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Diverse World of Unconventional Hydrogen Bonds

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ABSTRACT

This Account presents our view of unconventional intermolecular hydrogen bonds (HBs) for organometallic complexes and transition-metal or main-group hydrides. Over the past decade, low-temperature spectroscopic (IR, UV, and NMR) studies combined with theoretical calculations have disclosed the static and dynamic features of different HBs. Their guiding role in the proton-transfer processes was determined, as well as the energetic characteristics of HB intermediates and the activation barriers. Nevertheless, there is still much to explore in terms of the prediction of HB properties and control of protonation/deprotonation processes.

Introduction

The importance of hydrogen bonds (HBs) in many physical, chemical, and biological structures and processes can scarcely be exaggerated. Over the years, the hydrogen-bond concept evolved via not only an elucidation of the nature but also an extension of the range of hydrogen-bonding partners.[1] Thus, for a hydrogen bond $X^\delta-H^{\delta+}\cdots B$, the classical row of electronegative elements X (e.g., N, O, and F) has been broadened by the elements of periods III–IV (P, S, Cl, etc.). The same elements bearing lone electron pairs, as well as the π electrons of multiple bonds or arene rings, have been shown to be proton-accepting sites B. Discovery of unconventional basic centers specific for organometallic complexes has

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Lina Epstein received her Ph.D. degree at MSU (1967) and D.Sc. degree at INEOS (1985). She organized the Moscow Colloquium on Hydrogen Bonding (1975). In 1985–2000, she was Head of the Spectral Group in the lab of A. N. Nesmeyanov at INEOS. This group evolved into the Laboratory of Metal Hydrides at INEOS, where Professor Epstein is now leading researcher. Her research interests include structure/properties relationships for organometallic compounds, intermolecular interactions, especially hydrogen bonds and proton transfer, molecular spectroscopy, and theoretical studies.

opened a new page in the hydrogen-bond concept. Their fundamental and practical (catalysis, new materials) importance elicited studies from several research groups including our own. As the result, we are beginning to understand the organometallic HBs involved in proton-transfer processes.[2]

Our main interest in this area is in spectroscopic and theoretical studies of intermolecular interactions involving organometallic compounds. In this Account, we will describe the peculiarities of these unconventional HBs in comparison with the classical ones, discuss their structures and spectroscopic manifestations, and show recent developments in the field, especially the studies of the mechanism of proton transfer to organometallic hydrides.

Organometallic Compounds as Proton Acceptors in HBs

Three large classes of transition-metal or main-group compounds can serve as proton acceptors.

1. Complexes of Transition Metals. Complexes of transition metals have one unconventional basic site, the d electrons of a transition metal, that yields $XH^{\delta+}\cdots ML_n$ bonds. This class includes sandwich (Cp_2M, $Cp*_2M$) and semi-sandwich ($CpML_n$, $Cp*ML_n$, where L = CO, NO, Hal, N_2, PR_3, etc.) complexes of Group VI–VIII transition metals, as well as the coordination compounds (ML_n-(phosphine)$_m$). The ligands present in these complexes can also form HBs, but they do not differ much from classical $X^\delta-H^{\delta+}\cdots B$ bonds.

Thorough spectroscopic studies of $XH^{\delta+}\cdots M$ bonds in the traditional solvents of low polarity by our group have allowed us to determine their thermodynamics and to find some common features for $XH\cdots M$ and classical HBs.[3] The interesting investigations by Kazarian and Poliakoff in supercritical media have led to similar conclusions.[4] Studies of ionic hydrogen bonds ($M^-\cdots^+HN$) in the crystalline state and in solution have allowed Brammer and Crabtree to find the criteria by which HBs to a metal atom can be identified and distinguished from agostic interactions.[2c,5] A comparative theoretical study of the ionic and neutral systems is presented in ref 6.

2. Transition-Metal Hydride Complexes. Transition-metal hydride complexes have two unconventional basic sites: metal and hydride ligand. The last is unusual in possessing no lone pairs or π electrons but some negative charge at the hydride atom. The discovery that a hydride ligand can be an intermolecular hydrogen-bond acceptor $X-H^{\delta+}\cdots^{-\delta}HML_n$ in the solid state[7,8] and in solution[2b] has produced widespread interest. The term "dihydrogen bond" (DHB) is widely used now for this type of interaction.[2] The thermodynamic properties of such bonds in solution have been determined by low-temperature IR and NMR studies for many systems such as $CpMHL_n$, $Cp*MHL_n$, and MH_nL_m, where L = CO, NO, Hal, or a mono- or polydentate phosphine.[9–17] A family of ionic DHBs be-
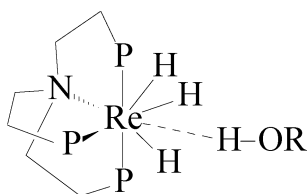
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Scheme 1
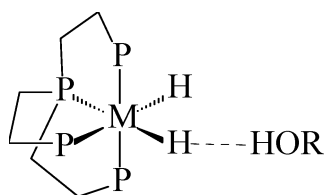
M = Fe, Ru, Os

I

II

tween the NH$^+$ groups of aza-crown ethers and the hydride ligands of polyhydride anions has been studied by Morris et al.[20] Some hydrides[18,19] of electron-rich transition metals do not form XH···HM but form XH···M hydrogen bonds (compare structures **I** and **II**, Scheme 1).

3. Main-Group Hydride Complexes. Main-group hydride complexes have only one unconventional basic site, hydride ligand. The formation of EH$^{\delta-}$···$^{\delta+}$HX bonds, which are DHBs as well, was found for the first time with boron hydrides.[8,21–23] Recently, some theoretical calculations for DHBs with other main-group hydrides and structural investigations of their crystalline state have been published.[2b,e] The spectral and thermodynamic characteristics of these bonds have been determined in our investigations of a series of boron hydrides and GaH$_4^-$ in solution.[23]

Organometallic Hydrides as Proton Donors in HBs

Many neutral hydrides are known to be strong acids. Therefore, it was supposed that a molecular MH$^{\delta+}$···B hydrogen bond between M–H bonds of neutral transition-metal hydrides and neutral bases (B) could be formed, as a HB of X–H acids. In this case, repolarization of a M–H bond (M–H$^{\delta+}$ instead of M–H$^{\delta-}$) could occur at the stage of HB formation. However, when Norton et al. studied the interaction between HCo(CO)$_4$ (a rather strong acid) and a series of bases, they found no evidence for such HB.[24]

Nevertheless, a cationic hydride, as we found, can be a proton donor in an ionic ([MH]$^+$···X$^-$) or ion-molecular ([MH]$^+$···B) hydrogen bond.[25–26] In these cases, some positive charge is more easily placed on the metal-bound hydrogen atom. The ionic HB was established for [Cp*$_2$-OsH]$^+$ and [WH$_5$(dppe)$_2$]$^+$ as proton donors and CF$_3$COO$^-$ as a base. The ion-molecular ([MH]$^+$···B) interaction was found with phosphine oxides as B; they are excellent proton acceptors, which combine great ability to form hydrogen bonds with weak basicity. Subsequently, IR

studies (in the ν_{MH} and ν_{PO} regions) of [IrH$_2$(PPh$_3$)$_2$L$_2$]BF$_4$ and PPh$_3$PO in the solid state were performed by Peris and Crabtree;[27] the NMR spectra were not studied. The changes in IR frequencies[25–27] were the same as for classical HBs, confirming that the polarization of the metal–hydrogen bonds is M–H$^{\delta+}$.

We are now searching for a HB with a neutral hydride complex. Low-temperature IR study of the interaction between CpW(CO)$_3$H and phosphine oxides has revealed[28] the lower-frequency ν_{WH} and ν_{PO} band shifts in WH···B complexes analogous to those observed for cationic hydrides. We suppose a partial positive charge is placed on the hydrogen when it interacts with polar bases; such repolarization is perhaps possible because of the presence of three electron-withdrawing CO ligands. This problem deserves further experimental and theoretical studies.

Spectroscopic (IR and ^{1}H NMR) Evidence for Unconventional HBs

Evidence of HB Formation. The most significant IR spectral changes upon unconventional HB formation for all of the above three classes are similar to those of classical hydrogen bonds: a decrease in intensity (A) of the ν_{OH}(free) band and the appearance of a low frequency ($\Delta\nu_{OH} > 100$ cm^{-1}) broad intense ν_{OH}(bonded) band. A downfield shift of the H(O) signal in the ^{1}H NMR spectra is also observed. However, these IR and NMR features give no information concerning the site of hydrogen-bond formation.

Determination of the HB Site: IR Spectra. The study of ligand IR stretching vibrations (ν_{MH}, ν_{EH}, and ν_L, where L = CO, NO, and M-Hal) in the presence of proton donors is convenient for this purpose. The rule is quite simple: the band of hydrogen-bond acceptor group (ν_{MH} or ν_L) shifts to lower frequency ($-\Delta\nu$), while all other bands shift to higher frequencies ($+\Delta\nu$). In the case of HBs to a metal atom, all diagnostic bands have a positive $\Delta\nu$ about 10–35 cm^{-1}.[2b,3] This experimental criterion has been confirmed by theoretical calculations.[13,16,23]

The two examples of OH···MH bonds for transition-metal hydrides found up to date [WH$_4$(dppe)$_2$,[18] [η^4-N(CH$_2$-CH$_2$PPh$_2$)$_3$]ReH$_3$ (**II**, Scheme 1)[19]] reveal $+\Delta\nu_{MH}$ in their low-temperature IR spectra in the presence of fluorinated alcohols R^{F}OH.

DHBs with monohydrides induce a low-frequency shoulder ($-\Delta\nu_{MH}$), as found for Cp*Fe(dppe)H.[14] Polyhydrides of classes 2 and 3 display a more complicated picture: the shift of ν_{MH}/ν_{EH}(bonded) bands to lower frequency in DHB complexes is accompanied by a shift of the bands of nonbonded groups to higher frequency ($+\Delta\nu_{MHn}$). Thus, distinct new high- and low-frequency bands were observed in the spectra of Cp$_2$NbH$_3$ in the presence of R^{F}OH at 200 K.[15] Similarly, the low frequency shoulders of the broadened ν_{EH} bands ($-\Delta\nu_{EH}$) in the IR spectra of neutral (BH$_3$L) and anionic (BH$_4^-$, B$_n$H$_n^{2-}$) boron hydrides[21,22] and GaH$_4^-$ [23] are accompanied by upward shifts ($+\Delta\nu_{EHn}$) of the initial bands because of the large number of free EH groups in the DHB complex.

[1]NMR Spectra. NMR data for XH···M complexes (class 1) are rare. Significant coupling between the OH⁻ or NH⁻ protons and the metal center (J_{MH}) has been observed for XH···Pt[II] hydrogen bonding.[2c]

The DHBs in class 2 have been more thoroughly studied, and two principal pieces of evidence for DHB formation have been found: an upfield shift of the hydride signal and a decrease in its relaxation time by a factor of 1.5−2.[2b] The δ_{MH} shifts are temperature- and alcohol-concentration-dependent and usually range from −0.2 to −0.8 ppm at 200−230 K in an excess of proton donors.[9,10] The regioselectivity of DHB with dihydrides PP₃OsH₂[13] [PP₃ = [η^4-P(CH₂CH₂PPh₂)₃], (**I**, Scheme 1)] and ReH₂(CO)(NO)-(PR₃)₂[29] was demonstrated: one of the hydride signals exhibits a significant upfield shift, while the second resonance remains practically unchanged. For the trihydride Cp₂NbH₃, both the central and lateral hydride ligands take part in DHB with (CF₃)₂CHOH at 180 K (the $\Delta\delta_H$ are −1.3 and −0.4 ppm, respectively; both $T_{1\,min}$ times decreased).[15] The larger shift of the first signal indicates the preferred coordination of the OH group to the central hydride (confirmed by DFT calculations). NMR changes because of the BH···HO bond formation observed for the system BH₃NH₃/(CF₃)₂CHOH have not been so pronounced.[21]

Quantum-exchange coupling has been proposed by Chaudret and Limbach[30] as an additional way of diagnosing DHB formation but has not become widely used.

Energies, Nature, and Structures of Unconventional HBs

Energy Values. The formation enthalpies ($-\Delta H$) of HBs formed by the three classes of complexes have been determined from van't Hoff's method (temperature dependence of formation constants obtained from IR or NMR data) or by assuming empirical correlations between $-\Delta H$ and IR spectral characteristics ($\Delta\nu_{OH}$ and $\Delta A^{1/2}$) like those found by Iogansen for organic systems.[31] The similarity of the enthalpy values determined by these two different approaches proves the applicability of empirical correlations for unconventional HBs.[3,9−17] All of these HBs are of medium strength ($-\Delta H = 4−7.6$ kcal mol⁻¹) except the neutral boron hydrides, which form HBs of only 2.5−3.3 kcal mol⁻¹.[21] The $-\Delta H$ values depend on the partner. Therefore, we find it more convenient to compare different unconventional bases using the characteristics of the proton-accepting ability, basicity factors (E_j) independent of the partners and media.[2b,32] The E_j values of transition metals reported up to date vary from 0.62 to 1.45, and those of hydride ligands are 0.54−1.66 and 0.41−1.37 (classes 2 and 3, correspondingly). Interestingly, hydrogen bonding has been shown to occur at the metal site for hydrides with rather high basicity factors ($E_j = 1.2−1.45$). Thus, there is no clear correlation between the hydrogen-bonding site preference and the basicity factor. An increase of E_j factors allows predicting a proton transfer from weaker XH acid.[2b]

Scheme 2
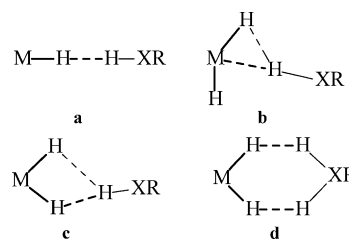
The theoretically estimated energies are as a rule higher than the experimental $-\Delta H$ values[6a,b] for several reasons. First, the calculations are usually carried out in the gas phase. Taking into account the solvent polarity, as was shown for CpRuH(CO)(PH₃), leads to a decrease of energy values from $-\Delta H$(gas phase) = 9.7 to $-\Delta H$(CH₂Cl₂) = 2.9 kcal mol⁻¹ and to a better agreement with the experimental value in a nonpolar solvent.[12] Second, the simplified models of the real systems have been used. Comparative study of the real Cp*Fe(dppe)H complex and its models shows that the H···H bond energies do not differ significantly, whereas the H···Fe bond energies are overestimated in the models because of the neglect of the steric hindrance caused by the phenyl substituents.[16] Third, the basis set superposition errors have not been determined in many cases, although they can be very large (up to 50%).[6,15]

Structures. A classical intermolecular HB is characterized by a linear geometry of the X−H···B fragment and an H···B distance shorter than the sum of the van der Waals radii. The X−H bond elongates upon HB formation.

The same features have been found in the recent theoretical calculations for DHBs of CpRuH(CO)PCy₃,[12] PP₃MH₂,[13] Cp₂NbH₃,[15] and EH₄⁻ (E = B, Ga).[21,23] The H···H distances are shorter than the sum of the van der Waals radii (2.4 Å). The M(E)−H and O(N)−H bonds are elongated, while the $H^{\delta-}$···$H^{\delta+}$−X moieties are practically linear (the angles range from 168° to 178°) (Scheme 2a). The M(E)−$H^{\delta-}$···$H^{\delta+}$ fragments are as a rule far from linear (about 100−130°), which has led to the description of DHB as a bent interaction between XH and the σ electrons of H−E bonds by some authors.[2e] However, the "hydrogen bond linearity" always refers to the B···$H^{\delta+}$−X angles. A linear correlation between the values of $-\Delta H$ and the distances r(H···H) has been theoretically obtained for various DHB complexes (Figure 1). Earlier, such correlations were found for small molecules by Grabovsky[33] and Alkorta et al.[34]

While DHBs have been extensively studied by theoreticians, the calculations on HB to a transition-metal atom have been limited.[2c,6] Our recent study of HB to Cp*FeH-(dhpe) (dhpe = 1,2-diphosphinoethane, Figure 2) provides for the first time a comparison of the M···HX and MH···HX bonding.[16] Thus, the Fe···H distances are less than the sum of the van der Waals radii (2.949−2.418 Å depending on the proton donor), as are the r(H···H). The Fe···H−X and H···H−X angles are close to linear. The metal-hydride bond shortens [Δr(Fe−H) = −0.004 to −0.007 Å] upon coordination of proton donor to the metal atom but elongates by 0.007−0.016 Å upon DHB forma-
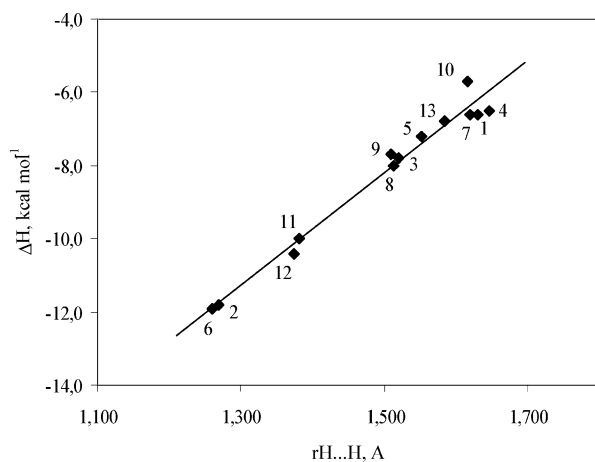
FIGURE 1. Correlation between the DHB enthalpy values and H···H distances for complexes of AlH_4^{-37} with CH_3OH (1), CF_3OH (2), CF_3CH_2OH (3), $BH_4^{-23,37}$ with CH_3OH (4), CF_3CH_2OH (5), GaH_4^- with CF_3OH (6), CH_3OH (7), CF_3CH_2OH (8), $Cp*FeH(dhpe)^{16}$ with $(CF_3)_2CHOH$ (9), FCH_2CH_2OH (10), $(CF_3)_3COH$ (11), CF_3COOH (12), and CF_3CH_2OH (13).
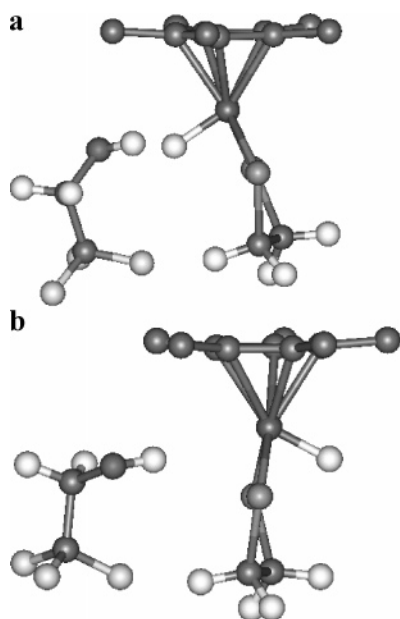

FIGURE 2. Optimized geometries of the hydrogen-bonded adducts at hydride and metal sites of $Cp*FeH(dhpe)$ with CF_3CH_2OH. Hydrogen atoms of $Cp*$ ring and PH_2 groups are omitted for clarity.

tion. In agreement with the experiment, the calculations show an energy preference for DHB adducts.[14,16]

The two calculated directions of proton donor coordination for the $Cp*FeH(dhpe)$ system, to the hydride ligand and to the metal atom, are mutually trans (Figure 2). In the case of polyhydrides, the proton donor approaches a hydride ligand or metal atom in such a way that additional interaction with the metal atom or neighbor hydride ligand is possible (bifurcated structures in parts b and c of Scheme 2). For example, with the $Cp*WH_3(dhpe)/(CF_3)_2$-CHOH system, the calculations show an energetic preference for HB to the metal atom (Scheme 2b) ($\angle W\cdots H-O$, 172.8°; $r(W\cdots H)$, 2.69 Å).[17] Although the H···H(O) distance is also short (2.03 Å), the H···H−O angle of 133.0° is not definitive for HB. We believe that in such situations other

parameters, e.g., bond overlap population or electron density at the H···H bond critical point, should be considered to elicit the true nature of the HB interaction. On the other hand, DHB to Cp_2NbH_3 can be regarded as asymmetrical bidentate coordination (Scheme 2c) by experimental data and calculations.[15] Interesting results were obtained for diprotic acids XH_2.[23] Minima on the potential energy surfaces for H_2O and CF_3NH_2 with GaH_4^- were achieved when two different hydride ligands coordinate with both hydrogen atoms of the XH_2 groups to form a symmetrical chelated structure (Scheme 2d). Such a DHB has nonlinear OH···H and NH···H moieties and induces less bond elongations. The H···H distances are longer than in the linear DHB complexes. With less acidic proton donors or less basic proton acceptors (BH_4^-), we obtained linear monodentate coordination (Scheme 1a); the interaction with the second hydrogen atom of the XH_2 group cannot be regarded as a DHB (H···H distance = 2.449 Å).

The additional interactions found theoretically for transition-metal polyhydrides are demonstrated in the solid state, although there are only a few DHB structures with well-determined hydrogen positions reported.[2b] The linearity of the central fragment has been shown by neutron diffraction studies for ionic $XH^+\cdots M^{-5}$ and neutral $NH\cdots HB$ bonds.[35] The spectral data obtained for intermolecular $M\cdots HX$ and $MH\cdots HX$ bonds in solution provide indirect evidence for the linear structure.[2b,3a]

Nature of the Bonding. The geometry changes during the different types of unconventional HB formation, as well as those in classical HBs, are accompanied by a mutual polarization of both partners with some charge transfer occurring from the base. As it has been demonstrated for many systems,[2b,e,13,16,21,23] both the positive charge on the acidic hydrogen and the negative charge on the metal or the hydride atom increase in value upon HB formation. Kitaura-Morokuma decomposition analysis of the bond energy contributions for the simple DHB ($LiH\cdots HX$)[36] as well as for $EH_4^-\cdots HX^{37}$ shows that the electrostatic term has the greatest impact on the total energy gain similarly to classical HBs. Both DHB[36,37] and $M\cdots H-O^{2c}$ complexes have considerably larger contributions of the polarization energy relative to classical HBs.

The positive overlap population of an H···H bond, which increases from 0.005 to 0.020 for BH_3NH_3/CH_3OH^{21} to 0.028−0.190 for EH_4^-/ROH,[23] as well as the charge density at the H···H bond critical point,[34] indicate a covalent component of DHB.

Mechanistic Aspects (Proton Transfer via Unconventional Hydrogen Bonds)
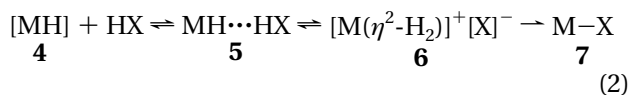
While classical $XH^{\delta+}\cdots B$ hydrogen bonds precede proton transfer in a classical system, unconventional hydrogen bonds have been shown to be intermediates in protonation reactions.

The protonation of transition-metal compounds yields classical cationic hydrides via intermediacy of HBs with the transition-metal atom (eq 1).[3,18] Under certain condi-

tions (low temperature, small amount of CF_3COOH in CH_2Cl_2), an ion pair stabilized by a hydrogen bond between a cationic hydride and a counteranion can be observed.[25] The reversibility of eq 1 has been shown, with the equilibrium shifting toward the ion pairs upon cooling or with an increase in the HX acid concentration. All species in eq 1 were observed in the case of sterically hindered sandwich compounds[25] and $WH_4(dppe)_2$,[18] while no free ions were found in the protonation of half-sandwich compounds in CH_2Cl_2[3] because of high HB formation constants. However, only the free cation $[Cp*Ir(CO)_2H]^+$ and the molecular complex $Cp*(CO)_2Ir \cdots HOR^F$ were found in neat $(CF_3)_2CHOH$ or in $(CF_3)_2CHOH$ or HCl diluted by supercritical xenon, probably because of dissociation of the hydrogen-bonded ion pair caused by the high polarity of these media.[4]

$$[M] + HX \rightleftharpoons M\cdots HX \rightleftharpoons MH^+\cdots X^- \rightleftharpoons [MH^+][X^-] \quad (1)$$
$$\mathbf{1} \qquad \qquad \mathbf{2} \qquad \qquad \mathbf{3}$$

In the case of transition-metal hydrides, just as there are two types of HBs, two pathways for proton transfer are possible. In addition to the direct protonation of the transition-metal atom yielding a classical polyhydride species (as in eq 1), the proton transfer may proceed via initial attack on the hydride ligand and dihydrogen bonding, followed by intracomplex proton transfer and nonclassical product formation (eq 2).

$$[MH] + HX \rightleftharpoons MH\cdots HX \rightleftharpoons [M(\eta^2\text{-}H_2)]^+[X]^- \rightharpoonup M-X$$
$$\mathbf{4} \qquad \qquad \mathbf{5} \qquad \qquad \mathbf{6} \qquad \qquad \mathbf{7}$$
$$(2)$$

In many cases, the nonclassical complex **6** is a kinetic product of protonation, evolving eventually to a classical polyhydride or organyloxo species **7**.[11]

Only two transition-metal hydrides have been found where the formation of the above-mentioned $XH\cdots MH$ bonds precedes the formation of classical cationic hydrides (eq 1).[18,19]

Examples of eq 2 are more numerous. A dynamic equilibrium between a DHB and an $(\eta^2\text{-}H_2)$ complex was observed for the first time by NMR[38] for the *trans*-RuH_2-$(dppm)_2/(CF_3)_2CHOH$ system. Later, this equilibrium was observed for the protonation of hydridocarbonyl complexes of Re[9] and Ru[10] and of PP_3MH_2 dihydrides.[13] By variable temperature IR spectroscopy, the reversibility of such equilibria has been shown; the equilibria shift toward the dihydrogen complexes upon cooling or increasing the HX concentration.

The formation of ion pairs $M-(\eta^2\text{-}H_2)^+\cdots X^-$ (X^- = CF_3COO^-, R^FO^-, and ArO^-), stabilized by hydrogen bonds between the dihydrogen ligand and counteranions, was detected for $CpRuH(CO)(PCy_3)$,[11,12] PP_3MH_2,[39] and $Cp*FeH$-$(dppe)$[16] complexes by IR and UV−visible spectroscopy. The ion-pair stability increases with the proton-accepting ability of the anion. For $CpRuH(CO)(PCy_3)$, the ν_{CO} band position thus depends on the nature of the anion.[12] The dissociation of the hydrogen-bonded ion pair in the reaction with CF_3COOH is assisted by the formation of homoconjugate anion $[CF_3COO(HOCOCF_3)_n]^-$.[11,12,16]

Scheme 3
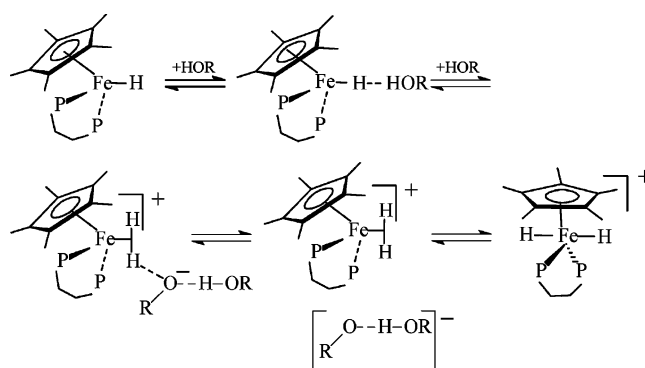
Recently, it was found experimentally that a second proton donor molecule may be necessary in an earlier stage of the reaction, the proton-transfer step itself. Norton et al. found that $PhNH_3^+$ is capable of protonating $CpHW(CO)_2(PMe_3)$ only because of the strong homoconjugate interaction of $PhNH_3^+$ with its conjugate base.[40] Intervention of a second proton donor molecule is similarly necessary for the protonation of $Cp*FeH(dppe)$ by fluorinated alcohols or *p*-nitrophenol[14,16] (Scheme 3). Theoretical studies[12,15,16] support this mechanism, showing that the coordination of the second HX molecule increases the strength of the primary dihydrogen-bonding interaction nonadditively (the so-called cooperative effect in hydrogen bonding[41]). The barrier is therefore lower, and the proton transfer can take place.

On the other side of the equilibrium, the second proton donor molecule stabilizes the protonation products via hydrogen bonding between the $(\eta^2\text{-}H_2)$ ligand of the cation and the anion. $[Cp*Fe(\eta^2\text{-}H_2)(dppe)]^+$ isomer is formed at 200 K and rearranges irreversibly into the *trans*-dihydride upon warming; the counteranion determines the temperature at which this rearrangement takes place.[14]

The mechanism of proton transfer to the main-group element hydrides resembles that of transition-metal hydrides (eq 2), yielding organyloxy derivatives.[23] However, $(\eta^2\text{-}H_2)$ complexes of main-group elements (B and Ga) are so unstable that they have been characterized only theoretically[2e,23] (with the exception of the $BH_3(\eta^2\text{-}H_2)$ complex observed by IR spectra in cryogenic matrixes at 13−27 K[42]). Recent calculations have found them as transition states or as very shallow minima on the potential-energy surface preceding a dihydrogen loss.[37]

Proton-Transfer Kinetics and Thermodynamics. Potential-Energy Surface

The equilibrium thermodynamic parameters for the stepwise protonation of the transition-metal hydrides in Table 1 have been obtained using a combination of different spectroscopic techniques.

These data allow us to present a general profile for the potential energy of proton transfer using the H−H distances as the reaction coordinate (Scheme 4). The experimental picture agrees with theoretical findings. Hydrogen-bond formation is a diffusion-controlled process with no energy barrier. This step makes a considerable contribu-

Table 1. Enthalpies (in kcal mol⁻¹) and Entropies (in eu) for Two Stages of Hydrides Protonation

hydride[a] (E_j)	R^{F}OH	dihydrogen bonding			proton transfer		
		$\Delta H°$	$\Delta S°$	rH···H[b]	$\Delta H°$	$\Delta S°$	rH−H[b]
triphosRe(CO)$_2$H (0.97)[9]	(CF$_3$)$_3$COH	−6.0	−22.7	1.83	−2.3	−8.4	0.80
Cp*FeH(dppe) (1.36)[14,16]	(CF$_3$)$_2$CHOH	−6.5	−18.6		−4.2	−8	
triphosRu(CO)H$_2$ (1.39)[10]	(CF$_3$)$_2$CHOH	−6.6	−23	1.81	−8.7	−42	0.93
RuH$_2$(dppm)$_2$ (1.40)[38]	(CF$_3$)$_2$CHOH	−6.8[c]			−10.2[d]		
Cp*MoH$_3$(dppe) (1.43)[17]	CF$_3$CH$_2$OH	−6.1	−20.4		−3.9	−14.4	
PP$_3$OsH$_2$ (1.67)[13]	CF$_3$CH$_2$OH	−6.8	−19.2	1.96	−2.5	−7.7	0.95

[a] triphos = CH$_3$(CH$_2$CH$_2$PPh$_2$)$_3$; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$; dppm = Ph$_2$PCH$_2$PPh$_2$; PP$_3$ = η^4−P(CH$_2$CH$_2$PPh$_2$)$_3$. [b] In angstroms. [c] Calculated by using $\Delta\nu_{XH}$ values from ref 38. [d] Calculated from the original value of −17 kcal mol⁻¹ obtained for transformation of free hydride into (η^2-H$_2$) complex.[38]

Scheme 4
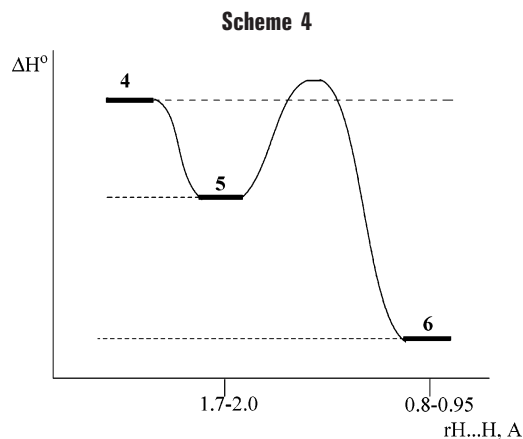
tion to the total energy gain and determines the direction of proton transfer. The depth of the second well depends on the stability of the nonclassical complex formed; it is a true minimum in most cases (Table 1). The (η^2-H$_2$) complex can lie above a DHB complex if it is unstable, like [CpRu(η^2-H$_2$)(CO)(PCy$_3$)]$^+$OR$^−$.[12]

The activation parameters associated with the proton-transfer step have been rarely measured. For Cp*FeH-(dppe)/(CF$_3$)$_2$CHOH in dichloromethane, $\Delta H^{\ddagger}$ = 3.9 kcal mol⁻¹ and $\Delta S^{\ddagger}$ = −40 eu, and for CpRuH(CO)(PCy$_3$)/(CF$_3$)$_3$-COH in hexane, $\Delta H^{\ddagger}$ = 11.0 kcal mol⁻¹ and $\Delta S^{\ddagger}$ = −19 eu. In other cases, the activation free energy $\Delta G^{\ddagger}$ has been estimated to be in the 12−16 kcal mol⁻¹ range, in agreement with the observation of two separate NMR resonances for the DHB and the (η^2-H$_2$) complexes. The barrier is particularly sensitive to the strength of the proton donor. When there are hydrogen-bonded inter-mediates in proton transfer to a transition-metal hy-dride, there is a correlation between the strength of the M−H···H interaction and the proton-transfer activation barrier. Calculations confirm that there is a barrier decrease with acid strength up to a barrierless reaction with strong acids.[16]

Another important issue is a correlation between HB characteristics (formation enthalpies or basicity factors) and parameters of proton transfer (enthalpies or pK_a). Such correlations for organic systems are linear for a given class of bases.

Such correlation may be found for transition-metal or hydride ligand protonation (Figure 3), but deviations from linearity are not rare for such bases. They can be explained by further transformations of the primary protonation products; e.g., the cis−trans isomerization occurs with
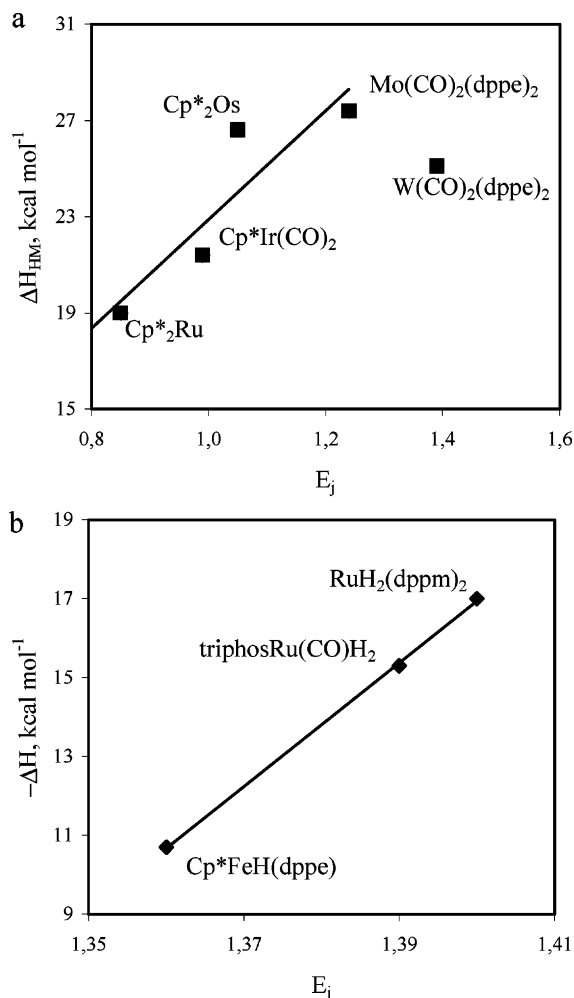
FIGURE 3. Correlations between the basicity factors E_j of transition-metal atom[3] (a) and of hydride ligand (b) and the enthalpies of their protonation by CF$_3$SO$_3$H in ClCH$_2$CH$_2$Cl (data from ref 43) and by (CF$_3$)$_2$-CHOH in CH$_2$Cl$_2$ (sum of two ΔH values in Table 1).

M(CO)$_2$(dppe)$_2$.[3] There may also be structural peculiarities in the protonation products. Thus, the enthalpies of DHB and E_j factors increase down the iron triad: H(Fe) < H(Ru) < H(Os) (for isostructural PP$_3$MH$_2$ hydrides),[13] although their ability to undergo protonation (judged by the relative content of protonated form in PP$_3$MH$_2$/p-nitrophenol equimolar mixture[39]) varies aperiodically H(Fe) ≪ H(Os) <H(Ru) as do the pK_a values of (η^2-H$_2$) ligands.[2a,44] This can be explained by a stronger (and then shorter) H−H bond in the ruthenium complex as compared to the osmium derivatives. Note, the E_j factors of transition

metals[2b,3] as well as the pK_a values of classical hydrides[44] increase down the group evenly.

Conclusion and Future Perspectives

This Account highlights unconventional HBs for organometallic complexes and transition-metal and main-group hydrides. Although these HBs were discovered only 10−15 years ago, their common spectral, structural, and thermodynamic features have been determined, as well as their intermediacy in proton transfer processes. All of the unconventional HBs studied to date are of medium or weak strength. A practically linear arrangement has been shown for the X−H⋯M, X−H⋯H(M), and X−H⋯H(E) moieties, with short H⋯M and H⋯H distances. Calculations suggest that polyhydrides can form some bifurcated or chelate structures with angles significantly less than 180°. Their electrostatic nature is similar to that of classical hydrogen bonds of the same energies. Only the polarization energy is more important for unconventional HBs than for classical HBs.

Two pathways of protonation for transition-metal hydrides have been studied: to the metal atom via HB as well as to the hydride ligand via DHB, yielding classical and nonclassical cationic polyhydrides, respectively. However, the conditions that determine which pathway is chosen for proton transfer are still unclear. The effects of metals, ligands, and solvent properties should be studied further. There are especially few data available for the first pathway. In the case of the EH⋯HX interaction, the mechanistic study of proton transfer demands new approaches, combining theoretical with spectral investigations. A future challenge is to study the equilibrium between these types of hydrogen bonding to steer the reaction along a desirable pathway. The different potential energy surfaces and the activation barriers await thorough study using experimental (involving kinetic) methods and theoretical work.

As more riddles are unraveled, this new lively world of HBs can be applied to the solution of catalytic, physical, and supramolecular problems in chemistry and biochemistry.

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