# Infrared Detection of M–H···OPPh$_3$ Hydrogen Bonds

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M–H···OPPh$_3$ hydrogen bonds are detected for a variety of cationic iridium hydrides of the type [IrH$_2$L$_2$(PPh$_3$)$_2$]$^+$ and [IrH(bzquin)L′(PPh$_3$)$_2$]$^+$ for which IR studies give estimates of the hydrogen-bond free energies of 10–13 kJ mol$^{-1}$, the strongest being associated with those compounds having more electron-withdrawing ligands.

Intramolecular[1] hydrogen bonding has recently been demonstrated in a number of metal hydrides, but in all these cases, the M–H bond has always behaved as the weak base or hydrogen-bond acceptor component of the bond. We have also reported[1e] the neutron-diffraction structure of [ReH$_5$(PPh$_3$)$_3$·indole] **1** which shows the presence of an intermolecular three-centre N–H···H$_2$Re hydrogen bond in which the proton is close to two ReH hydride ligands ($d_{HH}$ = 1.75 and 2.25 Å). Theoretical studies[1e] suggest that the interaction is strong (*ca.* 20.9 kJ mol$^{-1}$) in part due to the polarization of the Re–H bond which enhances the δ– character of the hydride, allowing it to behave as a weak base.

Some M–H bonds are known to have acidic properties,[2] and so hydrogen bonding in the opposite sense, with the M–H acting as the weak acid, or hydrogen-bond donor component, might be possible. The proximity of a weak base would be expected to cause a polarization of the M–H bond in the opposite sense to that present in **1**, and so enhance the interaction. In the case of **1**, we were able to demonstrate the interaction by growing a crystal containing both the metal complex and the hydrogen-bond donor, indole, but several analogous attempts to grow crystals with different metal hydrides and a variety of hydrogen-bond acceptors have not yet proved successful. In the absence of structural data, we have used an IR method to attempt to better characterize this new type of interaction and estimate the hydrogen-bond energies. A recent paper by Epstein *et al.*[3] has suggested that this new type of hydrogen-bonding interaction is possible in the case of the very acidic hydride, [OsH(η-C$_5$H$_5$)$_2$]$^+$; we have confined our study to hydride complexes of unexceptional acidity, of the sort that are much more commonly studied by inorganic chemists.

We find that evaporation of a CH$_2$Cl$_2$ solution of indole and OPPh$_3$ (1 : 1 molar ratio) on a KBr plate gives a film having an IR spectrum with a characteristic broad band (3208 cm$^{-1}$) due to the N–H stretching frequency of an indole···OPPh$_3$ hydrogen-bonded species. Iogansen's equation[4] allows us to estimate that $-\Delta H°$ for this interaction is 16.7 kJ mol$^{-1}$. The value of $-\Delta G°$ has been reported to be 10.5 kJ mol$^{-1}$.[5] In order to determine if there is any L$_n$M–H···OPPh$_3$ hydrogen bond to OPPh$_3$ for any given complex, L$_n$M–H, we have studied the competitive equilibrium of eqn. (1). The metal hydride, L$_n$M–H, competes

$$\text{indole}\cdots\text{OPPh}_3 + \text{L}_n\text{M–H} \rightleftarrows \text{indole} + \text{L}_n\text{M–H}\cdots\text{OPPh}_3 \quad (1)$$

with indole for hydrogen bonding with OPPh$_3$ in the system [indole···OPPh$_3$]. Typical spectra in the ν(NH) region are shown in Fig. 1.

As L$_n$M–H, we used the series of metal hydrides shown in Table 1. By using the technique described above, we obtained spectra of 1 : 1 : 1 molar ratio mixtures of indole : OPPh$_3$ : L$_n$M–H for the series of hydrides. The existence of the expected adduct, M–H···OPPh$_3$ can be easily detected by the appearance of the characteristic sharp N–H peak of free indole at 3469 cm$^{-1}$. By comparing the ratio of the integrated areas of the bands corresponding to the ν(N–H) of the free and hydrogen-bonded indole for the different metal hydrides used, we can estimate the hydrogen-bond energies in the series. Control experiments with [NEt$_4$]BF$_4$ and neutral hydride complexes such as [ReH$_7$(PPh$_3$)$_2$] show no free indole, so neither the counter ion nor the phosphines affect the indole···OPPh$_3$ adduct. Fig. 1 compares the spectrum of a mixture of indole : OPPh$_3$ : [IrH$_2$(bpy)(PPh$_3$)$_2$]BF$_4$ in 1 : 1 : 1 mole ratio with that of the indole : OPPh$_3$ adduct.

Experiments performed with the metal hydrides and OPPh$_3$ combined in 1 : 1 molar ratio (in the absence of indole) indicate the presence of a PO···H–M interaction. The ν(M–H) band shows a significant increase in intensity, but no significant shift in energy for any of the cationic systems studied. The strong ν(P–O) band at 1193 cm$^{-1}$ for free Ph$_3$PO is accompanied in the hydrogen-bonded adducts by a new band at 1167m cm$^{-1}$. These changes in ν(M–H) and ν(P–O) are in very close agreement with the previously reported results of Epstein *et al.*[3]

The results show that hydrogen bonds are indeed formed with all the cationic hydrides, the strongest being with [IrH$_2$(CO)$_2$(PPh$_3$)$_2$]BF$_4$, which would also be expected to be the most acidic in the series. For the rest of the series, there is a slight trend towards an increase of the free energy of the hydrogen bond with increasing electron-withdrawing character of the ligands. The neutral rhenium hydrides studied did not show free

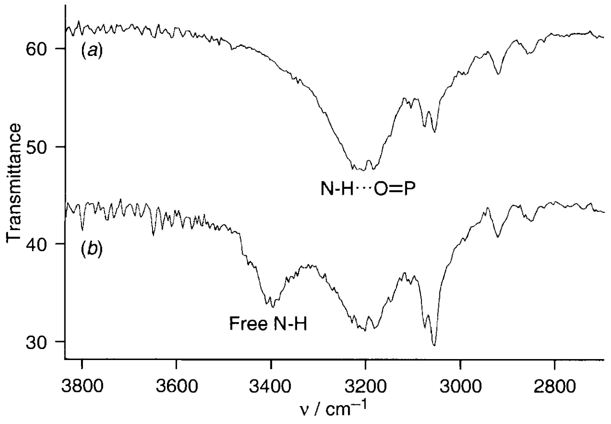

**Fig. 1** IR spectra in the ν(N–H) region of (*a*) indole + OPPh$_3$ (1 : 1 molar ratio) and (*b*) indole + OPPh$_3$ + [IrH$_2$(bpy)(PPh$_3$)$_2$]BF$_4$ (1 : 1 : 1 molar ratio). Transmittance in arbitrary units.

**Table 1** N–H intensity ratios and free energies (kJ mol$^{-1}$) estimated from IR data (errors from the standard deviation of a series of three measurements)

| Compound | $I$(N–H$_{free}$)/ $I$(N–H$_{H\text{-bonded}}$) | $\Delta G^a$ | $\Delta G^b$ |
|---|---|---|---|
| Indole | 0.78 | 0 | 10.5 |
| [IrH$_2$(Me$_2$CO)$_2$(PPh$_3$)$_2$]BF$_4$ | 0.66 | −0.4 | 10.1 ± 0.3 |
| [IrH$_2${P(OMe)$_3$}$_2$(PPh$_3$)$_2$]BF$_4$ | 0.86 | 0.5 | 11.0 ± 0.2 |
| [IrH$_2$(bpy)(PPh$_3$)$_2$]BF$_4$$^c$ | 0.85 | 0.4 | 10.9 ± 0.2 |
| [IrH$_2$(CO)$_2$(PPh$_3$)$_2$]BF$_4$ | 1.21 | 2.2 | 12.7 ± 0.3 |
| [IrH(CH$_3$CN)(bzquin)(PPh$_3$)$_2$]BF$_4$$^d$ | 0.70 | −0.5 | 10.0 ± 0.2 |
| [IrH(CO)(bzquin)(PPh$_3$)$_2$]BF$_4$ | 0.82 | 0.3 | 10.8 ± 0.2 |
| [ReH$_7$(AsPh$_3$)$_2$] | $^e$ | | |
| [ReH$_7$(PPh$_3$)$_2$] | $^e$ | | |
| [ReH$_5$(PPh$_3$)$_3$] | $^e$ | | |
| [IrH$_2$(CF$_3$CO$_2$)(PPh$_3$)$_2$] | $^e$ | | |

[a] Values referred to the indole–OPPh$_3$ free energy. [b] Absolute values using the ΔG for indole–OPPh$_3$ obtained from the data in ref. 5. [c] bpy = 2,2′-bipyridyl. [d] bzquin = 1,8-benzoquinolinato-*C,N*. [e] No hydrogen bond formed.

indole and so these, with their more basic hydrides, are incapable of hydrogen bonding significantly to $OPPh_3$.

We have also studied the analogous equilibrium using the much stronger hydrogen-bond donor, 2-*tert*-butyl-6-methylphenol, for which the $O–H\cdots OPPh_3$ bond energy is *ca.* 25.1 kJ $mol^{-1}$ ($-\Delta H^\circ$, Ioganser equation). As expected, in no case did we see displacement of the free phenol from the phenol$\cdots OPPh_3$ adduct.

Hydrogen bonds have been detected between $OPPh_3$ and a variety of cationic iridium hydrides and their strengths have been estimated by IR studies on equilibria of the type shown in eqn. (1); neutral rhenium hydrides gave no evidence for hydrogen bonding. This is the reverse of the situation for $N–H\cdots H–M$ hydrogen bonding, studied previously,[1] where hydrogen bonding took place only for the neutral rhenium species but not for the cationic iridium complexes of Table 1. This is consistent with the $N–H\cdots H–M$ hydrogen bonding requiring hydridic character and $M–H\cdots OPPh_3$ hydrogen bonding requiring protonic character for the MH hydrogen. Theoretical studies are in progress.[6]

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## Footnote

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