_3H$) become weak and attack hydride ligands in a molecular form.[11] For this reason, various unusual H-bonded intermediates can be located on the reaction coordinate of the proton transfer to the hydride ligand, leading to a relatively high energy barrier for the process.

### Dihydrogen Bonding

The interaction between hydrogen atoms carrying opposite charges, known as dihydrogen bonding,[12] is a common phenomenon in modern chemistry. H···H bonds play an important role in crystal packing and molecular aggregation in the solid state[13a,13b] and also in the stabilisation of conformational molecular states in solution.[13c] The X–H···H–Y binding energy depends on the nature of the electropositive and electronegative elements X and Y and covers the $-\Delta H^0$ region from 1[13b] to 7 kcal/mol.[2] Recent data [2,14] have demonstrated that dihydrogen bonding is an important pre-organising factor in solid-state proton transfer. In fact, heating the solid complex, $NaBH_4$·triethanolamine, containing B–H···H–X bonds, results in loss of $H_2$ (Figure 1). Subsequently, the Lewis acidic and basic subunits, remaining in close proximity, combine to form new strong covalent bonds.[2] Likewise, dihydrogen-bonded adducts formed in solution by HX protons and negatively charged hydride ligands[15] (Scheme 3) may participate in the first step of proton transfer. In fact, such aggregates formed by $[CpRuH(CO)(PH_3)]$ or $[Cp_2NbH_3]$ and the relatively weak proton donors $CF_3COOH$ and $(CF_3)_3COH$ have recently been located at energy minima in DFT calculations, even in the gas phase.[9,10]

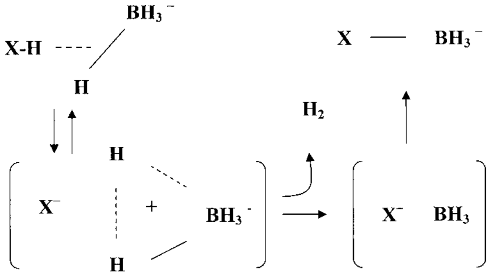
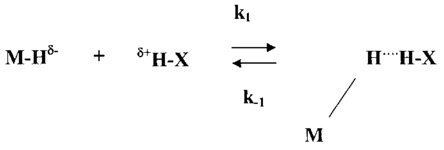


Figure 1. Schematic representation of the solid-state proton transfer to a hydridic hydrogen of the $BH_4^-$ group via the dihydrogen bond[2]



Scheme 3

Both IR and NMR techniques can be used to detect M–H···HX bonds. A combination of the two spectroscopic methods is best.[5c,5d] In the IR spectra, commonly recorded at low temperatures to avoid $H_2$ elimination, dihydrogen bonding is indicated by the new lower-frequency $\nu_{M-H}$ bands (or shoulders) which are shifted by 20–40 cm$^{-1}$ from the corresponding values in the initial hydrides. The timescale of IR spectroscopy allows observation of both the free and H-bonded hydride molecules. In contrast, resonances from the free and coordinated hydrides in the $^1$H NMR spectra are usually averaged even at low temperatures. However, upon dihydrogen bond formation, the signals of initial hydrides undergo remarkable high-field shifts ($\approx$ 0.5–1 ppm) and their spin-lattice relaxation times ($^1$H $T_1$) are diminished due to additional proton-hydride dipole-dipole interactions.[16] It should be emphasised that the concurrent observation of both the effects is required for establishing a reliable NMR criterion for the presence of dihydrogen bonds. In rare cases, the application of Freon solvents "stops" the MH···HX bond formation even on the $^1$H NMR timescale. For example, the ReH resonance of

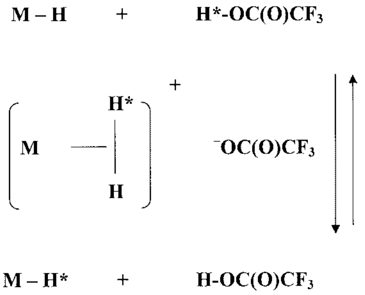


Figure 2. Schematic representation of a proton/hydride exchange occurring via a short-lived dihydrogen complex

[Cp*ReH(CO)(NO)] decoalesces in the presence of acidic alcohols at 96 K giving two resolved lines at –7.54 and –8.87 ppm, assignable to the free and dihydrogen bonded hydride, respectively.[17] A similar difference in the chemical shifts of M–H and M–H···HX has been reported for the [(triphos)Ru(CO)$H_2$]/$(CF_3)_2CHOH$ system in TDF.[18] The difference in the chemical shifts is not as big as in the case of systems with classical hydrogen bonds, possibly due to insignificant electronic perturbations on the target nuclei. However more theoretical investigations of this NMR effect are needed.

According to DFT calculations,[9,10,15] dihydrogen bonding leads to slight elongations of M–H and X–H bonds in proportion to the acidity of the proton donors. For example, the M–H bond length in [M(NO)$(CO)_2(PH_3)_2$H···HX] adducts (M = Mo, W) increases by 0.04 Å. H···H distances in dihydrogen bonded species have been determined as 1.6–2.2 Å by $^1$H $T_1$ relaxation time measurements in solution[5c,5d,16,18] and DFT calculations in the gas phase.[9,10,15] The $H^{\delta+}\cdots{}^{\delta-}H$–M angles have been calculated to be between 130° and 180°. Finally, polyhydride molecules such as [$Cp_2NbH_3$] can form bifurcated dihydrogen bonds[10] where coordination of HX molecules to the central and lateral hydride ligands occurs.

An unusually short H···H distance of 1.43 has been recently reported for the H-bonded complex [CpRu($PP^{Ph}PF$) H···$HO_2CCF_3$] which has been proposed as a new intermediate in proton transfer.[19] The H···H value has been determined by $^1$H $T_1$ time measurements in [D$_6$]acetone. However, the $^1$H and $^{31}$P NMR spectra of the initial hydride [CpRuH($PP^{Ph}PF$)] in the absence and in the presence of the acid were indistinguishable. Therefore, the short $^1$H $T_1$ relaxation times measured for the hydride (RuH) and proton ($CF_3COOH$) resonances (49 ms, 234 K, 300 MHz), are rather due to proton/hydride exchange occurring on the NMR timescale via a short-lived dihydrogen complex (Figure 2). Note that the same relaxation effect has previously been observed in a $CD_2Cl_2$ solution of the dihydride [$ReH_2$(CO)(NO)$(PO\mathit{i}Pr_3)_2$] with $CF_3COOH$ in which the dihydrogen complex was invisible.[20] However, this complex, with a very short $^1$H $T_1$ time (5 ms, 200 MHz, 193 K), can be clearly detected by $^1$H and $^{31}$P NMR spectroscopy in the presence of a twentyfold excess of $CF_3COOH$.

The driving force for the formation of MH···HX bonds is the electrostatic attraction between the electrons of the polar M–H σ-bonds and $H^+$ from the proton donors. As in the case of classical H-bonds, the electrostatic component provides a dominant contribution to the total dihydrogen bonding energy[15,21] which depends on the nature of the transition metal hydrides, acids and solvents used. Enthalpies ($-\Delta H^0$), measured for the formation of MH···HX bonds in solution, vary between 2.0[22] and 7.6 kcal/mol.[5d] The influence of hydrides on dihydrogen bonding can be quantitatively scaled in terms of the basicity factor, $E_j$, determined via Equation (1)

$$E_j = \Delta H_{ij}/\Delta H_{11}P_i \tag{1}$$

where $\Delta H_{ij}$ are bond energies determined by IR spectroscopy, $P_i$ is the proton donor ability of the OH acids and $\Delta H_{11}$ is the enthalpy of the standard H-bonded phenol complex.[5d] On this scale, the $E_j$ factor varies in the range between 0.54 and 1.67. Effects of the metal are expressed, for example, as $E_j$ = 1.09, 1.32 and 1.67 as recently obtained for $PP_3FeH_2$, $PP_3RuH_2$ and $PP_3OsH_2$, respectively.[23]

A good illustration of the solvent influence on dihydrogen bond formation is provided by the $-\Delta H^0$ values of 6.2, 5.8 and 3.1 kcal/mol for the interaction of [$ReH_2$(CO)(NO)$(PMe_3)_2$] with $(CF_3)_3COH$ in $C_7D_{14}$, hexane and [D$_8$]toluene, respectively.[7a,22b,22c] A similar trend was reported for the [CpRuH(CO)$(PCy_3)$]/$(CF_3)_2CHOH$ system showing $-\Delta H^0$ values of 6.3 and 5.1 kcal/mol in hexane and the more polar $CH_2Cl_2$, respectively.[5d,9] The effects of the acidic component are demonstrated by the $-\Delta H^0$ values calculated as 8.4 and 9.7 kcal/mol for the interaction of [CpRu(CO)-$(PH_3)$] with $CF_3COOH$ and $(CF_3)_3COH$, respectively.[9]

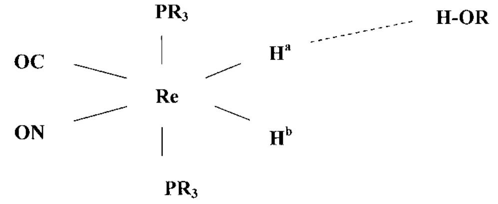
Data on H···H bond formation rates is rather limited since the process is usually too fast for studies by standard kinetic techniques. Nevertheless, some estimations are possible from the low-temperature $^1$H NMR experiments in Freon solutions.[17] As mentioned above, the Re–H signal of [Cp*ReH(CO)(NO)] decoalesces in the presence of acidic alcohols at 94 K. Under these conditions, the life time of the MH···HX complexes, τ, can be calculated via Equation (2)

$$\tau = 1/k_1 = \sqrt{2}/\pi\cdot\Delta\nu \tag{2}$$

where Δν is the chemical shift difference for the free and bonded state expressed in Hz.[24] The calculation gives $\tau \approx 10^{-3}$ s, corresponding to the rate constant, $k_1$, of ca. $10^4$ L/mol·s for concentrations of acidic alcohols of $< 10^{-1}$ mol/L.

## Regioselective Dihydrogen Bonding

The location of the spectroscopically observed MH···HX adducts on the reaction coordinate of the proton transfer process is well supported by the variable-temperature IR and NMR spectra of the hydrides [$RuH_2(dppm)_2$], [MeC$(CH_2PPh_2)_3$Re$(CO)_2$H], [Cp*Ru$(PCy_3)H_3$] and [(Cp-N)RuH$(PPh_3)_2$] in acidic solution in which MH···HX species and dihydrogen complexes $[M(\eta^2\text{-}H_2)]^+$ $[X]^-$ coexist



Scheme 4

in a slow equilibrium.[5d,22a] An additional possibility is that of a regioselective attack on a hydride ligand with the formation of MH···HX bonds, ending in a proton/hydride exchange (see below).

Regioselective dihydrogen bonding has been observed for $[ReH_2(CO)(NO)(PR_3)_2]$ (R = Me, Et) in the presence of $(CF_3)_2CH\text{-}OH$ or $(CF_3)_3COH$ by variable-temperature $^1H$ NMR spectroscopy in $[D_8]$toluene or $[D_{14}]$methylcyclohexane.[22b] A fivefold excess of $(CF_3)_3COH$ causes a high-field shift of the $ReH^a$ resonance (Scheme 4) by 1.24 ppm (193 K) while the $ReH^b$ resonance is shifted by 0.04 ppm only. The same spectroscopic behaviour can be observed for the trihydride $[Cp_2NbH_3]$ upon addition of $(CF_3)_2CH\text{-}OH$. The central hydride ligand acts as a proton acceptor.[10]

Scheme 4 shows the $(CF_3)_3COH$ attack on the $H^a$ ligand located trans to NO in $[Re(CO)H_2(NO)(PR_3)_2]$ ending in the formation of $H\cdots H^a$ bonds with $-\Delta H^0$ values of 6.2 and 3 kcal/mol in $[D_{14}]$methylcyclohexane and $[D_8]$toluene, respectively. In contrast, the weaker proton donor, $(CF_3)_2CH\text{-}OH$, binds to both the hydride ligands. Nevertheless, even in this case, the $H\cdots H^a$ bonds are more preferable: $-\Delta H^0(H\cdots H^a) = 2.1$ kcal/mol and $-\Delta H^0(H\cdots H^b) = 1.7$ kcal/mol. All these effects, not explainable in steric terms, are directly associated with different electronic properties (hydridicity) of the hydride ligands. Finally, it should be pointed out that the oxygen atoms of the NO groups in $[Re(CO)H_2(NO)(PR_3)_2]$ can accept a proton while no Re···H bonds have been found for these hydrides.[22c]

## Contact H-bonded Ion Pairs

Protonation of the heteroatom Y of an organic base consists of a proton shift along a linear H-bond, O–H···Y, with the formation of an intimate ion pair, $O^- \cdots H\text{-}Y^+$, as the product of partial proton transfer. This H-bonded ion pair then converts to a solvent-separated ion pair to finally give free ions when the solvent polarity is sufficient for full proton transfer. In the limits of this concept, proton transfer to hydride ligands can be represented by Figure 3 where the reaction ends with the formation of solvent-separated ion pairs due to the relatively small permittivities of the solvents (THF, toluene, $CH_2Cl_2$) usually applied for protonation of transition metal hydrides.

The best experimental method for observing intimate ion pairs, $M(\eta^2\text{-}H_2)^+ \cdots X^-$, is IR spectroscopy in which the positions of indicator bands (for example, $\nu_{MH}$ or $\nu_{CO}$) attributable to contact ion pairs markedly depend on the nature of the proton donor HX, i.e. on H-bonded anions $X^-$.[5d]

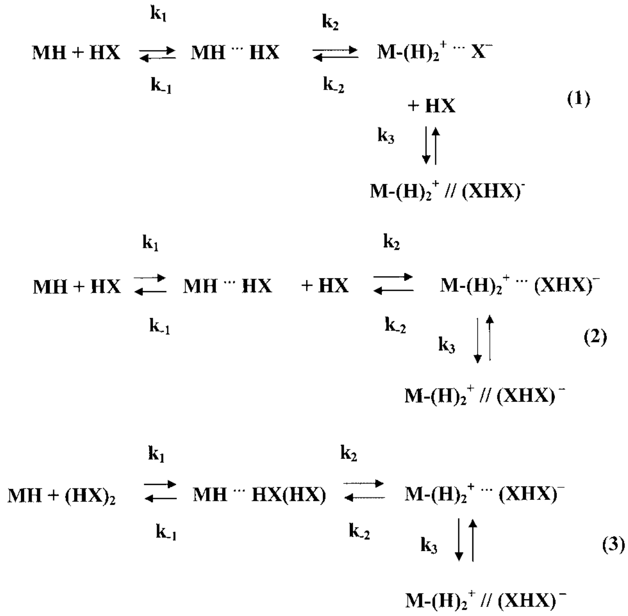


Figure 3. The schemes illustrating proton transfer to a hydride ligand via dihydrogen bonds with participation of two proton donor HX molecules: dimer $(HX)_2$ forms the dihydrogen bond (pathway 3); the second HX molecule initiates the formation of the solvent-separated or contact ion pair [pathway (1) or (2), respectively]

Such pairs have been found in hexane solutions of the hydride $[CpRuH(CO)(PCy_3)]$ protonated with $(CF_3)_2CHOH$, $(CF_3)_3COH$ and $CF_3COOH$, the IR spectra of which have shown $\nu_{CO}$ bands at 1972, 1978 and 2004 $cm^{-1}$, respectively.[9] In addition, the $\nu_{CO}$ frequencies of MH···HX complexes, simultaneously detected in these solutions, also depend reasonably on $X^-$ (1931, 1935 and 1940 $cm^{-1}$) whereas the $\nu_{CO}$ bands of the solvent-separated ion pairs $[CpRu(H_2)(CO)(PCy_3)]^+//CF_3COO^-$ and $[CpRu(H_2)(CO)(PCy_3)]^+//BF_4^-$ cannot be distinguished (2020 $cm^{-1}$, $CH_2Cl_2$).

As expected, increasing the solvent polarity from hexane to $CD_2Cl_2$ should lead to displacement of the positions of the equilibria in Figure 3 towards contact ion pairs due to stabilisation of species with a larger charge separation. In accord with this, the $CH_2Cl_2$ IR spectra of $[CpRuH(CO)(PCy_3)]$ in the presence of $(CF_3)_3COH$ exhibit $\nu_{CO}$ bands belonging only to contact ion pairs. In addition, the $[CpRuH(CO)(PCy_3)]/CF_3COOH$ system can show only intimate ion pairs, only solvent-separated ion pairs or both species simultaneously as a function of the $CF_3COOH$/hydride ratio.[5d,9] Unfortunately, thermodynamic aspects of conversions of H···H complexes to contact ion pairs remain unstudied. However, according to preliminary data,[7c] contact ion pairs are energetically preferable by only 0.2 kcal/mol, for example in $CH_2Cl_2$ solutions of the $[CpRuH(CO)(PCy_3)]/(CF_3)_3COH$ system.

In spite of reliable experiments concerning observations of contact ion pairs, the gas-phase DFT calculations[9,10] of the ion-pair structures $[CpRu(CO)(PH_3)(H_2)]^+ \cdots OC(CF_3)_3^-$ and $[CpRu(CO)(PH_3)(H_2)]^+ \cdots OCOCF_3^-$ or $[Cp_2NbH_2(H_2)]^+ \cdots OC(CF_3)_3^-$ and $[Cp_2NbH_2(H_2)]^+ \cdots OCOCF_3^-$ have

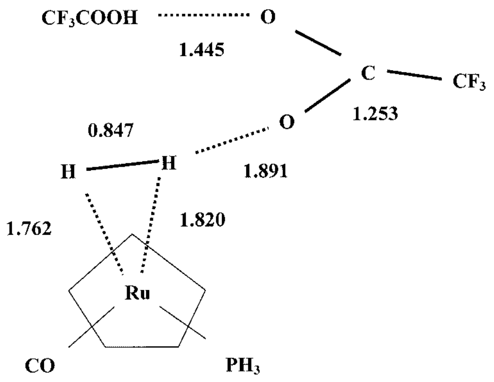


Figure 4. The DFT-optimised geometry of the hydrogen-bonded contact ion pair, $[CpRu(CO)(PH_3)(H_2)]^+\cdots[CF_3C(O)O\cdots H\cdots O(O)CCF_3]^-$ stabilised by the $[CF_3C(O)O\cdots H\cdots O(O)CCF_3]^-$ anion in the gas phase; the distances are given in Å

ended up in the initial dihydrogen-bonded complexes. In addition, the products of full proton transfer, i.e. free ions, were thermodynamically unstable and their energies were higher with respect to the reagents by 100 kcal/mol. Polar solvents could stabilise the charged species. In fact, calculations modelling $CH_2Cl_2$ led to reduced energies of the systems containing free ions. Nevertheless, the products of proton transfer remained 22 kcal/mol above the initial compounds. Again, no energy minima have been located for contact ion pairs. However, these intermediates have been calculated with minimal energies even in the gas phase if homoconjugated anions, $[RO\cdots H\cdots OR]^-$, are taken into consideration as an additional factor for charge stabilisation. Note that this factor has been well demonstrated by kinetic experiments on the protonation of transition metal hydrides in solution.[6] The calculations led to the structures $[CpRu(CO)(PH_3)(H_2)]^+\cdots[RO\cdots H\cdots OR]^-$ and $[Cp_2NbH_2(H_2)]^+\cdots[RO\cdots H\cdots OR]^-$, the optimised geometries of the former are shown in Figure 4. As can be seen, one of the dihydrogen atoms in $[CpRu(CO)(PH_3)(H_2)]^+\cdots[CF_3C(O)O\cdots H\cdots O(O)CCF_3]^-$ acts as a proton donor forming the H-bond with a length of 1.891 Å.[9] The corresponding Ru–H distance (1.820 Å) is slightly longer with respect to the free cationic dihydrogen complex (1.765 and 1.775 Å) while the H···H separations in the $(H_2)$ ligands are very similar in both the species (0.847 Å). Finally the H–O bond in the ion pair involved into H-bonding is significantly elongated with respect to that in the free proton donor (1.253 Å and 0.98 Å, respectively).

Hartree–Fock calculations of the dihydrogen-bonded $Li{-}H^{\delta-}\cdots{}^{\delta+}H{-}F$ complex have shown that an electric field, applied along the molecular axis, leads to transfer of H atoms between two heavy atoms to give the dihydrogen $Li^+\cdots H{-}H\cdots F^-$ system.[25] Thus the transformation of the M–H···HX species to contact ion pairs can be interpreted as movement of two hydrogen atoms, under the field due to the charges, towards the state with a larger charge separation if the latter can be stabilised by a polar solvent and/or by homoconjugated anions. In contrast to proton transfer to usual organic bases, these movements require strong electronic perturbations. A priori, this circumstance should lead to significant energy barriers, separating dihydrogen-bonded complexes and contact ion pairs.

## 3. Kinetic Experiments

Table 1 lists kinetic data for the protonation of transition metal hydrides, obtained by the spectroscopic (NMR, UV, IR) and electrochemical methods with the application of usual or stopped-flow mixing techniques. The kinetic experiments have mostly been performed under pseudofirst-order conditions in which acids have been added in large excess.[11,26a–26d] The $[ReH_2(NO)(CO)(PR_3)_2]/CF_3COOH$ systems have been studied with comparable concentrations of the reagents.[26e] In all cases, the overall kinetic order has been found to be close to 2.

The data in Table 1 illustrate the dependences of the rate constants on the nature of the acid used. For example, the rate of proton transfer to [Cp*Fe(dppe)H] strongly increases with the acidity of the proton donor as $CF_3CH_2OH < (CF_3)_2CHOH < (CF_3)_3COH < CF_3COOH$.[26d] At the same time, the *cis*-hydride $[FeH_2PPh_3]$ shows very insignificant changes in the k values in the order $CF_3COOH < HCl < HBr$.[11] In addition, the rate constants are smaller for the stronger acids $HBF_4$ and $CF_3SO_3H$. The same effect has been reported for $[RuH_2(dppe)_2]$[26a] and $[ReH_2(NO)(CO)(PMe_3)_2]$ protonated with $CF_3COOH$ and $[\{3,5\text{-}(CF_3)_2C_6H_3\}_4B]^-[H(OEt_2)]^+$.[26e] Thus, in common cases, the rate of proton transfer and the acid strength do not correlate. This result can be explained by the relatively small permittivities of the solvents (THF, toluene, $CH_2Cl_2$) where even strong acids exist in an equilibrium between molecular forms, ion pairs and free ions (Scheme 5). If free $H^+$ attacks a hydride, then proton transfer should be suppressed by the addition of $X^-$ ions. However, $NBu_4BF_4$ does not affect protonation rates of *cis*-$[FeH_2PPh_3]$ by the action of $HBF_4$ in THF. This is good evidence for the parallel attack of the molecular form HX and the ion pair where ion pairs react slower than HX.[11]

Kinetic experiments on the acids HX and DX, carried out under pseudofirst-order conditions, have revealed inverse kinetic isotope effects, $k_H/k_D$ (Table 2). The results can be interpreted either as the kinetic effects measured for a single-step proton transfer or as the inverse thermodynamic isotope effects in fast preequilibria.[11] In contrast to the effects on usual H-bonds,[27] the effects of deuterium on the thermodynamics of dihydrogen bonding are unknown. On the other hand, under pseudofirst-order conditions, the position of the kinetic preequilibrium should be completely shifted towards the dihydrogen bonds. Therefore, the hypothesis of a single-step proton transfer via a late transition state could be successful for interpreting the observed isotopic effects. A structure, similar to that of the contact ion pairs in Figure 4 with almost complete formation of new bonds, could represent such a transition state. The $k_H/k_D$ values can then be calculated by Equation (3),[11] where $\nu_i(H)$ and $\nu_i^{\neq}(H)$ are the stretching frequencies in the

Table 1. The second-order rate constants ($k$, 25 °C) for protonation of transition metal hydrides with formations of dihydrogen complexes in solution

| Complex | HX | $k$ L/mol·s | Solvent | Ref. |
|---|---|---|---|---|
| $[FeH_2PPh_3]$ | $HBF_4$ | $1.7\times 10^{-4}$ | THF | [11] |
| | $CF_3COOH$ | $0.112 \times 10^{-2}$ | | |
| | $CF_3SO_3H$ | $0.176 \times 10^{-2}$ | | |
| | HCl | $1.32 \times 10^{-2}$ | | |
| | HBr | $3.4 \times 10^{-2}$ | | |
| $[FeH_2(dppe)_2]$ | $HBF_4$ | $9.7 \times 10^{-3}$ | THF | [26b] |
| | $CF_3COOH$ | $1.39 \times 10^{-2}$ | | |
| | $CF_3SO_3H$ | $2.1 \times 10^{-2}$ | | |
| | HCl | $4.8 \times 10^{-2}$ | | |
| $[CpW(CO)_2(PMe_3)H]$ | $[Me_2NHC_6H_4C(Me_3)]^+[BF_4]^-$ | $2.7 \times 10^{-3}$ (a) | $CD_2Cl_2$ | [6] |
| $[CpRuH(dppm)]$ | $HBF_4$ | $1.86 \times 10^{2}$ | THF | [26c] |
| $[CpRuH(dppe)]$ | $HBF_4$ | $0.70 \times 10^{2}$ | THF | [26c] |
| $[CpRuH(PPh_3)_2]$ | $HBF_4$ | $1.69 \times 10^{2}$ | THF | [26c] |
| $[RuH_2(dppe)_2]$ | $HBF_4$ | $1.1 \times 10^{3}$ | THF | [26a] |
| | $CF_3COOH$ | $9.2 \times 10^{4}$ | | |
| | HCl | $1.7\ 10^{6}$ | | |
| $[ReH_2(NO)(CO)(PiPr_3)_2]$ | $CF_3COOH$ | $4.4 \times 10^{2}$ (b) | $CD_2Cl_2$ | [26e] |
| $[ReH_2(NO)(CO)(PMe_3)_2]$ | $CF_3COOH$ | $192 \times 10^{2}$ (c) | $CD_2Cl_2$ | [26e] |
| $[Cp^*Fe(dppe)H]$ | $CF_3COOH$ | very fast | $CH_2Cl_2$ | [26d] |
| | PFTB | $1.56 \times 10^{2}$ | $CH_2Cl_2$ | |
| | HFIP | 5.4 | $CH_2Cl_2$ | |
| | $CF_3CH_2OH$ | $1.5 \times 10^{-3}$ | $CH_2Cl_2$ | |

[a] At –10 °C. [b] At –80 °C. [c] At –90 °C.

$$\mathbf{H\text{-}X} \rightleftarrows \mathbf{H^+/X^-} \rightleftarrows \mathbf{H^+ + X^-}$$

Scheme 5

Table 2. Kinetic isotope effects [$k$(H)/$k$(D)] measured for protonation of transition metal hydrides in solution

| Complex | HX | Solvent | $k$(H)/$k$(D) ($T$ °C) | $k$(H)/$k$(D) calcd. | Ref. |
|---|---|---|---|---|---|
| $[FeH_2(dppe)_2]$ | $CF_3SO_3H$ | THF | 0.21 (25) | 0.87 | [26b] |
| | HCl | | 0.36 (25) | 0.47 | |
| | HBr | | 0.55 (25) | 0.39 | |
| $[FeH_2PPh_3]$ | $CF_3SO_3H$ | THF | 0.45 (25) | 0.87 | [11] |
| | HCl | | 0.62 (25) | 0.47 | |
| | HBr | | 0.64 (25) | 0.39 | |
| $[RuH_2(dppe)_2]$ | $CF_3COOH$ | THF | 0.80 (25) | 0.87 | [26a] |
| | HCl | | 0.38 (25) | 0.47 | |
| $[ReH_2(NO)(CO)(PiPr_3)_2]$ | $CF_3COOH$ | $CD_2Cl_2$ | 1.4 (–80) | 0.87 | [26e] |

fundamental and transition states, respectively. As can be seen, Table 2 shows good agreements between the theoretical and experimental $k_H/k_D$ values.

$$k(H)/k(D) = \exp\{7.06\ 10^{-4}[\Sigma_i \nu_i(H) - \Sigma_i \nu_i^{\neq}(H)]\} \tag{3}$$

As in the case of classical organic bases, proton transfer to a hydride ligand is not a single-step process and occurs via dihydrogen-bonded intermediates. It follows from the previous section that the factor of the basicity, $E_j$, characterising the formation of H···H bonds, changes from 0.54 to 1.67. The effects of solvents on dihydrogen bonding are also insignificant. Thus dihydrogen bonding is a weak preorganising interaction which cannot be responsible for very big variations in rate constants of proton transfers (Table 1). For example, the $k$ constant, measured for proton transfer from $CF_3COOH$ to $[FeH_2PPh_3]$, $[ReH_2(NO)(CO)(PMe_3)_2]$ and $[RuH_2(dppe)_2]$, increases by six orders from $0.112\ 10^{-2}$ (25 °C) to $192\ 10^{2}$ (–90 °C) to $9.2\ 10^{4}$ (25 °C) 1/mol.

IR monitoring of the $[CpRuH(CO)(PCy_3)]/(CF_3)_3COH$ (1:2) system has directly shown a slow (≈30 min) conversion of H···H complexes to intimate H-bonded ion pairs in nonpolar hexane.[9] The $^1H$ NMR spectra, recorded for the same hydride in the presence of 12 and 100 equivalents of $(CF_3)_3COH$ in $CDClF_2/CDF_3$ (2:1),[7c] support this observation. It is important to emphasise that the formation of H···H bonds is very fast on the NMR timescale even at 120 K. In contrast, the hydride signal, averaged between the intimate and solvent-separated ion pairs, is strongly broadened at 120 K, indicating retardation of ionpair transformations on the NMR timescale.

The schemes in Figure 3 represent proton transfers to hydride ligands with the participation of two proton donor molecules, emphasising the role of homoconjugated $[X\cdots H\cdots X]^-$ species in the kinetics of the process. Note that the second HX molecule initiates the formation of the solvent-separated or contact ion pair, corresponding to pathway (1) or (2).

Formally pathway (1) can be expressed via Equation (4). Since the formation of contact ion pairs is rate-determining (i.e. $k_2 << k_{-1}$ and $k_3[HX] >> k_{-2}$), the equation becomes

Table 3. Activation parameters for proton transfer to hydride ligands in solution

| System | $\Delta H^{\neq}$ kcal/mol | $\Delta S^{\neq}$ e.u. | Solvent | Ref. |
|---|---|---|---|---|
| $CpRuH(CO)(PCy_3)$/PFTB (1:2) | 11.0 | –19 | hexane | [9] |
| $ReH_2(NO)(CO)(PiPr_3)_2$/ $CF_3COOH$ (1:1) | 11.1 | 12.0 | $CD_2Cl_2$ | [26e] |
| $ReH_2(NO)(CO)(PMe_3)_2$/ $CF_3COOH$ (1:1) | 13.5 | 36.8 | $CD_2Cl_2$ | [26e] |
| $ReD(PMe_3)_4(CO)$/ $CF_3COOD$ (1:1) | 14.4 | 14.8 | $CH_2Cl_2$ | [26e] |

Equation (5) and thus the reaction represents a first-order process with respect to the acid. It is easy to show that under the pseudofirst-order conditions (when the preequilibrium is shifted completely to H···H complexes) the measured rates become independent of HX concentration.

$$d[MH]/dt = -\{k_1k_2k_3[MH][HX]^2\}/\{k_{-1}k_{-2} + k_{-1}k_3[HX]\} + k_2k_3[HX] \quad (4)$$

$$d[MH]/dt = -(k_1/k_{-1})\cdot k_2[MH][HX] \quad (5)$$

Experimentally, this pathway has been well established from the IR spectra of the $[CpRuH(CO)(PCy_3)]/(CF_3)_3OH$ system in $CH_2Cl_2$ in which large variations in hydride/alcohol ratios did not affect a slow transformation of H···H complexes to H-bonded ion pairs with $k$ values between 1.4 $10^{-3}$ and 1.6 $10^{-3}$ $s^{-1}$.[7a] Activation parameters for this step (Table 3) have been determined in hexane.[9] It is probable that such a mechanism operates for the protonation of the hydrides $[ReH_2(NO)(CO)(PR_3)_2]$ with $CF_3COOH$ (Table 3) in $CD_2Cl_2$ where the reaction corresponds to first order kinetics on the acid at hydride/acid ratios ≥ 1.[26e]

In contrast, UV monitoring of the hydride [Cp*Fe(dppe)-H] protonated with a 30–200 fold excess of $(CF_3)_3COH$ or $(CF_3)_2CHOH$ ($CH_2Cl_2$) (pseudofirst-order conditions) led to the first-order dependence of the measured rates on the alcohol concentration.[26d] In the framework of pathway (1) the result can be interpreted according to Equation (6) obtained from equation (5) by assuming $k_3[HX] << k_{-2}$. It is clear that under the pseudofirst-order kinetic measurement conditions, this equation will show a first order dependence on the acid concentration.

$$d[MH]/dt = -(k_1/k_{-1})(k_2/k_{-2})k_3[MH][HX]^2 \quad (6)$$

On the other hand, the above data can be rationalised in the context of pathway (2) where a slow transformation of the H···H complexes to contact ion pairs is accompanied by the second HX molecule [Equation (7)].

$$d[MH]/dt = -\{k_1k_2k_3[MH][HX]^2\}/\{k_{-1}k_{-2} + k_{-1}k_3 + k_2k_3[HX]\} \quad (7)$$

Then, at $k_2$ [HX] << $k_{-1}$, Equation (7) converts to Equation (8).

$$d[MH]/dt = -\{k_1k_2k_3[MH][HX]^2\}/k_{-1}(k_{-2} + k_3) \quad (8)$$

The latter will correspond to the first-order process under the pseudofirst-order kinetic measurement conditions. Finally, the gas-phase and solution DFT calculations have revealed that proton transfer in the $[CpRu(CO)(PH_3)H]/CF_3COOH$ system is energetically preferable if the second HX molecule participates in each step of the process.[9] When the acid is initially a dimer, this situation corresponds, in kinetic terms, to Equation (9) [$(HX)_2$ = DM] showing first order kinetics for the DM acid.

$$d[MH]/dt = -k_1k_2k_3[MH][DM]/\{k_{-1}k_{-2} + k_{-1}k_3 + k_2k_3\} \quad (9)$$

To account for the dimerisation of $CF_3COOH$,[28] this scheme cannot be excluded when interpreting the kinetic data collected for the $[ReH_2(NO)(CO)(PR_3)_2]/CF_3COOH$ (1:1) system in $CD_2Cl_2$.[26e] It is clear that only detailed kinetic measurements for large variations in reagent concentrations can distinguish pathways 1–3. For obvious reasons, such experiments are often impossible. However, on the basis of the data presented in this section, pathway (1) can be taken as a general mechanism of proton transfer.

## 4. Proton/ HydrideExchange as a Measure of Proton Transfer

Intra- and intermolecular positional exchanges with the participation of hydride ligands are widely known.[6,29] Proton/hydride exchanges similar to those in Figure 2 are manifested in the $^1H$ NMR spectra as broadenings and coalescences of the hydride and HX resonances upon heating and can be quantitatively characterised with the help of a lineshape analysis or saturation transfer experiments.[24] As in the case of proton transfer, the exchange rates in Table 4 strongly depend on the nature of the hydrides and are sensitive to isotope displacements. The overall kinetic order of the exchanges is also equal to 2[6,26e] in agreement with almost negative activation entropies. The nature of the acids also has a significant influence on exchange rates: the exchange is faster when the anion of HX is capable of assistance.[26e]

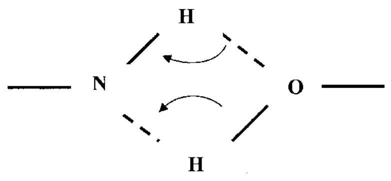
According to the $^1H$ NMR spectroscopic data collected for an isomeric mixture of the hydride $[CpW(CO)_2(PMe_3)$-H] in the presence of $[PhNH_3(OEt_2)]^+{}_{1-2}[B(Ar^f)_4]^-$, the proton/hydride exchange is fast only for the *trans* isomer.[6] It is obvious that this selective proton/hydride exchange is a good test for a proton attack on the hydride ligand.

The exchanges are highly regioselective in $[D_8]$toluene solutions of the $[ReH_2(NO)(CO)(PR_3)_2]/CF_3COOH$ system where only the H ligands, located *trans* to NO, are involved in the exchange (Table 4).[26e] Since this effect correlates

Table 4. Kinetic parameters of proton/hydride exchanges, determined by $^{1}H$ NMR in solution[6,26e]

| System | $k$(exch) ($T$, °C) (L/mol·s) | $\Delta H^{\neq}$ (kcal/mol) | $\Delta S^{\neq}$ e.u. | Solvent |
|---|---|---|---|---|
| $[CpW(CO)_2(PMe_3)H]/[(CH_3)_3C_6H_4N(CH_3)_2D]^+$ | $1.8 \times 10^{-4}$ (–10) | 10.7 | –35.2 | $CD_2Cl_2$ |
| $[CpW(CO)_2(PMe_3)D]/[(CH_3)_3C_6H_4N(CH_3)_2H]^+$ | $8.9 \times 10^{-4}$ (–10) | 11.2 | –30.2 | $CD_2Cl_2$ |
| $[ReH_2(NO)(CO)(PiPr_3)_2]/CF_3COOH$ | $33.7 \times 10^{2}$ (–70)[a] | 7.7 | –2.3 | $[D_8]$toluene |
| $[ReD_2(NO)(CO)(PiPr_3)_3]/CF_3COOD$ | $16.0 \times 10^{2}$ (–70)[a] | – | – | toluene |
| $[ReH_2(NO)(CO)(POiPr_3)_2]/CF_3COOH$ | $20.7 \times 10^{2}$ (–66) [a,b] | 7.4 | –5.5 | $CD_2Cl_2$ |
| $[ReD_2(NO)(CO)(POiPr_3)_2]/CF_3COOD$ | $4.6 \times 10^{2}$ (–70)[a] | 7.1 | –10.3 | toluene |
| $[ReD_2(NO)(CO)(POiPr_3)_2]/CF_3COOD$ | $3.6 \times 10^{2}$ (–70)[a] | 6.0 | –16.6 | $CD_2Cl_2$/toluene (1:1) |
| | $0.93 \times 10^{2}$ (–60)[b] | 7.7 | –13.9 | $CD_2Cl_2$/toluene (1:1) |
| $[ReH_2(NO)(CO)(PMe_3)_2]/CF_3COOH$ | $250 \times 10^{2}$ (–73)[a] | 7.8 | 0 | $[D_8]$toluene |
| $[ReD(PMe_3)_4(CO)]/CF_3COOD$ (1:1) | $0.92 \times 10^{2}$ (–60) | 6.3 | –19.2 | $CH_2Cl_2$ |

[a] *trans* to the NO group. [b] *cis* to the NO group.



Scheme 6

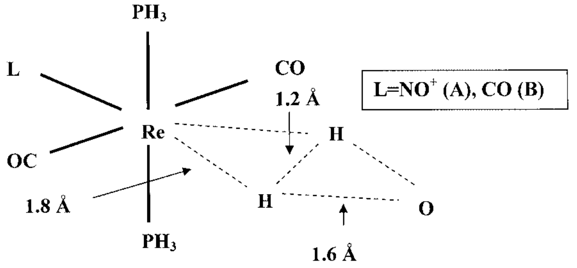


Figure 5. The models of the transition states **A** and **B**, suitable for proton/hydride exchange processes, obtained by EHT calculations on the basis of symmetrical pseudooctahedral geometry ($H^+$ and $O^{2-}$ represent the acid)[26e]

with the regioselective dihydrogen bonding and Re···HOR bonds are not observed, the dihydrogen-bonded adducts can be taken as a starting point for the proton/hydride exchange process.

A priori, a hydride atom and an acidic proton can exchange their positions if both H atoms are bound to a metal centre in a transition state or an intermediate. It is clear that the solvent-separated ion pairs, $M(H_2)^+//X^-$, could play the roles of such states. Experimentally this statement can be supported by the equal rates measured for the proton/hydride exchange and the formation of dihydrogen complexes. This case is documented for the $[ReH_2(NO)(CO)(PiPr_3)_2]/CF_3COOH$ system in the relatively polar $CD_2Cl_2$:[26e] a line-shape analysis of the hydride resonances (a test for the exchange) and the $^{31}P$ NMR signals of $[ReH_2(NO)(CO)(PiPr_3)_2]$ and $[ReH(H_2)(NO)(CO)(PiPr_3)_2]^+$ $[CF_3COO]^-$ (a test for the formation of dihydrogen complexes) gave very similar rate constants (15–20 $10^2$ L/mol·s, –70 °C). In is clear that under these conditions, the proton/hydride exchange is a good probe for full proton transfer to a hydride ligand.

However, as in the case of usual organic bases, the situation can change. In fact, proton exchanges in organic acid/base pairs can occur without charge separation via the cyclic nonpolar transition states in Scheme 6 where N-H is a base and H-O is an acid. As a result, for example, the dihydrogen complexes $[ReH(H_2)(CO)(NO)(PR_3)_2]^+$ $[CF_3COO]^-$ are formed *slowly* in nonpolar toluene on the $^{31}P$ NMR timescale while *fast* proton/hydride exchanges still occur on the $^{1}H$ NMR timescale.[26e] The same effect can be observed in a $CH_2Cl_2$ solution of $[ReD(PMe_3)_4(CO)]$ and $CF_3COOD$. As follows from Table 4, the activation energies $\Delta H^{\ddagger}$ necessary for the exchanges are remarkably smaller than those for the formation of dihydrogen complexes (Table 3). In contrast, the isotopic effect $k_H/k_D$ for the exchange is larger. It becomes obvious, that in spite of the same starting point (dihydrogen bonded complexes), both processes occur via different transition states and thus such a type of exchange is not a measure of proton transfer and only accompanies the latter. Structures **A** and **B** in Figure 5 could be models of exchange transition states for the Re hydrides, where $H^+$ and $O^{2-}$ represent the acid.[26e] The structures obtained by EHT calculations are not optimised but they do exhibit feasible features for the orbital interactions and explain the selectivity of the exchanges. For example, state **A** with a *trans* NO has a reasonable HOMO/LUMO gap (≈2.5 eV) and crucial participation of the oxygen orbitals in the binding of the $H_2$ unit to the metal centre. The orbital interactions are built up from $d_{XY}$ and σ-type functions on the Re centre by the two $s_H$ hydrogen orbitals and $s$, $p_X$ and $p_Y$ orbitals from the oxygen atom. Thus the appearance of H···H bonding is a main feature of the exchange transition state with participation of hydride ligands in contrast to the transition state in Scheme 6 which is typical of usual organic bases.

## 5. Energy Profile of Proton Transfer to Hydride Ligands

The discussed spectroscopic, kinetic and thermodynamic data are quite sufficient to describe, semiquantitatively, the energy profile of proton transfer to a hydride ligand in solution.[5c,5d,30] Figure 6 shows the energy as a function of the proton–hydride distance varying from an initial state to a

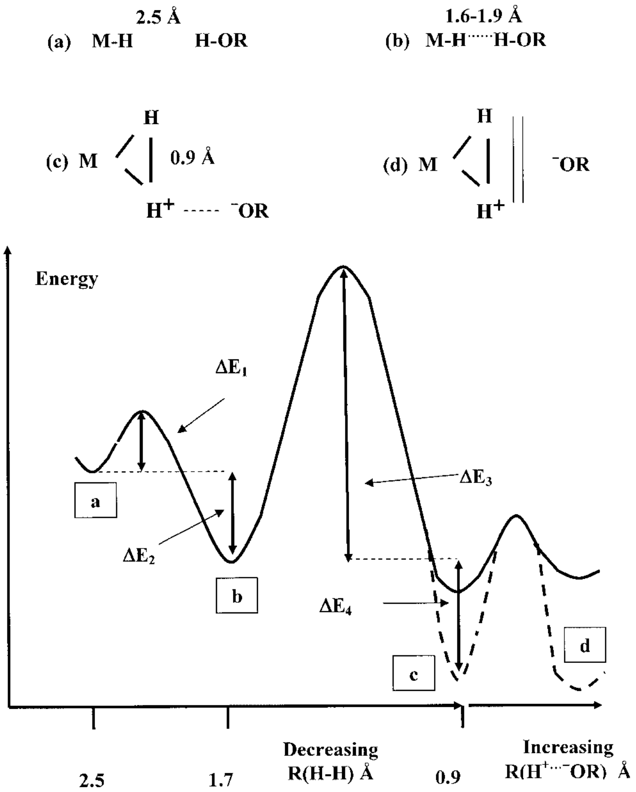


Figure 6. Energy profiles of proton transfer to a hydride ligand of a transition metal complex in solution: $\Delta E_1$ = +3–4 kcal/mol, $\Delta E_2$ = –5 to –7 kcal/mol, $\Delta E_3$ = +10–14 kcal/mol and $\Delta E_4$ = –7 kcal/mol, respectively; the energy is a function of the proton–hydride distance varying from an initial state (2.5 Å) to the final product (0.9 Å); conversion of the intimate ion pair to the solvent/separated ion pair is shown as a function of the $H^+\cdots O^-$ distance

final product. The averaged structural parameters of the initial hydrides and intermediates have been taken from the experimental measurements and DFT calculations. Since proton-hydride contacts of $\leq$ 2.4 Å, found for different compounds in the solid state, correspond to the appearance of weak bonding interactions,[13b] the H···H distance of 2.5 can be regarded as the starting point with zero energy. The proton transfer process ends with a structure in which the $H^{\delta+}\cdots{}^{\delta-}H$ distance becomes 0.9 Å, a typical value for dihydrogen ligands.[3]

The pattern in Figure 6 contains four energy minima occupied by the initial hydride, the dihydrogen-bonded complex, the intimate ion pair and the solvent-separated ion pair as a final product of the reaction. For simplicity, homoconjugated species, $[RO\cdots H\cdots OR]^-$, assisting proton transfer and stabilising the protonated products can be ruled out.

Usually, the formation of the H-bonded complexes is regarded as a very fast and diffusion-controlled process with no energy barrier.[5d] On the other hand, even ultra fast molecular reorientations in solution require energy for reorganisation of molecular environments. Since transition metal complexes reorient in solutions with energies of 3.0–4.5 kcal/mol, this magnitude can be taken as a reasonable first barrier, separating the free hydride molecules and the H···H complexes. Dihydrogen bonding results in systems with H···H separations between 1.6 and 1.9 Å. The energy of these systems is reduced by 2.0–7.6 kcal/mol. Note that the latter remarkably depends on the nature of hydrides and acids while the solvent influence is insignificant. The M–H and H–O bonds in the dihydrogen bonded adduct are only slightly elongated with respect to the initial hydride and the acid. The electronic perturbations are minimal and do not require significant energies. The next energy minimum is populated by contact ion pairs and stabilised by H-bonds with anions. This intermediate has the H···H separation very close to that in the dihydrogen complex and its H···O bond is strongly elongated. In spite of the significant structural changes, the depths of the energy minima occupied by dihydrogen- bonded complexes and contact ion pairs are very similar. Since the ion pair species were not localised in the gas-phase DFT calculations, the effect is certainly consistent with their stabilisation by polar solvents or homoconjugated anions $[RO\cdots H\cdots OR]^-$.

As in the case of classical acid/base pairs, the formation of contact ion pairs $M(H_2)^+\cdots X^-$ is the step of proton transfer. However, for transition metal hydrides this step requires significant changes in the M–H–H–X geometry and the H···H and X–H bond lengths. For this reason, the energy barrier separating the M–H···H–X and $M(H_2)^+\cdots X^-$ species increases to 11–13 kcal/mol (Table 3) in very good agreements with the DFT calculations[9] modelling proton transfer in the $[CpRuH(CO)PH_3]/CF_3COOH$ and $[CpRuH(CO)PH_3]/(CF_3)_3COH$ systems (heptane, $CH_2Cl_2$). Note that this step is responsible for the total kinetics of proton transfer and the large variation in the *k* constants in Table 1. The solvent-separated ion pair finishes the process with enthalpy changes between –2.4 and –9 kcal/mol.[7,5d,30] The NMR experiments on the $[CpRuH(CO)(PCy_3)]/(CF_3)_3COH$ system in $CDClF_2/CDF_3$ (2:1)[17] showed a low energy barrier separating the contact and solvent-separated ion pairs. Therefore, in the absence of quantitative kinetic data on the last step, the barrier between $M(H_2)^+\cdots X^-$ and $M(H_2)^+//X^-$ can be taken to be small.

## 6. Conclusion

The concept of hydrogen bonding, known since the beginning of the 20 century, has played a very important role in the understanding of the nature and properties of chemical compounds. The problem of dihydrogen bonding, as an interaction between oppositely charged hydrogen atoms, is significantly younger.[12a,13c,31] In spite of this, its fundamental significance in catalysis, bio-organic and supramolecular chemistry has been well recognised.

This microreview, ignoring details of hydride chemistry and focusing on key physicochemical data, discusses possible kinetic schemes for the protonation process and formulates a general mechanism whereby dihydrogen bonding is the preorganising interaction in proton transfer and proton/hydride exchanges. Protonation of hydride ligands occurs via intermediates, H···H complexes and H-bonded contact ion pairs, and ends in dihydrogen complexes as solvent-separated ion pairs or free ions. General rules governing proton transfer to hydride ligands and conventional organic bases are very similar. The difference between the two is quantitative rather than qualitative in character and is apparent in the contact ion pair formation step. In the case of transition metal hydrides, this step, which determines the kinetics of the process, requires significantly larger activation energies and for this reason the total rate of proton transfer is remarkably slower.

In spite of the numerous studies considered in this article, some important mechanistic details of proton transfer are still unclear and could be the subject of further investigations, one of these being the regularity governing the participation of homoconjugated $[X\cdots H\cdots X]^-$ species. For example, it remains uncertain as to which intermediate step needs such $[X\cdots H\cdots X]^-$ assistance for dictating the total kinetic order of the process. Thermodynamic aspects of conversions of $H\cdots H$ complexes to contact ion pairs are also practically unstudied. To answer these fundamental questions, additional experimental and theoretical investigations are needed. Among various experimental approaches, NMR experiments at extremely low temperatures[8] seem to be very appropriate.

As in the case of conventional organic bases, proton/hydride exchanges in transition metal hydrides can be considered as a probe for full proton transfer. In this context, further theoretical work investigating models of transition states for both processes will be most interesting.

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