d^0 and d^2 Polyhydrides as Unconventional Proton Acceptors in Intermolecular Hydrogen Bonding

Eduardo Peris, Jeremy Wessel, Ben P. Patel and Robert H. Crabtree*

Yale Chemistry Dept., 225 Prospect St., New Haven, CT 06511, USA

Intermolecular hydrogen bonds form between a variety of weak proton acids such as indole and 2,4,6-$Me_3C_6H_2OH$ and the transition-metal hydrides $[ReH_5(PPh_3)_3]$, $[ReH_7(Ph_2PCH_2CH_2PPh_2)]$ and $[WH_4(PMePh_2)_4]$; the strengths of the hydrogen-bond interactions are compared by IR data.

Intramolecular hydrogen bonding[1] has recently been demonstrated[2,3] between an OH or NH bond as weak acid (or proton donor) and an M–H bond as weak base (or proton acceptor). We were interested to know if an intermolecular version of this interaction would be possible and have very recently described[4] the neutron-diffraction structure of $[ReH_5(PPh_3)_3$·indole] **1** which shows the presence of an intermolecular three-centre N–H···H_2Re hydrogen bond in which the proton is close to two ReH hydride ligands (d_{HH} 1.75, 2.25 Å). For a variety of other hydrogen-bond donors, cocrystallization to give diffraction quality crystals has not yet proved possible, so we have looked for an alternative method to characterize the interaction.

We now find that evaporation of a CH_2Cl_2 solution of $[ReH_5(PPh_3)_3]$ containing 1 mol equiv. of indole gives a film having an IR spectrum similar to that of the fully characterized $[ReH_5(PPh_3)_3$·indole] single crystal. In both the film and the crystal, the ν(NH) vibration of the indole is shifted to lower energy and broadened in a way typical[1] for hydrogen bonding. In such a case, the Δν(NH) is known[5] to correlate quantitatively with the $\Delta H°$ of the hydrogen bond interaction. This method therefore allows us not only to tell rapidly whether an intermolecular hydrogen bond can form in any particular case but also to estimate the $\Delta H°$ of the interaction.

All the prior cases of N–H···H–M and O–H···H–M hydrogen bonds have involved metals with an electronic configuration of d^2 or higher, where the metals have non-bonding electron pairs. We were not previously able to eliminate the possibility that these electron pairs might at least contribute to, or perhaps even dominate, the hydrogen-bond interaction. In apparent accord with this picture, such hydrogen bonds are often strongly bent at the metal hydride, with M–H–H angles far from 180°; for example, in **1** this angle is 117.1°. Such bending may have resulted from the NH group being attracted to the non-bonding electron pair site. However, our earlier *ab initio* electronic structure calculations[4] on **1** suggested that the non-bonding electron pair of the d^2 Re is localised in a position sufficiently removed from the indole NH so as to suggest it is not significantly involved in the hydrogen-bond interaction.

The IR film method has now allowed us to compare the hydrogen bond strengths for the d^2 $[ReH_5(PPh_3)_3]$ with those for the analogous d^0 complex $[ReH_7(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), as well as the d^2 $[WH_4(PMePh_2)_4]$. The results show that hydrogen bonding takes place in all three hydrides including the d^0 complex, and therefore the presence of a metal electron pair is not essential for an interaction to occur. The hydrogen bond strengths are slightly lower for $[ReH_7(dppe)]$ and $[WH_4(PMePh_2)_4]$ than for $[ReH_5(PPh_3)_3]$. Shubina *et al.*[6] have recently reported hydrogen bonding between O–H donors and $[WH_4(dppe)_2]$ which they ascribe to O–H···M hydrogen bonding *via* the metal electron pair; from our results O–H···H–M hydrogen bonding may be more likely.

The film IR method has also allowed us to show that the intermolecular interactions found in **1** are general for a variety of proton donors and the metal polyhydrides $[ReH_5(PPh_3)_3]$, $[ReH_7(dppe)]$ and $[WH_4(PMePh_2)_4]$ (Table 1). The $\Delta H°$ of the interaction depends on the pK_a of the proton donor[7] (Fig. 1) although the steric properties of the donor may also play a role. This correlation would be expected[1] if we are correct in considering this X–H···H–Ir interaction (X = O, N) as a hydrogen bond and suggests that all the adducts are of a similar type. The position of the hydrogen-bonded absorption does not vary upon changing the polyhydride molar ratio and formation of 1 : 1 adducts as found in **1** is most likely.

Control experiments in the absence of metal hydride were necessary to eliminate the possibility that the hydrogen-bonded band ν(XH) is the result of self association. In this context, we find that one of the hydrogen-bond donors we have studied,

Table 1 Hydrogen bond energies (kcal mol^{-1}) for the complexes $[ReH_5(PPh_3)_3]$, $[ReH_7(dppe)]$ and $[WH_4(PMePh_2)_4]$ according to IR data

H-Bond donor	$\nu(XH_{free})^a$	$\nu(XH_{H\text{-bonded}})$	Δν	$-\Delta H^{0b}$	$pK_a{}^c$
$ReH_5(PPh_3)_3$					
PhNHMe	3433	3334	99	3.0	29
PhNHBn	3422	3320	102	3.1	27
PhNHPh	3400	3287	113	3.3	25
Pyrrole	3477	3234	243	4.8	23
Indole	3469	3328	141	3.6	21
2-Bu^t-6-MeC_6H_3OH	3597	3237	360	5.8	19
2,4,6-$Me_3C_6H_2OH$	3600	3270	330	5.6	18
$ReH_7(dppe)$					
PhNHPh	3400	3381	19	1.3	25
Pyrrole	3477	3351	126	3.4	23
Indole	3469	3351	118	3.3	21
2-Bu^t-6-MeC_6H_3OH	3597	3413	184	4.2	19
2,4-6-$Me_3C_6H_2OH$	3600	3362	238	4.7	18
$WH_4(PMePh_2)_4$					
PhNHMe	3433	3421	12	1.1	29
Pyrrole	3477	3446	31	1.7	23
Indole	3469	3430	39	1.9	21
2-Bu^t-6-MeC_6H_3OH	3597	3322	275	5.1	19
2,4,6-$Me_3C_6H_2OH$	3600	3317	283	5.2	18

[a] Δν(XH,free) (± 2 cm^{-1}) from our own experimental data (X = O or N). [b] In kcal mol^{-1} (± 0.2 kcal mol^{-1}) by the method of ref. 5. [c] pK_a values from ref. 7.

2-*tert*-butyl-6-methylphenol, is particularly useful in that it does not self associate at all.

The results show that intermolecular hydrogen bonding is not limited to complex **1** and that the major interaction is that between the M–H bond and the hydrogen-bond donor, with the metal electron pair playing, at most, a minor role, at least in the cases studied here. This picture is confirmed by our very recent finding[8] that short B–H···H–N hydrogen bonds are present in a variety of amine boranes, in which there are no non-bonding electron pairs, and for which d(H···H) is 1.7–1.9 Å and the bond strength is *ca.* 7 kcal mol^{-1} (1 cal = 4.184J).

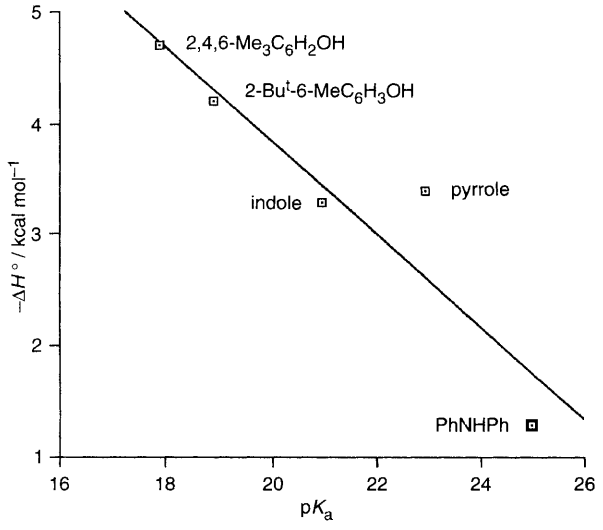

Fig. 1 A plot of the ΔH^0 of hydrogen bond strength between [ReH_7(dppe)] and a variety of hydrogen-bond donors, *versus* pK_a of the donor. The ΔH^0 values were estimated[5] from IR data.

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