A New Intermolecular Interaction: Unconventional Hydrogen Bonds with Element−Hydride Bonds as Proton Acceptor

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This Account describes a new type of intermolecular interaction, the H···H or dihydrogen bond, which operates between a conventional hydrogen bond donor such as an NH or OH bond as the weak acid component and an element−hydride bond as the weak base component, where the element in question can be a transition metal or boron. The interaction, which involves a close approach of protonic and hydridic hydrogens, has been characterized by crystallography, including neutron diffraction, and by physical and theoretical methods.

These interactions occur in the so-called second or outer coordination sphere of a metal complex, as distinct from the first or inner sphere of the ligands directly bound to the metal. Taube[1] has drawn attention to the importance of the outer solvent sphere in certain electron transfer processes, but otherwise very little is known about the structure and energetics of the outer sphere, and little attention[2] has been given to the possibility of its control and organization. By selectively stabilizing the transition state, such interactions might be capable of accelerating specific reactions and so provide a general strategy with useful applications in catalysis.

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Conventional hydrogen bonds are formed between a proton donor, such as an OH or NH group, and a proton acceptor, such as an oxygen or nitrogen lone pair,[3] but in all such cases a nonbonding electron pair acts as the weak base component. In rare cases, π-bonds[4] and even metal atoms in metal complexes[5] have also been shown to act as weak proton acceptors.

A wide variety of element−hydrogen σ bonds, such as B−H and M−H (M = transition metal), act as unexpectedly efficient hydrogen bond acceptors toward conventional proton donors, such as O−H and N−H groups. The resulting E−H···H−X systems have close H···H contacts (1.75−1.9 Å) and they have therefore been termed "H···H or dihydrogen bonds".[6] Their heats of interaction are substantial (3−7 kcal mol^{-1}) and lie in the range found for conventional H-bonds. Both inter- and intramolecular versions have been identified, and a number of reactions involving these new H-bonds have also been found. A significant feature of the work has been the close cooperation among synthetic, physical, crystallographic, and theoretical approaches.

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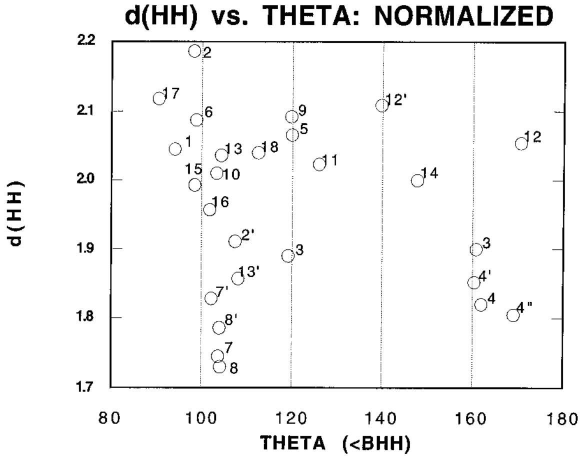

Figure 1. Dependence of the B–H–(HN) angle (θ) on the H···H distance (d_{HH}) in some aminoboranes found in the Cambridge Crystallographic Database. Distances were normalized. The numbers refer to the following structures listed by their CSD filenames: 1, AZIBOR; 2, CESHIR 10; 3, DITSUU; 4, DUJYOW; 5, EMOBOR; 6, FUDHIV01; 7, FUDHOB; 8, FUDHOB02; 9, FUZSEY; 10, GACWUC; 11, GALGIJ; 12, GALGOP; 13, GEWWEK; 14, JUJKUU; 15, KACRAH; 16, KADMEH; 17, SORGEL; 18, VIJLEF. Primes refer to second and third H-bonds within a single structure. Reprinted with permission from ref 6. Copyright 1995 American Chemical Society. The θ values are most often in the range 95–120°, but some structures have higher values.

Main Group H-Bonds

The Case of B–H···H–N H-Bonds. A comparison of the melting points of H_3CCH_3 (−181 °C) and of the isoelectronic species H_3BNH_3 (**1**; +104 °C), which differ by nearly 300 °C, suggested the possibility that unusually strong interactions were present in **1**. Of course, **1** is polar, but the polar but non-H-bonding molecule CH_3F, also isoelectronic with ethane, has a melting point of −141 °C, only 40 °C higher than that of ethane. Because **1** lacks lone pairs, it cannot form conventional hydrogen bonds, and so we suspected H···H bonds were present.[7a]

The Cambridge Crystallographic Database (CSD) was searched for close intermolecular B–H···H–N contacts,[6] of which 26 were found in the range 1.7–2.2 Å in 18 amine–boranes. As X-ray structures, we had to normalize the N–H and B–H distances to their true internuclear separation by preserving the X-ray derived bond angles, but elongating the NH and BH distances to their *n*-diffraction distances of 1.03 and 1.21 Å, respectively. This normalization procedure[3] avoids systematic underestimation of *d*(H···base). Figure 1 shows the distribution of normalized B–H···(HN) angles[7c] versus *d*(H···H). These *d*(H···H) values are much smaller than those for normal nonbonding H···H contacts, which are ca. ≥2.4 Å, or twice the van der Waals radius for H, and this suggests that an attractive interaction is indeed present. Classical H-bonds tend to be linear, but Figure 1 shows that many of the B–H···(HN) angles are strongly bent, falling in the range 95°–120°; others are nearer to being linear, but this is believed to result from the molecular conformation.[7d]

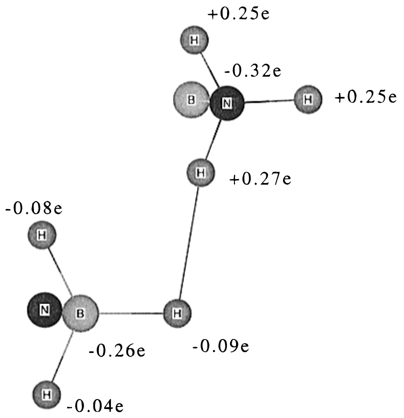

Figure 2. Lowest energy structure found for the gas phase dimer $[H_3BNH_3]_2$ as determined by PCI-80/B3LYP methods. One of two identical B–H..H–N bonds is shown. The calculated Mulliken charges on the atoms help explain the structure adopted. Reprinted with permission from ref 6. Copyright 1995 American Chemical Society.

Is the interaction really attractive, what is its strength, and why does the B–H···(HN) angle tend to be strongly bent? We modeled the B–H···H–N H-bond theoretically by looking at the mutual interaction of two H_3BNH_3 fragments in the gas phase dimer $[H_3BNH_3]_2$ by PCI-80/B3LYP theoretical studies, an empirically parametrized density functional theory.[8] The lowest energy structure found, assumed to be the global minimum, contains two identical short BHHN interactions, one of which is shown in Figure 2. The structure is no doubt influenced by the constraints of the cyclic structure, but the theoretical results nevertheless closely reproduce the experimental structural results from the database. The interaction strength is a surprisingly large 12.1 kcal/mol for the structure as a whole, corresponding to 6.1 kcal/mol for each H···H interaction. The calculated charge distribution, shown in Figure 2, gives an indication of the origin of the structural preferences found. The N–H bond is strongly dipolar in the sense $N^-{-}H^+$, and this may be the reason the N–H···(HB) angle is close to the values (160–180°) normally found in conventional hydrogen bonds. In contrast, both atoms of the B–H bond are negatively charged, and the bond is only weakly dipolar with the boron as the negative end. This may explain why the BH dipole avoids a linear B–H···H–N arrangement which would give rise to an unfavorable mutual disposition of the dipoles. By bending, the protonic NH can approach the strongly negatively charged B and maximize the attractive Coulombic interaction.

*Intra*molecular B–H···H–N hydrogen bonds have very recently been identified in certain boronated heterocycles, such as *N*1-(cyanoboryl)cytosine, originally prepared in connection with boron neutron capture therapy, and theoretical studies were carried out to confirm the nature of the binding.[9]

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(7) (a) A brief report on the structure of BH_3NH_3 has appeared,[7b] but we are currently redetermining it by neutron diffraction. (b) Boese, R.; Niederprüm, N.; Bläser, D. In *Molecules in Natural Science and Medicine*; Maksic, Z. B., Eckert-Maksic, M., Eds.; Horwood: Chichester, 1994; Chapter 5. (c) The term B–H···(HN) angle refers to the angle between the B–H and H···H vectors. (d) In these cases, several H···H bonds are formed and geometrical constraints prevent them from adopting the usual bent B–H···(HN) angle.

(8) (a) This method has recently been discussed in detail.[8b] (b) Siegbahn, P. E. M.; Blomberg, M. R. A.; Svensson, M. *Chem. Phys. Lett.* **1994**, *223*, 35; Siegbahn, P. E. M.; Svensson, M.; Boussard, P. J. E. *J. Chem. Phys.* **1995**, *102*, 5377.

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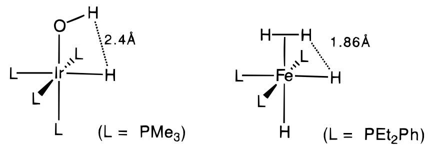


Figure 3. Two complexes having short H···H distances as determined in neutron diffraction studies. In the Ir complex, a weak dipole–dipole interaction probably accounts for the H···H distance of 2.4 Å, but the short distance of 1.86 Å suggests a much stronger interaction in the case of the iron species.[10,11]

Transition Metal M–H···H–N and M–H···O–H H-Bonds: Intramolecular Cases

Early Examples. Two early examples of M–H bonds acting as proton acceptors were reported in 1990 (Figure 3). In the neutron diffraction structure of $[Ir(PMe_3)_4(H)(OH)]^+$ by Bau, Milstein, and Koetzle, a d(H···H) of 2.4 Å was found between the OH proton and the Ir–H hydride.[10] This long d(H···H) probably represents a weak dipole–dipole interaction. The neutron diffraction structure[11] of $[Fe(H)_2(H_2)(PEt_2Ph)_4]$ showed the presence of the molecular hydrogen[12] ligand previously predicted[13] from T_1 NMR spectroscopic studies. In addition, a close d(H···H) of 1.862(13) Å was found between one of the H_2 protons and the hydrogen of a *cis*-Ir–H group, because the H_2 ligand adopts a conformation in which the H–H bond is coplanar with and parallel to the *cis*-Fe–H bond. This attractive interaction was termed a "*cis* effect", but as Morris[14a] has also recognized, it could equally well be considered as an intramolecular hydrogen bond. Dihydrogen complexes are known[15] to be effective proton donors because the M–(H_2) bonding involves net electron transfer from the H_2 ligand to the metal and many H_2 complexes lose a proton relatively easily.

Morris and co-workers[14] independently discovered a series of Ir–H···H–N species simultaneously with our own work.[16] For example, they showed how reversible protonation of a pendant pyridyl group can switch intramolecular N–H···H–M hydrogen bonds on and off. In related work, they find that two N–H bonds of two different pendant pyridinium groups can both simultaneously bind to one Ir–H bond. In recent theoretical work, Lin and Hoffmann[17] have confirmed the attractive nature of the interaction.

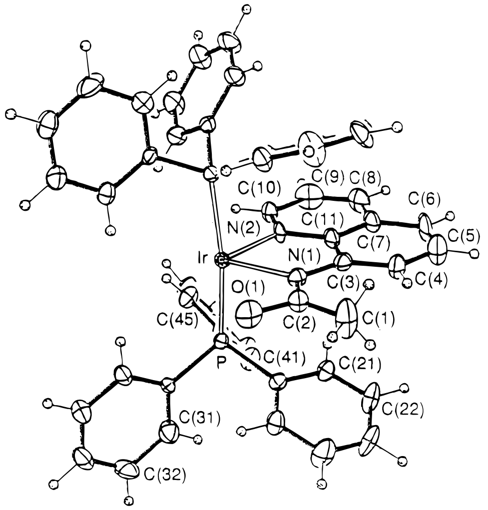
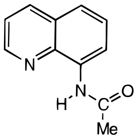
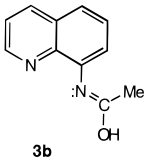


Figure 4. Structure of complex **2**. The Ir–H and O–H hydrogens were not located, but spectroscopic data suggest they are located as shown in eq 2. Reprinted with permission from ref 16a (*J. Am. Chem. Soc.*). Copyright 1994 American Chemical Society.

An Ir–H···H–O H-Bond and Its Chemistry. Our 1994 X-ray diffraction structure of **2a** (R = Me), shown in Figure 4,[16a] was the unanticipated result of an attempt to make a complex with an "agostic" N–H···Ir group, of a type which is still unknown. In fact, the amide **3** does not bind directly to the metal in the amide form **3a** but first tautomerizes to the very rare iminol form **3b** before binding to the metal via the nitrogen lone pair. The *syn*-orientation of the iminol OH in **2a** allows the OH proton, not located in the refinement, to approach very close to one of the iridium hydrides and accounts for the unexpectedly large coupling ($J_{HH'}$ = 2–4 Hz) between the OH and IrH protons, suggesting the presence of a direct H···H interaction.



3a
(amide form)



3b
(iminol form)

Confirmation of the interaction was obtained from spectroscopic studies. As expected for a hydrogen bond, the ν(OH) IR band of the iminol group appears in the range 3310–3409 cm^{-1}, at lower energy than expected for the free iminol OH. The ν(IrH) IR band not only shifts from 2252 cm^{-1} in the starting complex $[IrH_2(Me_2CO)_2(PPh_3)_2]^+$ to 2150–2180 cm^{-1} for the iminol compounds, but also becomes significantly broader, also as expected for H-bonding.

The best evidence for the close approach of the OH and Ir–H protons comes from their abnormally low minimum T_1 values in the ^1H NMR spectrum. The 4.0 s^{-1} excess T_1 relaxation rate we observe can be quantitatively interpreted[18] in terms of an internuclear distance of 1.8 Å between the OH and MH protons. Morris[14] has also used this method in his systems and finds very similar excess relaxation and H···H distances.

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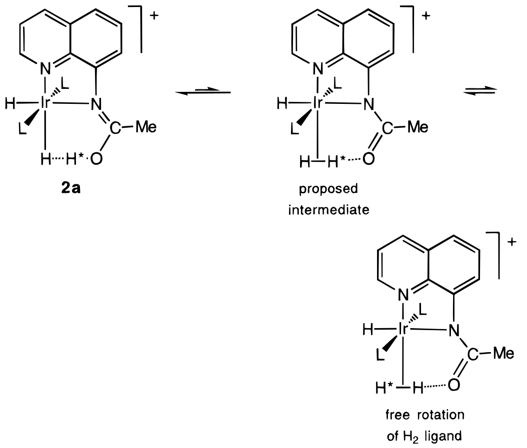
The presence of the M−H···H−O H-bond facilitates proton transfer. As shown by VT NMR studies, the OH and MH protons exchange readily with a $\Delta G^{\ddagger}$ of 15 kcal/mol for **2a** (R = 3,4-$C_6H_3F_2$). We propose that proton transfer from the acidic iminol OH group to the basic hydride leads to a dihydrogen complex, which is expected to undergo rotation[19] about the M−(H_2) bond, followed by back transfer of a proton, thus accounting for the exchange (eq 1).



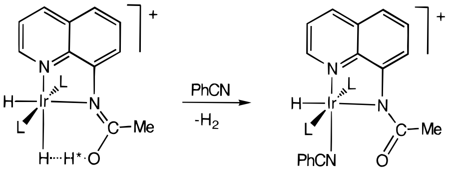
2a

proposed intermediate

free rotation of H_2 ligand

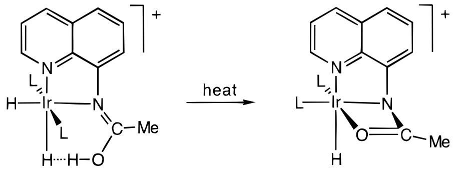
(1)

If an H_2 complex is indeed an intermediate in this process, a suitable ligand should be able to displace it, since H_2 is often very labile. Benzonitrile indeed gives a substitution of this type (eq 2), but more interestingly, on thermolysis in the absence of added ligand, the complex cyclometalates with rearrangement of the phosphines from *trans* to *cis* to give **4** (eq 3). Here, the adjacent C=O group acts as a nucleophile to replace the H_2. The H_2 liberated in this reaction can be considered as arising from the protonic OH combining with the hydridic M−H. The facility of cyclometalation may help explain why these new H-bonds have only recently been discovered; in prior cases cyclometalation may have been too rapid for the intermediate H-bonded species to be detected.



2a

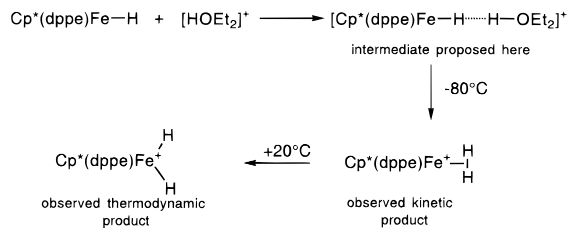
(2)



2a **4**

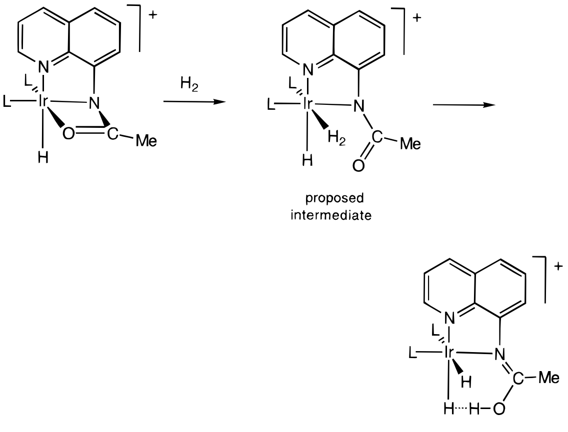
(3)

M−H···H−X systems generally seem to lose H_2 readily and indeed such H···H-bonded intermediates may lie on the pathway whenever a hydride undergoes protonation. If H-bonding to a hydride ligand takes place prior to proton transfer, then protonation of that ligand might be facilitated. Lapinte and co-workers[20] have found (eq 4) that Et_2OH^+ selectively protonates [Cp*FeH(dppe)] at the hydride ligand at −80 °C to give the dihydrogen complex $[Cp^*Fe(H_2)(dppe)]^+$ even though the complex rearranges to the more stable, metal-protonated form $[Cp^*Fe(H)_2(dppe)]$ on warming. Formation of a hydrogen-bonded precursor provides a plausible path for kinetic protonation at the hydride, even when, as here, the metal itself is more basic.



(4)

The loss of hydrogen from **2a** is reversible: reaction of the cyclometalated species with H_2 at room temperature regenerates an iminol complex, although not **2a** itself, but an isomer (**2b**) in which the cis geometry of the phosphines is retained (eq 5). This kinetic product reverts to **2a** after 1 day. This is an example of the "σ bond metathesis" reaction.[21] Reversibility arguments suggest that an H_2 complex, formed after dissociation of the carbonyl oxygen from the metal, may be an intermediate in the hydrogenolysis.

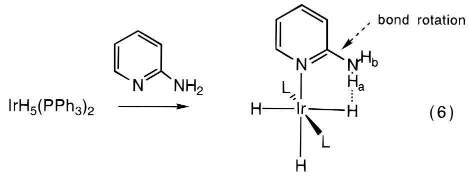


proposed intermediate

2b

(5)

An Ir−H···H−N Example and the H-Bond Strength. Are these interactions really strong enough to be considered full-fledged H-bonds? To look at this, we designed a new system, $[IrH_3(PPh_3)_2(2\text{-aminopyridine})]$ (**5**), to allow measurement of the H···H interaction energy.[16b] The new species was readily prepared by reaction of 2-aminopyridine with $IrH_5(PPh_3)_2$ (eq 6), and NMR and IR studies confirmed that a very



5

(6)

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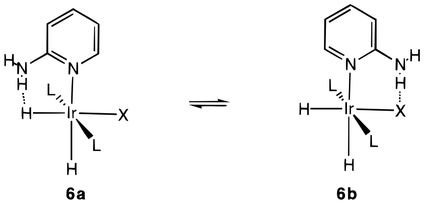
similar H···H interaction is present. Exchange between H_b and H_a was observed by ^1H NMR for **5**, for which line shape studies gave a barrier of 10.8 kcal/mol. This barrier is the sum of the H···H bond energy and the intrinsic C–N bond rotation barrier for the bound ligand. The latter was estimated to be 5.8 kcal/mol by a combination of model compound studies and theoretical work. This in turn leads to a value of 5.0 kcal/mol for the H-bond strength, a very substantial number for an H-bond involving NH, and comparable to that of $N-H\cdots OH_2$. This implies that M–H is a very effective proton acceptor, comparable to a lone pair in water.

In the halo complexes **6**, we find that the two H-bonded isomers **6a** and **6b** are in equilibrium (eq 7) and we are able to directly compare the H-bonding abilities of Ir–H and F from the ratio of **6a** and **6b** and the results of the C–N bond rotation study. Surprisingly only the N–H···F bond is stronger (5.2 kcal/mol) than the strongest N–H···H–Ir bond (5.0 kcal/mol), but only by a small amount. The constraints of chelation may somewhat disfavor H-bonding to F, however. The high polarizability of the MH bond is illustrated by the fact that the nature of the ligand, X, *trans* to the Ir–H group greatly affects the strength of the Ir–H···H–N interaction, which increases in the following order of X: F > Cl > Br > I > CN > CO > H.



(7)

Transition Metal H-Bonds: Intermolecular Cases

$ReH_5(PPh_3)_3$·Indole. Are intermolecular N–H···H–M H-bonds possible? To definitively characterize such a system, we felt we needed a neutron diffraction study, which in turn requires that a suitable proton donor cocrystallize with a suitable hydride. Of course, most solute mixtures do exactly the opposite and crystallize separately; this is the principle of recrystallization. In order to promote cocrystallization, we used a solvent having weak association with the two solutes, and chose solutes having minimal tendency for self-association. As H-bond proton donor, we therefore preferred a liquid like indole, a substance which has little tendency to self-associate because it is a strong proton donor but weak acceptor. As metal hydride, we chose $ReH_5(PPh_3)_3$, a complex that crystallizes poorly to form small crystals. In the presence of indole, however, this pentahydride rapidly crystallizes from a benzene solution to give very large yellow prisms of the ternary adduct $ReH_5(PPh_3)_3$·indole·C_6H_6 (**7**). As a control experiment, we showed that $ReH_5(PPh_3)_3$ does not cocrystallize with indene, a molecule having the same shape as indole, but in which the key NH bond is replaced by a CH_2 group.

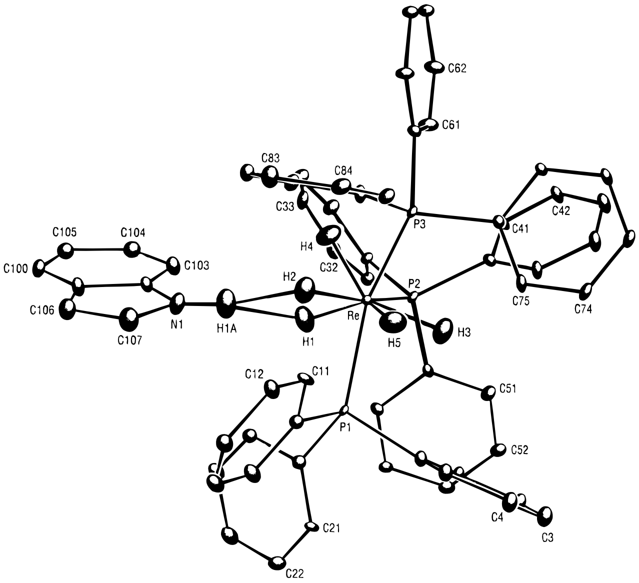


Figure 5. Structure of $[ReH_5(PPh_3)_3$.indole] (**7**). The neutron diffraction results are shown here. Reprinted with permission from ref 22. Copyright 1995 VCH.

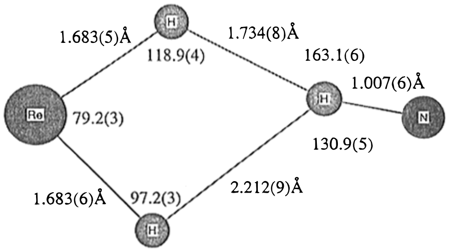


Figure 6. Details of the $N-H\cdots H_2Re$ interaction from the neutron diffraction data of $[ReH_5(PPh_3)_3$·indole] (**7**). Reprinted with permission from ref 22. Copyright 1995 VCH.

X-ray and neutron diffraction studies[22] (Figure 5) on **7** show the presence of an N–H···H–N hydrogen bond. This can be considered as a three-center H-bond, with one hydrogen tightly bonded ($d(H\cdots H) = 1.734$ (8) Å) and one very weakly bound ($d(H\cdots H) = 2.212(9)$ Å). The Re–H···(HN) angles are strongly bent (118.9(4)° for the stronger and 97.2(3)° for the weaker interaction), like we saw in the B–H···H–N cases. The N–H points toward the Re–H bond to which it is most strongly bound ($\angle(N-H\cdots HRe) = 163.1(6)°$), indicating the major interaction takes place with this bond (Figure 6). The ν(NH) band in the IR moves from 3437 cm^{-1} in free indole to 3242 cm^{-1} in **7**, a shift corresponding[23] to a heat of interaction of 4.3 kcal/mol. Very recently, Epstein, Berke, and coworkers[24] have reported spectroscopic evidence for intermolecular H-bonding between acidic alcohols and a tungsten hydride.

We were able to carry out[22] a high-level density functional theory calculation on the model system $[ReH_5(PH_3)_3$·$NH_3]$, which closely reproduced both the geometry and energy of the H bond and suggested that the interaction is indeed attractive and that the

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[22] Wessel, J.; Lee, J. C.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int Ed. Engl.* **1995**, 34, 2507.

[23] Kazarian, S. G.; Hamley, P. A.; Poliakoff, M., *J. Am. Chem. Soc.* **1993**, *115*, 9069; Iogansen, A. V.; Kurkchi, G. A.; Furman, V. M.; Glazunov, V. P.; Odinokov, S.E. *Zh. Prikl. Spectrosk.* **1980**, *33*, 460.

[24] Shubina, E. S.; Belkova, N. V.; Krylov, A. N.; Voronstov, E. V.; Epstein, L. M.; Gusev, D. G.; Nidermann, M.; Berke, H. *J. Am. Chem. Soc.* **1996**, *118*, 1105.

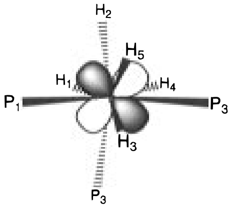


Figure 7. Location of the HOMO in **7** showing it is somewhat removed from H1−H2, the site of H⋯H bond formation, which lie behind the plane of the paper, which is also the plane of the orbital in question.

Table 1. H-Bond Energies (kcal/mol) for the 1:1 Adducts of a Variety of Proton Donors and the Complexes $ReH_5(PPh_3)_3$ and $ReH_7(dpe)$, according to IR Data in a Thin Film[a]

H bond donor	ν(free)[b]	ν(H-bonded)	$\Delta\nu$	$-\Delta H°$	pK_a
		$ReH_5(PPh_3)_3$			
PhNHMe	3433	3334	99	3.0	29
pyrrole	3477	3234	243	4.8	23
indole	3469	3328	141	3.6	21
2-^{t}Bu-6-MeC_6H_3OH	3597	3237	360	5.8	19
2,4,6-$Me_3C_6H_2$OH	3600	3270	330	5.6	18
		$ReH_7(dpe)$			
PhNHPh	3400	3381	19	1.3	25
pyrrole	3477	3351	126	3.4	23
indole	3469	3351	118	3.3	21
2-^{t}Bu-6-MeC_6H_3OH	3597	3413	184	4.2	19
2,4,6-$Me_3C_6H_2$OH	3600	3362	238	4.7	18

[a] Data from ref 24. dpe = $Ph_2PCH_2CH_2PPh_2$. [b] $\Delta\nu$(free) from our own experimental data.

structure is not just an artifact, a result of crystal packing forces.

Apart from its relevance to these H-bonding studies, indole is likely to be a useful crystallization reagent whenever a molecule having H-bonding proton acceptor groups does not crystallize well under conventional conditions.

Role of the Nonbonding Electrons on the Metal

The hydrides studied above have d^6 (Ir(III)) or d^2 (Re(V)) electronic configurations which mean that they possess nonbonding electron pairs. Since metals can act as H bond proton acceptors using such electron pairs,[6] it might be the case that the interaction with the hydride is incidental and that the H bond proton donor is primarily interacting with nonbonding metal electrons. That this is not the case is suggested by the strong H⋯H bonds formed by amine−borane and the fact that the nonbonding pair in **7** is located in a position somewhat removed from the indole NH (see Figure 7).

If this idea is correct, d^0 polyhydrides should form H⋯H bonds with proton donors. Cocrystallization proved ineffective in this case, and we turned to IR studies on films formed by evaporation of CH_2Cl_2 solutions of proton donor and proton acceptor.[25a] These studies (Table 1) showed that intermolecular adducts were formed between the d^2 polyhydride [$ReH_5(PPh_3)_3$] or the related d^0 polyhydride [$ReH_7(PPh_3)_2$] and a variety of NH and OH proton donors. 2-*tert*-Butyl-6-methylphenol is a particularly useful acid in that it has no tendency to self-associate. In the case of **7** we find an essentially identical IR spectrum in the film and in the crystal, validating the procedure. The adducts formed with the d^0 polyhydride are almost as strongly bound as with the d^2 polyhydride, suggesting that the H⋯H interaction is predominant.

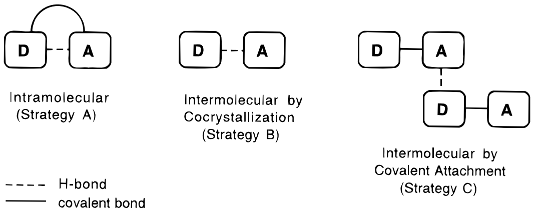
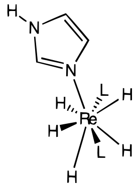


Figure 8. Strategies used in obtaining crystallographic evidence for the interactions discussed. Reprinted with permission from ref 25a Copyright 1995 Royal Society of Chemistry.

Strategy for Structural Studies

In initial work on **2**, **5**, and **6**, we tied the donor (D) and acceptor (A) together in such a way that they could form an intramolecular H bond (strategy A in Figure 8). This has the disadvantage that the structure observed may be modified by the constraints of chelation. To avoid these problems, we moved to the case in which the proton donor and acceptor are distinct molecules that we attempt to cocrystallize from solution (strategy B). This proved successful in the case of compound **7**, where we were able to obtain neutron crystallographic data that completely characterized the structural aspects of the interaction. Unfortunately, we found that this approach is not general, because no proton donor we tried other than indole gave a cocrystal with $ReH_5(PPh_3)_3$; instead the donor and acceptor crystallized separately.

We have now moved to a third strategy (shown as C in Figure 8) in which the donor and acceptor are covalently linked in such a way that intramolecular interactions are disfavored. In such a case, we expected that, by guaranteeing a cocrystallization of the donor and acceptor in a 1:1 ratio, we would encourage the formation of intermolecular donor−acceptor interactions. This strategy was tested in the case of complex **8**, where the imidazole ligand acts as the proton donor N−H function.



8

A crystal was studied by X-ray crystallography,[25b] with the key result shown in Figure 9. The packing diagram shows that the D−A molecules do indeed line up head-to-tail in the lattice, but that the H⋯H distances are all >2.4 Å and so are too long to be H-bonding. Remarkably, the crystal also contains free imidazole (occupancy 0.5) from an adventitious imidazole impurity in the recrystallization solvent. The free imidazole is strongly H-bonded to a $ReH_5(PPh_3)_2$(L) molecule, with the closest d(H⋯H) being 1.7 Å (Figure 10). Strong H-bonding is confirmed by the

(25) (a) Peris, E.; Wessel, J.; Patel, B. P.; Crabtree, R. H. *J. Chem. Soc., Chem. Comm.* **1995**, 2175. (b) Patel, B. P.; Yao, W.; Yap, G. P. A.; Rheingold, A. L.; Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1996**, 991.

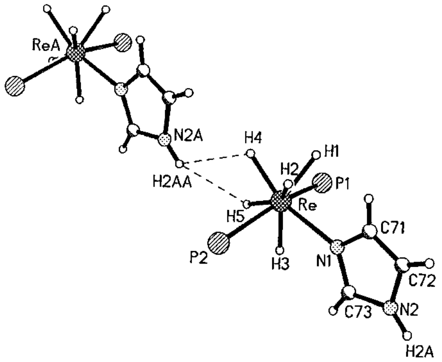


Figure 9. Packing of molecules of [$ReH_5(PPh_3)_2$(imidazole)] in the X-ray crystal structure of **8**, showing the N–H···H2Re interaction, following strategy C of Figure 8. Selected distances (Å): H(2AA)···H(4), 3.55(7), H(2AA)···H(5), 2.60(8); all distances normalized. Reprinted with permission from ref 25a. Copyright 1995 Royal Society of Chemistry.

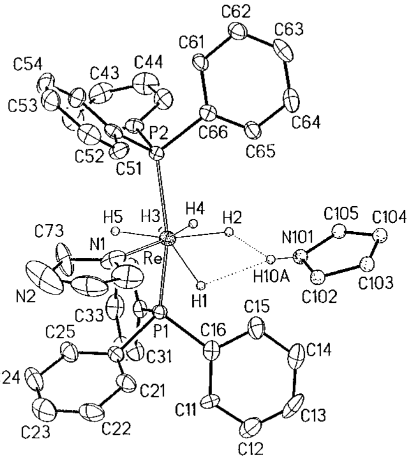


Figure 10. Interaction between the imidazole of crystallization and the metal hydrides in the X-ray crystal structure of **8**. Selected distances (Å): H(10A)···H(2), 1.68(2), H(10A)···H(1), 1.99(8); all distances normalized. Reprinted with permission from ref 25a. Copyright 1995 Royal Society of Chemistry.

shift of the ν(N–H) band in the IR spectrum of the adduct which corresponds[23] to a ΔH of interaction of 5.3 kcal/mol. Growing crystals in the absence of free imidazole does not lead to the formation of a strongly H-bonded head-to-tail polymer, as shown by IR spectroscopy. This suggests that the imidazole may be too rigid a link between the Re–H and N–H bonds, and we are now trying more flexible systems.

Future Prospects

Hydrogen-binding is ubiquitous in enzymes, where it is believed to enhance selectivity by binding the substrate(s), and to accelerate reactions by strong binding of the transition state. So far, hydrogen-bonding has been employed very little in homogeneous catalysis, but it is possible that useful applications of H-bonding may be found in the future.

Conclusion

Unconventional hydrogen bonds are formed between proton donors with OH and NH bonds and a variety of metal hydrides, including boron hydrides, as proton acceptors. This illustrates the basicity[26] of M–H bonds. The CSD can be used as a source of information on outer sphere interactions, even in cases where the original authors did not identify them. In this way we were able to characterize the B–H···H–N H-bond. The strength of the interaction, in the range 3–7 kcal/mol, is comparable with those of conventional N–H···N H-bonds. A variety of strategies have been developed for the structural characterization of these new H-bonds. We find that the X–H···(HM) angle is normally close to linear, but the (XH)···H–M angle is usually strongly bent. The H···H distance is usually in the range 1.7–1.9 Å. The H-bonding gives rise to a number of reactions, including proton transfer and σ bond metathesis. Such species are probably intermediates in protonation reactions of metal hydrides. Intermolecular versions of the interaction are also strong. It may be possible to use intra- and intermolecular H-bonds to influence structure, equilibria, and reactivity in transition metal complexation and catalysis, in molecular recognition, and in designing catalysts for such reactions as asymmetric hydrogenation. After all, Nature uses hydrogen bonds very successfully in enzymes, so we might benefit by introducing them into our synthetic catalysts.

R.H.C. particularly thanks Dr. Jesse Lee, who discovered the complex **2** *that began our work, Dr. Jeremy Wessel who grew the crystal of* **7***, Professor Eduardo Peris (Castellón, Spain) and Mr. Thomas Richardson for key contributions, Professor Kenneth G. Caulton for valuable discussions, Professor Paul Pregosin for help in the spectroscopy, the National Science Foundation for funding, and the CNRS for funding a stay in O.E.'s laboratory. O.E. thanks Gjergji Sini, A.L.R. thanks Dr. Glenn Yap, and T.F.K. thanks Professor Alberto Albinati (Milan), Mr. Jeffery Fortin, and Professor John Ricci (University of Southern Maine) for their collaboration, and the U.S. DOE, Office of Basic Energy Sciences, for support under Contract DE-AC02-76CH00016.*

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[26] (a) Significant Lewis base character for M–H bonds is also evident in their ability to back-bond to the CO π^* orbital in stabilizing such d^0 hydrides as [$Cp_2Zr(H)_2(CO)$], where one would normally not expect CO binding to be possible.[26b] (b) Brintzinger, H. H., *J. Organomet. Chem.* **1979**, *171*, 337.