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Recent advances in hydrogen bonding studies involving metal hydrides

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Abstract

Neutral transition metal hydrides tend to act as proton acceptors towards conventional H-bond proton donors. The resulting species can be precursors of dihydrogen complexes. The BH bonds of boranes are also effective H-bond acceptors. Cationic metal hydrides, in contrast, can act as proton donors toward conventional H-bond acceptors, such as $OPPh_3$. © 1998 Elsevier Science S.A. All rights reserved.

In their reactions, metal hydrides can act as proton donors, hydrogen atom donors or hydride donors, depending on the nature of the hydride and of the reagent with which it reacts [1]. Since 1990, a number of studies have shown how various metal hydrides can take on the roles either of the weak acid (proton donor) or the weak base (proton acceptor) component of a hydrogen bond. The classical hydrogen bond [2] of type A–H···B, a weak electrostatic attraction between a weak acid, AH, and a weak base, B, requires the presence of a lone pair on the base and both A and B to be electronegative atoms or groups. Of the two new types of hydrogen bonds discussed here, the M–H···B type is the most directly related to the classical hydrogen bond, except that AH is replaced by a suitable weakly acidic metal hydride. In the other type, A–H···H–M, the role of the weak base is taken by a weakly basic metal hydride. This is an unusual situation because in such a case there is no lone pair on B—the sigma bonding electron pair of the M–H bond (or more generally an element–hydrogen bond, EH) instead acts as the base. Another way of looking at these interactions is to consider them as arising from the attractive interaction between a protonic and a hydridic hydrogen atom.

1. The A–H···H–E hydrogen bond

Examples of this type, which we have called dihydrogen bonding, are now known where AH is an acidic NH or OH bond and E is Re, Ir or even B, but any electropositive element E should in principle be capable of forming similar bonds.

1.1. Structural aspects

Data on many interactions of this type probably exist unsuspected in the literature. The Cambridge Crystallographic Database (CSD) allows easy access to both intramolecular and intermolecular cases, and in one early study, the CSD was used to provide evidence for

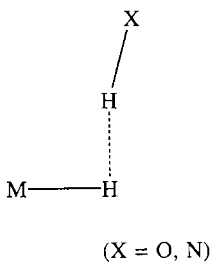

Fig. 1. The typical geometry of a dihydrogen bond, showing the side-on approach of the weak acid AH group to the weak base EH bond.

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the existence of intermolecular N–H···H–B hydrogen bonds [3]. In the case of the adduct between indole and [$ReH_5(PPh_3)_3$], a high quality neutron diffraction structure is available [4]. This and other recent work indicates that the typical range of H···H distances is 1.7–2.2 Å, although the upper limit is not sharp because very weak dihydrogen bonds shade imperceptibly into close nonbonding contacts. Such H···H distances can be compared with 2.4 Å [5], the sum of the van der Waals (vdW) radii for two hydrogens. In the typical geometry, shown in Fig. 1, there is a side-on approach of the weak acid AH group to the weak base EH bond to give E–H···H angles of 90–120°. This means that the E···HA distance is also short and raises the question of the importance of the E···H interaction, a topic considered in more detail in a later section. For the moment we can say that because N–H···H–B cases are well established and boron has no lone pairs, dihydrogen bonding can exist in the absence of any classical N–H···(lone pair) hydrogen bonding contribution.

Attractive A–H···H–M interactions appear to have been first suggested to account for the close contact (H···H, 2.4 Å) found between the OH proton and the Ir–H hydrogen in a neutron-diffraction (n-diffraction) study of *cis*-[$Ir(OH)H(PMe_3)_4$] [6], although in this case the H···H distance is equal to the sum of the vdW radii and the interaction must be relatively weak.

There is some discussion about the appropriate vdW radius to use in cases of dihydrogen bonding. In their studies of C–H···H–B interactions, Contreras and coworkers [7] preferred a larger vdW radius for hydridic hydrogens, 1.45 Å, and therefore consider H···H distances below 2.65 Å as being associated with attractive interactions. We suspect that 1.45 Å may be too big a vdW radius, at least for transition metal hydrides, because the presumably essentially nonbonding contacts in both crystal forms of $HMn(CO)_5$, 2.29 Å (by n-diffraction), [8] indicates a radius in the range 1.15–1.2 Å may be more appropriate. Until the situation is better understood, we have preferred to use a more conservative d(H···H) of ≤ 2.2 Å as prima facie evidence of dihydrogen bonding, but we recognize that this value may well need revision in the future.

One other very early example of close H···H distances deserves special comment. A d(H···H) of 1.86 Å was found by n-diffraction in the crystal structure [9] of *mer*-[$Fe(H)_2(H_2)(PEt_2Ph)_3$], a study originally carried out to check our earlier spectroscopic assignment [10] of this species as a dihydrogen complex. The H_2 ligand was found to be eclipsed with the *cis*-Fe–H bond in such a way that the protonic hydrogen of the dihydrogen ligand is close to the hydridic terminal hydride hydrogen. Eisenstein recognized the origin of the attractive interaction and used the term '*cis*-effect' for this phenomenon but it can now be alternatively seen as a special case of the dihydrogen bonding phenomenon because the short H···H distance puts this squarely into the dihydrogen bonding range.

1.2. Energetic aspects

On the basis of the significant fall-off in hydrogen bonding energies [2] on moving from the classical lone pair type, N–H···(lone pair), with an interaction energy of 4–8 kcal mol^{-1}, to the case in which the proton acceptor is a π-bond, such as an arene, the N–H···π type (≤ 2 kcal mol^{-1}), one would expect that any N–H···σ type would have a negligible bond energy (< 1 kcal mol^{-1}). In favorable cases, where E in N–H···H–E is an electropositive element such as B or a transition metal, we find interaction energies of 4–7 kcal mol^{-1} which are almost as large as for the N–H···(lone pair) case. The reasons for the energies being so large are still not entirely clear, however.

Approximate bond strengths have been obtained via IR spectroscopy using the Iogansen equation [11] which relates the low energy shift of the ν(NH) or ν(OH) band in the IR spectrum to the interaction energy. As applied [4] to [$ReH_5(PPh_3)_3$·indole] (3.6 kcal mol^{-1}), and [$ReH_5(PPh_3)_3$·ArOH] (5.6–5.8 kcal mol^{-1}), the method appears to give reasonable results. Epstein, Berke and coworkers [12] have applied the method to intermolecular association between acidic alcohols such as $(CF_3)_2CHOH$ and the hydride, [$WH(CO)_2(NO)(PMe_3)_2$], where enthalpies of association of ca. 5.5 kcal mol^{-1} were obtained. That the site of association was the WH bond was determined spectroscopically. A useful feature of this work was that the values derived from the Iogansen equation were checked by looking at the equilibrium constants for the same systems, which led to an interaction energy of 4.9 kcal mol^{-1}. In terms both of ΔH^0 and ΔS^0, the tungsten hydride was found to be closely comparable to the strong H-bond acceptor DMF in its hydrogen bonding propensity.

In almost all the transition metal examples of dihydrogen bonding, the metals have a d^6 or a d^2 electronic configuration and so the metals have nonbonding electrons which could in principle act as proton acceptors. The side-on approach of the weak acid allows a direct AH···M interaction and so it was important to determine if this played a significant or even predominant part in the overall interaction. Indeed, Brammer and coworkers [14] have clearly demonstrated that direct N–H···M hydrogen bonding is possible in a number of cases. We looked at this problem by measuring the $\Delta\nu$(NH) and $\Delta\nu$(OH) values for the interaction of a variety of proton donors with the closely related metal polyhydrides shown in Table 1, where the pentahydride is a d^2 metal and has the opportunity to engage in X–H···M hydrogen bonding but the heptahydride is

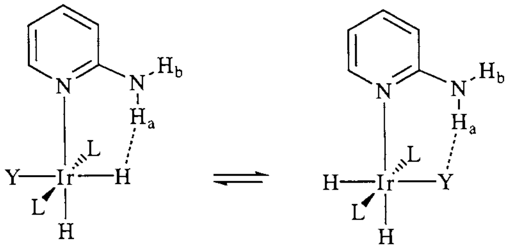
Table 1
Approximate dihydrogen bond strengths (kcal mol^{-1}), deduced from $\Delta\nu$(NH) and $\Delta\nu$(OH) IR spectroscopic data, for adducts of the d^0 and d^2 complexes shown with typical proton donors, indicating that direct X–H··M hydrogen bonding is not predominant; data taken from ref. [4]

H-bond donor	$[ReH_5(PPh_3)_3]$	$[ReH_7(dpe)]$
Indole	4.3	3.3
$2,4,6\text{-}Me_3C_6H_2OH$	4.5	4.7
d^n configuration	d^2	d^0

dpe, $Ph_2PCH_2CH_2PPh_2$.

an authentically classical d^0 molecule and although the metal may make an electrostatic contribution it lacks nonbonding electrons and cannot give a Brammer type of interaction. As can be seen in Table 1, the interaction energies deduced from the $\Delta\nu$(NH) and $\Delta\nu$(OH) values are similar for the d^0 and d^2 cases and therefore direct Brammer type X–H···M hydrogen bonding plays only a minor role and the main interaction must therefore be of the X–H···σ type [4].

In intermolecular cases, NMR methods can be used. For example, in the case of complex **1a**, the barriers to exchange between H_a and H_b were determined and associated with relative values of H···H interaction energies [13]. By estimating the intrinsic C–N rotation barrier in the absence of dihydrogen bonding, it was possible to estimate the absolute values of the hydrogen bond strength.



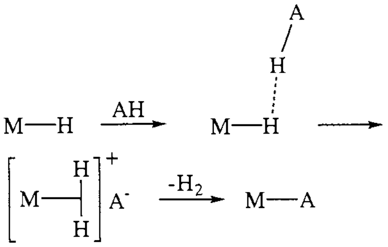
(1)

1a **1b** (L = PPh_3)

In the case of **1a** the C–N rotation barriers proved to be strongly dependent on the nature of the *trans* ligand, Y, indicating the presence of a substantial trans effect on the H···H interaction. In the most favorable case, where Y is H^-, the H···H bond energy was estimated to be 5.0 kcal mol^{-1} but as more electron withdrawing groups are substituted for Y, the interaction energy falls until for $Y = F^-$, the energy is < 2.9 kcal mol^{-1} (Table 2). The presence of the other isomer, **1b**, allowed the N–H···Y hydrogen bond strengths to be determined and even for $Y = F^-$, this proved to be only just a little more (5.2 kcal mol^{-1}) than for the N–H···H–Ir bond where $Y = H^-$ (5.0 kcal mol^{-1}). The system was designed to be most favorable for formation of an N–H···H–Ir dihydrogen bond, however, so there is probably some size mismatch for the larger Y groups. Fluoride being very similar in size to hydride, however, a valid comparison is probably possible in this case.

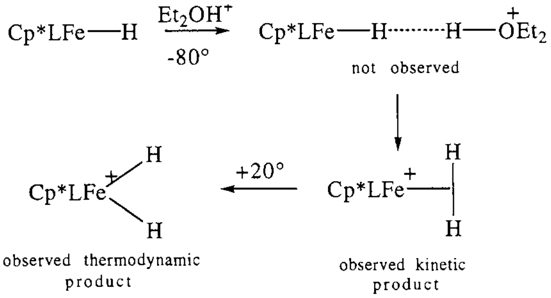
1.3. Reactivity

The basic character of hydrides had long been recognized but in early work (pre 1984) only complete proton transfer from the acid to the hydride with loss of H_2 was generally recognized. The discovery of dihydrogen complexes by Kubas made a dihydrogen complex a likely intermediate in such processes. Now, with the discovery of the dihydrogen bond, 2, a new intermediate can be added to the general reaction pathway (Eq. 2).



(2)

The presence of such an intermediate may help account for the faster protonation of a terminal hydride even when protonation at the metal is thermodynamically preferred, as in the case shown in Eq. 3 [15].

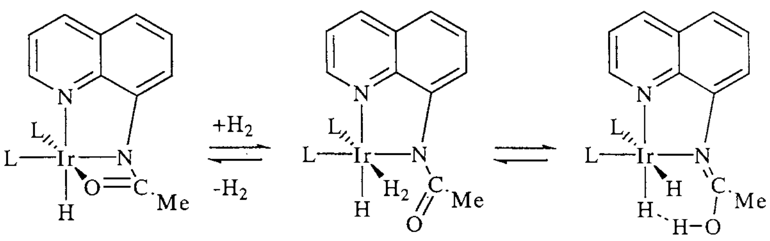


(3)

Table 2
Some dihydrogen bond strengths for complex **1** taken from ref. [13]

Y	H···H bond strength (kcal mol^{-1})
H^-	5.0
CO	3.7
CN^-	3.4
I^-	3.3
MeCN	3.1
Br^-	3.0
Cl^-	2.9
F^-	<2.9

Reversible proton transfer to and from a terminal hydride was proposed [13] to explain the reversible dihydrogen activation pathway shown in Eq. 4, where the proposed dihydrogen bonded intermediates are directly observed.



(4)

Chaudret and coworkers [16] have recently detected an equilbrium between $RuH_2(dpm)_2$ {dpm = $Ph_2PCH_2PPh_2$} and the corresponding dihydrogen complex as a result of proton transfer from an acidic alcohol such as $(CF_3)_2CHOH$ (Eq. (5)).

$$RuH_2(dpm)_2 \cdot HOR \rightleftharpoons [RuH(H_2)(dpm)_2]^{+}[OR]^{-} \quad (5)$$

1.4. Spectroscopy and bonding

Although the $\nu(NH)$ and $\nu(OH)$ IR bands of the proton donors show the expected shift on adduct formation, the $\nu(MH)$ bands do not seem to be strongly affected. Many of the systems studied to date are polyhydrides, however, and more work needs to be done on monohydrides. In the Epstein study [12] on the $(CF_3)_2CHOH/[WH(CO)_2(NO)(PMe_3)_2]$ system, small changes were noted in the $\nu(MH)$ and $\nu(MD)$ IR bands, where low energy shoulders were observed.

Since the IR does not definitively establish the site of adduct formation, we turned to NMR spectroscopy [13], where several lines of evidence point to the existence of very short $H \cdots H$ contacts in the adducts. In intramolecular cases, $J(H,H')$ coupling in the range of 2–7 Hz has been observed. While this is small compared with the $J(H,H')$ of 280 Hz expected for H_2 itself (if the protons were inequivalent) it is larger than would be expected ($J \sim 0$) for purely electrostatic interactions. This is unlike the situation found for classical hydrogen bonds [1] and may indicate there is a small but nonzero covalent contribution to the $H \cdots H$ bonding. Indeed, Eisenstein [13] found a small but nonzero overlap integral (0.012) in her studies on the model system $[IrH_3(formamide)(PH_3)_2]$.

In what is perhaps a better test of the presence of close $H \cdots H$ distances, a substantial excess T_1 relaxation has been detected by our own group [13] and by that of Morris [17] for H and H′ in the NMR spectrum of a number of compounds containing intramolecular $X\text{-}H \cdots H'\text{–}M$ dihydrogen bonds. The magnitude of the effect can be interpreted in terms of an $H \cdots H$ distance of about 1.8 Å.

Solvatochromic shifts in the UV–vis spectra have been associated with hydrogen bonding interactions in organic compounds and in recent work [18], the MLCT band of $[ReH_5(pyridine)(PPh_3)_2]$ was shown to be red-shifted in more polar solvents. This is believed to result from stabilization of the more polar excited state by polar solvents and is not related to hydrogen bonding. Protic solvents, capable of $X\text{–}H \cdots H\text{–}Re$ dihydrogen bonding, gave blue shifts relative to the MLCT position expected from their polarity. This was ascribed to stronger dihydrogen bonding in the ground state; in the excited state the Re is expected to have cation radical character and so the dihydrogen bonding is expected to be less efficient.

Chaudret, Limbach and coworkers [19] have recently shown that dihydrogen bonding effects can alter the quantum exchange coupling observed in the NMR spectrum of $[Cp^*(PCy_3)RuH_3]$.

Theoretical work on the gas phase BH_3NH_3 dimer, which exhibits two $B\text{–}H \cdots H\text{–}N$ dihydrogen bonds, suggests that the side on approach of the NH (Fig. 1) may result from the charge distribution in the molecule. This direction of approach allows the very positively charged NH proton to approach both the BH boron and hydrogen atoms, both of which are negatively charged. In other words, it is indeed the BH sigma bond which is the proton acceptor [3].

1.5. C–H···H–M dihydrogen bonding

Relatively acidic CH bonds such as those of aryl CH groups have been shown to give classical $C\text{–}H \cdots$base hydrogen bonds with a strength of about 60% of those of the corresponding $O\text{–}H \cdots$base case [2]. It is therefore not surprising to find weak attractive interactions in the $C\text{–}H \cdots H\text{–}M$ case as well [20]. IR spectroscopic detection of an interaction between $ReH_5(PPh_3)_3$ and PhCCH was indicated by a low energy shift of the $\nu(CH)$ band; C_6F_5H showed no similar effect, however. Short intramolecular $CH \cdots HRe$ distances ($d\{H \cdots H\} < 2$ Å) in the n-diffraction structure of $[ReH_5(PPh_3)_3]$ were recently associated with the presence of weak attractive $C\text{–}H \cdots H\text{–}Re$ interactions [20]. Morris et al. found $d\{H \cdots H\}$ values of 2.0–2.2 Å in a number of Ir and Ru hydrides [21].

1.6. *M–H···base hydrogen bonds*

Certain acidic hydrides, especially ones with a cationic charge, have been shown to form M–H···base hydrogen bonds with suitable proton acceptors. Epstein and coworkers [22] provided strong IR spectroscopic evidence for such interactions in the case of the very acidic hydride, $[Cp_2OsH]^+$ and $OPPh_3$ as proton acceptor. In some cases the bases caused deprotonation leading to the suggestion that the M–H···base hydrogen bonding adduct is an intermediate in the deprotonation of the hydride. The IR data suggesting the nature of the interaction was the increase in intensity of the ν(MH) band and the decrease in intensity of the ν(PO) band together with the presence of a ν(PO) shoulder at low energy.

Peris et al. [23] were able to detect an interaction between $OPPh_3$ as proton acceptor and a variety of cationic complexes such as $[IrH_2(bipy)L_2]BF_4$ and $[ReH(MeCN)_3L_3](BF_4)_2$ ($L = PPh_3$; bipy = 2,2-bipyridyl). In this work the appearance of 'free' [24] indole in the equilibrium was ascribed to preferential binding of the metal complex to $OPPh_3$.

Concomitant changes in the ν(PO) and ν(MH) bands resembled those reported by Epstein et al. [22] and were therefore ascribed to the formation of an M–H···$OPPh_3$ adduct. Related neutral hydrides such as $[IrH_2(O_2CMe)L_2]$ did not give any effect so the cationic charge was assumed to be important in promoting the interaction.

This class of hydrogen bond remains little studied and no structural information is yet available, so much work remains to be done.

1.7. *Future developments*

In principle, it should be possible to combine the two types of hydrogen bond to produce an M–H···H′–M′ interaction, but for the moment, no examples are known. Such a complex could be the precursor to an M–M′ bonded cluster by loss of H_2 and by reversibility arguments might be formed by hydrogenolysis of an M–M′ cluster.

2. Conclusion

Neutral transition metal hydrides tend to act as proton acceptors towards conventional H-bond proton donors. The resulting species can be precursors of dihydrogen complexes. The BH bonds of boranes are also effective H-bond acceptors. Cationic metal hydrides, in contrast can act as proton donors toward conventional H-bond acceptors, such as $OPPh_3$.

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