# An Unusual Type of H···H Interaction: Ir−H···H−O and Ir−H···H−N Hydrogen Bonding and Its Involvement in σ-Bond Metathesis

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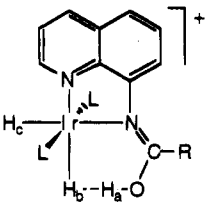
**Abstract:** A series of metal hydride complexes is described (**1**, **6**, and **7**) containing X−H···H−Ir (X = O or N) hydrogen bonds. The H···H distance is short, about 1.8 Å, as in the N−H···H−Ir system independently discovered recently (1994) by Ramachandran and Morris, but much shorter than the prior (1990) O−H···H−Ir system of Milstein et al. A *J*-coupling of 2−4 Hz in the NMR spectrum is often found between $H_a$ and $H_b$ in X−$H_a$···$H_b$−Ir. Exchange between $H_a$ and $H_b$ occurs on the NMR time scale, probably via proton transfer to give hydrogen complexes X···($H_2$)−M as intermediates. The interaction activates the Ir−H bond for reactions such as substitution, and cyclometalation. NMR data indicates an H-bond strength of 4.3 ± 0.8 kcal/mol in one case (**7**). The species give σ-bond metathesis reactions and easily lose $H_2$ to give a cyclometalated derivative, a reaction which is reversible in some cases. Reasons for the formation of a strong H-bond in this case are proposed: the close approach possible for $H_a$ and $H_b$; the absence of lone pair repulsion; and the high polarizability of the Ir−H bond.

## Introduction

Hydrogen bonding is a well-recognized phenomenon of wide significance.[1] It normally involves a weak acid, AH, binding to a weak base, B, with an interaction energy of 2−10 kcal/mol to give a near-linear A−H···B structural arrangement, as in the water dimer, HO−H···$OH_2$. The case in which an element−hydride bond acts as the weak base component (B) is of special interest because it leads to a close H···H interaction.

We briefly reported such a case[2] (**1a**) in which an apparent hydrogen bond is formed between an RO−H group as weak acid and a metal hydride as weak base; the H···H distance was estimated at 1.8 Å. A much weaker O−H···H−Ir interaction ($d$(H···H) = 2.4 Å, based on neutron diffraction[3b]) was reported in 1986 by Milstein et al.,[3a] and an N−H···H−Ir example ($d$(H···H) = 1.8 Å) recently independently discovered by Ramachandran and Morris[4] may be of similar strength to our own.

We now report the full details for a series of complexes of type **1**, and report on a related series of H-bonded species (**6** and **7**). We show how H-bonding can activate the Ir−H bond for reactions such as isotope exchange, substitution, and cyclometalation.



**1**

R = Me, **a**; n-Bu, **b**; p-tolyl, **c**; Ph, **d**; p-$FC_6H_4$, **e**; 3,4-$F_2C_6H_3$, **f**.

## Results and Discussion

Neutral amides, normally poor ligands for platinum metals, can bind via O or N.[5] In the reaction of [$IrH_2$(acetone)$_2$($PPh_3$)$_2$]-$SbF_6$ (**2**)[6] with *N*-quinolin-8-ylacetamide (**3a**), it seemed unlikely that **3** could bind via O, and we expected it to give an N−H···Ir system.[7] Instead, the amide tautomerizes to the iminol form **3′**, which binds to Ir and takes part in an unexpected O−H···H−Ir hydrogen bond. Iminol complexes such as [(dien)PtNH=C(OH)Me]$^{2+}$ have so far only been detected spectroscopically.[8]

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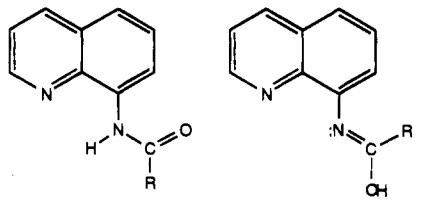
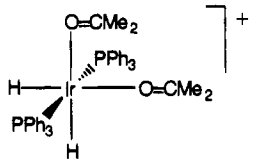


**3** **3'**

R = Me, **a**; n-Bu, **b**; p-tolyl, **c**; Ph, **d**; p-$FC_6H_4$, **e**; 3,4-$F_2C_6H_3$, **f**; t-Bu, **g**.

**Synthesis and Structure of 1.** Complex **2** reacts with amide **3a** to give the pale yellow microcrystalline dihydrido(quinoline-8-acyliminol)bis(triphenylphosphine)iridium(III) compound **1a** (71%).



**2**

Crystals were grown from $CH_2Cl_2$–hexanes under $H_2$ for an X-ray diffraction study, which has been reported elsewhere.[2] The results show that the amide group of **3a** has tautomerized to the iminol form (**3'a**) so that the essentially planar iminol can bind via the imine nitrogen. The O–$H_a$ hydrogen, although not detected in the X-ray structure, gives a feature at a position (+9.54 ppm, intensity 1H) in the $^1$H NMR spectrum expected[8] for an iminol OH. The Ir–$H_b$ hydrogens were not detected in the X-ray structure, but the cis $^2J$(P,H) coupling shows that they complete the octahedron expected for Ir(III).

The OH proton is coupled {$^1J(H_a,H_b)$ = 3 Hz} to one of the Ir–H resonances, assigned as $H_b$ in **1**; this was confirmed by decoupling $H_b$. If there were no hydrogen bond, the observed H,H coupling of 3 Hz would have to result from transmission through five bonds, which seems unlikely. H,H coupling was not reported in either the Milstein or Morris X–H···H–M compounds, however.[3,4] The X-ray structure shows that the OH oxygen is located close to the position occupied by the Ir–$H_b$ hydride.

The H···H distance in the hydrogen bond, calculated from the Ir–$H_b$ and O–$H_a$ positions on the basis of an octahedral geometry with $d$(Ir–H) = 1.65 Å, $d$(O–H) = 1.00 Å, and planarity of the ligand, is 1.58 Å. The H-bonded protons show somewhat short $T_1$ values (Ir–$H_b$, 262 ms at 300 MHz and 183 K; O–H, 202 ms). Although a minimum $T_1$ could not be obtained for this compound (but see later for a successful measurement on a related compound), similar compounds show minima around this temperature. If we assume we are near the minimum at 183 K, these data are most consistent[9] with a $d$(H···H) of about 1.8 Å; this would be compatible with the crystal structure if the OH proton were located slightly out of the quinoline plane.

The C–O bond in **1** is *syn* to the N–Ir group, in sharp contrast to the *anti* arrangement of C=O and N–H always found in unconstrained amides. This is likely to be a result of the intramolecular hydrogen bonding, only possible in the *syn* conformation, or may indicate that iminols, unlike amides, do not show a strong preference for an anti conformation.

**Table 1:** Key Spectral Data for the Quinoline Complexes

| | $^1$H NMR (ppm): $\delta$ OH, $^1J(H_a,H_b)$ $\delta$ Ir–$H_a$, $\delta$ Ir–$H_b$ | IR (film) (cm$^{-1}$): $\nu$(O–H) $\nu$(Ir–H) |
|---|---|---|
| **1a** (R = Me) | 9.54 (d), $J$ = 3.0 Hz[a] | 3310 |
| | −19.09 (td), −19.29 (m) | 2152.0 |
| **1b** (R = *n*-Bu) | 9.70 (d), $J$ = 3.6 Hz[a] | 3362 |
| | −19.11 (td), −19.23 (m) | 2164.9, 2117.6 |
| **1c** (R = *p*-tolyl) | 9.90 (d), $J$ = 3.8 Hz[b] | 3445 |
| | −18.94 (td), −19.12 (m) | 2181.1, 2122.3 |
| **1d** (R = Ph) | 9.98 (d), $J$ = 3.8 Hz[b] | 3403 |
| | −18.94 (td), −19.05 (m) | 2175.2, 2115.7 |
| **1e** (R = *p*-$FC_6H_4$) | 9.90 (d), $J$ = 3.8 Hz[c] | 3386 |
| | −18.98 (td), −19.09 (m) | 2170.9, 2121.1 |
| **1f** (R = 3,4-$C_6H_3F_2$) | 9.98 (d), $J$ = 3.9 Hz[c] | 3409 |
| | −19.02 (br t) | 2181.8, 2122.8 |

[a] Observed at 20 °C. [b] Observed at −20 °C. [c] Observed at −40 °C.

A series of related complexes was prepared by the same synthetic route but replacing amide **3a** with amides having R = *n*-Bu, **3b**; *p*-tolyl, **3c**; Ph, **3d**; *p*-$FC_6H_4$, **3e**; 3,4-$F_2C_6H_3$, **3f**. Complexes of type **1** (**1b–f**) were isolated in each case. The spectral data are reported in Table 1. The $J(H_a,H_b)$ value is not always resolved at 20 °C due to fast exchange between OH and IrH, but can be clearly observed at lower temperatures. Particularly notable is **1f**, where $^1J(H_a,H_b)$ is 3.9 Hz at −40 °C, the largest value we have seen; larger $^1J(H_a,H_b)$ values presumably indicate stronger H-bonding. These trends are reasonable: as R becomes more electron-withdrawing, the acidity of the OH group, and therefore the strength of the H-bond, is expected to increase. As in **1a**, the Ir–H stretching frequencies of **1b–f** all appear around 2120 cm$^{-1}$, lower than in **2** (2252 cm$^{-1}$), and are significantly broader than for the non-H-bonding Ir–H.

In the case of the reaction of **2** with **3g** (R = *t*-Bu), the H-bonded species **1** is not formed. Examining models suggests that the *t*-Bu group of **3g** would interfere with the adjacent aryl-C–H bond in a complex of type **1**. Instead, an Ir–NH species is formed in which the amide tautomer **3g** binds to Ir via the quinoline N and the amide N lone pair. This type of species is also observed by NMR for **1a–f** when the reaction of **2** and **3a–f** is carried out at −80 °C. Conversion of the Ir–NH intermediate into **1** takes place smoothly at 20 °C. The characterization of the species bound via the amide N lone pair has been carried out by X-ray structural and $^{15}$N NMR studies and is fully described in another paper.[10]

If the O–H···H–Ir interaction can properly be described as a hydrogen bond, it should be possible to break it with a sufficiently powerful H-bond acceptor. We find that the presence of $Ph_3PO$ (0.15 mM) does indeed cause loss of the $^1J(H_a,H_b)$ coupling in **1a**, which we ascribe to O–H···OPPh$_3$ hydrogen bonding. No breakage of the O–H···H–Ir interaction is observed with the weaker H-bond acceptors, acetone or ethanol.

**Proton Exchange in 1.** The H-bonding activates the Ir–H bond for a number of reactions. The simplest reaction of **1** is exchange between the O–$H_a$ and the Ir–$H_b$ protons. This can be followed by line broadening and coalescence studies in the NMR spectrum. $H_a$ and $H_b$ exchange much more slowly with $H_c$, consistent with a specific activation of the Ir–$H_b$ bond by H-bonding. The results (Table 2) show that $\Delta G^{\ddagger}$ values go

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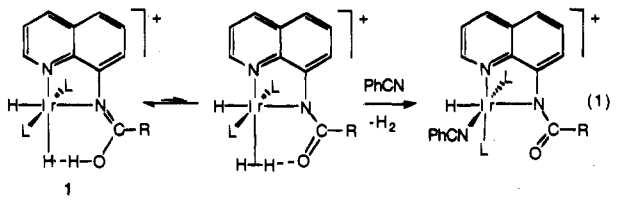
**Table 2:** Thermodynamic Data for the Proton Exchange in Complexes of Type 1, Obtained from VT NMR Data[a]

| | $\Delta G^{\ddagger}_{293K}$ (kcal/mol) | $\Delta H^{\ddagger}$ (kcal/mol) | $\Delta S^{\ddagger}$ (eu) |
|---|---|---|---|
| **1b** (R = *n*-Bu) | 18 ± 4 | 16 ± 3 | −7 ± 3 |
| **1c** (R = *p*-tolyl) | 19 ± 3 | 16 ± 3 | −8 ± 3 |
| **1d** (R = Ph) | 17 ± 2 | 16 ± 2 | 6 ± 3 |
| **1e** (R = *p*-$FC_6H_4$) | 16 ± 3 | 14 ± 2 | 7 ± 4 |
| **1f** (R = 3,4-$C_6H_3F_2$) | 15 ± 2 | 15 ± 2 | 0 ± 3 |

[a] Proton exchange in **1a** is too slow to be accurately calculated by the line-broadening method under accessible temperatures.

down as the R group becomes more electron-withdrawing. This is consistent with a mechanism in which exchange occurs by proton transfer from the OH group to the Ir−$H_a$ to give an $H_2$ complex of general type $[Ir(H_2)H(PPh_3)_2(L\text{-}L)]^+$ (L-L = chelating ligand), which we have previously studied.[11] Rotation of the $H_2$ and back proton transfer to the amide oxygen completes the exchange (eq 1). A similar mechanism had been postulated by Milstein et al. in an Ir system.[12]

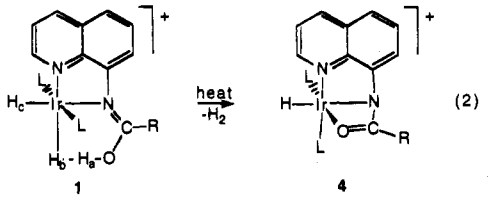



Since $H_2$ complexes are often labile, we thought that the presence of a potential ligand might lead to net displacement of $H_2$. With PhCN (0.02 mM; 1.1 equiv) a benzonitrile complex is formed from **1a** (eq 1). The Ir−H resonance at −17.59 ppm shows cis coupling to two P nuclei ($J$(P,H) = 20 Hz). The $^{31}$P NMR shows two inequivalent P nuclei with a typical cis coupling ($J$(P,P′) = 22 Hz). In the complexes $[IrH_2LL'(PPh_3)_2]^+$ the hydride chemical shift has proved to correlate well[6] with the nature of the trans ligand. In the benzonitrile complex, the hydride shift is most consistent with the amide nitrogen being the trans ligand, and so we prefer the stereochemistry shown in eq 1. The other benzonitrile complexes behave similarly: ppm (H) = −17.54 (R = *p*-tolyl), −17.64 (R = Ph), −17.60 (R = *p*-$FC_6H_4$), −17.66 (R = 3,4-$F_2C_6H_3$) all having $^2J$(P,H) = 20 Hz. We cannot exclude H being trans to quinoline N, however.

For **1f**, where R is the electron-withdrawing 3,4-$C_6H_3F_2$ group, the rate of formation of the PhCN complex ($3 \times 10^{-1}$ $s^{-1}$ at 20 °C) is about 10 times that for **1a** with its electron-donating methyl group ($5 \times 10^{-2}$ $s^{-1}$ at 20 °C). This is consistent with the higher acidity of the OH group in **1f** favoring the formation of the proposed $H_2$ intermediate. Complexes **1a**−**f** do not exchange with $D_2$ on the same time scale, however, and so $H_2$ does not dissociate rapidly. This implies that the PhCN reaction has associative character, implicating an I type mechanism. We verified that the rate of substitution in eq 1 is first order in PhCN.

The proposed proton transfer from the OH group to the M−H bond in **1** is consistent with our prior finding that the $H_2$ ligand is the stronger kinetic acid in a related complex of iridium, $[IrH(H_2)bq(PR_3)_2]^+$ (bq = benzoquinolinate), where M−H and M−($H_2$) must have the same thermodynamic acidity because they share the same conjugate base.[11b] Lapinte et al.[13] have shown that at −80 °C [CpFeH(dppe)] protonates faster at the M−H bond to give $[CpFe(H_2)(dppe)]^+$ as intermediate, which converts irreversibly to $[CpFe(H)_2(dppe)]^+$ at −40 °C (dppe = $Ph_2PCH_2CH_2PPh_2$). In no case has quantum exchange[14] been seen between $H_a$ and $H_b$.

**Reversible Hydrogen Loss from 1.** Although $H_2$ is not lost rapidly from **1** at 20 °C, heating in a sealed tube at 80 °C for 5 h does cause loss of $H_2$ to give **4**, in what is essentially a σ-bond metathesis, as shown in eq 2. Only **1c** (R = *p*-tolyl) loses $H_2$ completely; in the other cases some starting material is always left when irreversible decomposition of the complex sets in. The identification of **4** as a chelate rather than as a 5-coordinate species comes from the IR data which show that the ν(C=O) is shifted from 1678 $cm^{-1}$ in free **3** to 1476 $cm^{-1}$ in **4**. The ν(C=O) absorption of the benzonitrile complex in eq 1, which does have an uncomplexed amide carbonyl, appears at 1601 $cm^{-1}$. The cis arrangement of the phosphines follows from the $^{31}$P NMR, which shows two inequivalent phosphorus nuclei with a characteristic cis coupling ($J$(P,P′) = 22 Hz). This stereochemistry may be favored because it allows the $sp^3$ amide N to become pyramidal. Attempts to grow crystals have so far failed, so the stereochemistry shown is tentative.




We wondered whether this reaction might be reversible and find that **4a** indeed reacts with $H_2$ at 20 °C in $CH_2Cl_2$ over 10 min to give **1′a**, an isomer of **1a** (eq 3). Like **1a**, **1′a** is also an IrH···HO species because the OH and IrH protons are coupled in the proton NMR. The OH appears as a doublet at 9.81 ppm with $^2J(H_a,H_b)$ = 3.0 Hz. Ir−$H_b$ is an unresolved broad triplet ($J$(P,$H_{cis}$) = 15.0 Hz) at −19.90 ppm; the two resonances are mutually coupled because decoupling $H_b$ causes the $H_a$ resonance to collapse to a singlet. Ir−$H_c$ appears as a doublet of a doublet of doublets at −10.86 ppm ($^2J$(P,$H_{trans}$) = 145.7 Hz. $^2J$(P,$H_{cis}$) = 24.0 Hz. $^2J$(H,H′$_{cis}$) = 5.7 Hz). Upon standing (1 day, 20 °C), isomer **1′a** quantitatively reverts to **1a**. The conversion of **1′** to **1** could result from proton transfer to Ir−H, dissociation of $H_2$ and rearrangement.

The reaction of eq 3 is an example of Ir−O bond hydrogenolysis, again a σ-bond metathesis. Since **4** is an 18e complex, dissociation of a ligand is expected to occur before $H_2$ can bind and be activated. In view of our proposed mechanism of $H_2$ loss from **1**, the most likely mechanism for the hydrogenolysis is heterolytic Ir−O bond breaking, coordination of $H_2$ presumably as an $H_2$ complex, and then proton transfer from the bound $H_2$ to the adjacent amide oxygen (eq 3). This is consistent with the high acidity found for closely related $H_2$ complexes, such as $[IrH_2(H_2)_2(PR_3)_2]^+$ and $[IrH(H_2)bq(PR_3)_2]^+$.[11]

If $H_2$ can break the Ir−O bond, we thought that a silane might also do so. **4a** indeed reacts with $Et_3SiH$ at 20 °C in $CH_2Cl_2$ over 10 min to give **5a**, a compound related to **1′a** but with a silylated iminol OH (eq 4). Since silanes readily bind to Ir(III)

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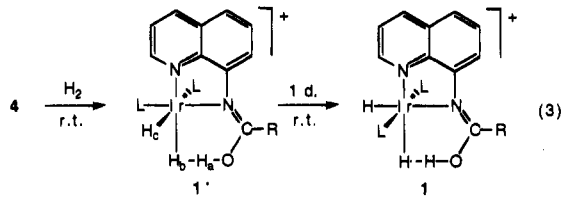
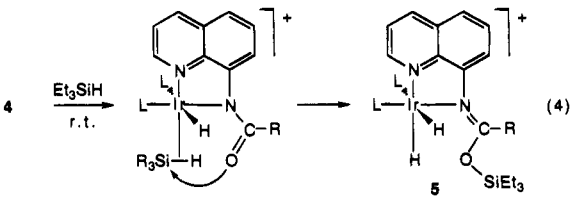
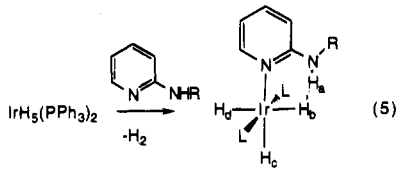



to form $\sigma$-bond complexes[15a] and these complexes readily undergo attack at Si by nucleophiles, the formation of **5** is consistent with the proposed mechanism of eq 4. In both metatheses, $H_2$ and silane, a $\sigma$-bond complex[15b] is the probable intermediate.




**H-Bonded Species with 2-Aminopyridines.** The reaction of the much weaker acid, 2-(phenylamino)pyridine (pyNHPh), with $IrH_5(PPh_3)_2$ at 80 °C in benzene did indeed give the H-bonded derivative **6** in 75% yield. The NMR spectrum in $CH_2Cl_2$ at 20 °C shows three IrH resonances of unit intensity at −9.8, −10.0, and −22.3 ppm, each showing a cis $J$(P,H) coupling of ca. 16 Hz to the two $PPh_3$ groups as well as mutual $J$(H,H′) couplings of ca. 4 Hz. We were surprised to find a trans H,H coupling of this low magnitude; Fryzuk et al. have seen a similar coupling in an Ir(III) compound,[16a] but Morris et al. have found 18.2 Hz for an Fe(III) complex.[16b] One of the IrH protons ($H_b$) is coupled to the NH proton at 10.5 ppm with a $J$(H,H′) of 2.6 Hz, as expected for an H-bonded system. Decoupling and COSY experiments confirm that the NH and IrH are mutually coupled. As expected[16c] for an H-bonded N−H, there is a significant low-field shift in the N−H resonance to 10.5 ppm from the free ligand value (8.2 ppm); no significant shifts are observed in the hydride signals, however.



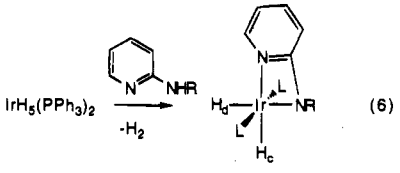

2-Aminopyridine ($pyNH_2$) reacts with $IrH_5(PPh_3)_2$ at 80 °C in benzene to give **7** in 81% yield, a complex similar to **6**, the spectrum of which shows the usual three Ir−H NMR peaks at −90 °C. Exchange phenomena (see below) lead to broad line widths and so the $J$(H,H′) coupling is not directly available, but decoupling $H_b$ does lead to a decrease in the line width of the $H_a$ resonance, suggesting that unresolved coupling is present. As for **6**, the $H_a$ resonance appears at much lower field (7.8 ppm at 183 K) than for the free ligand (4.7 ppm at 183 K) or for the non-H-bonded NH proton (4.4 ppm at 183 K), also evidence for H-bonding.

**The H···H Distance.** The lower $T_1$ (min) values for $H_a$ and $H_b$ in compound **7** ($H_a$, 127 ms at 300 MHz and 213 K; $H_b$, 130 ms at 233 K) versus the other hydride protons ($H_c$, 251 ms at 193 K; $H_d$, 288 ms at 233 K) imply an excess relaxation rate for $H_a$ and $H_b$ of 4.0 $s^{-1}$. Using the standard equations[9] and assuming that the $H_a-H_b$ vector rotates with the molecule as a whole, the $H_a\cdots H_b$ distance can be estimated at about 1.8 Å; a similar $H_a\cdots H_b$ distance was estimated in the same way by Morris.[4]

**Exchange in 6 and 7.** As in the case of **1**, exchange occurs on the NMR time scale between $H_a$ and $H_b$ in **6** and **7**. Once again, proton transfer to give an intermediate $H_2$ complex as the most likely mechanism. Exchange between $H_b$, $H_c$, and $H_d$ also occurs, but on a time scale of minutes, as shown by adding $CD_3OD$ to an NMR sample at 20 °C. The resonances for $H_a$ and $H_b$ disappear at once, followed by a slower disappearance of the signals for $H_c$ and $H_d$. The unsubstituted pyridine complex $[(IrH_3(py)(PPh_3)_2]$ exchanges only slowly (1 h) with $CD_3OD$ under comparable conditions, so the H-bonding gives **6** and **7** a way to exchange rapidly with MeOD. This implies that H-bonding specifically activates the Ir−$H_b$ bond for exchange.

**Strength of the H-Bond.** In the case of **7** (R = H), the two H substituents of the $NH_2$ group (4.4 and 7.8 ppm at 183 K) undergo exchange with a coalescence temperature of 253 K (300 MHz), which corresponds to a $\Delta G^{\ddagger}$ of 10.8 ± 0.2 kcal/mol for the rotation about the C−N bond. This value, slightly higher than those observed in the literature for the bond strengths of conventional H-bonds (2−10 kcal/mol), must represent the sum of the H-bond strength and the intrinsic rotation barrier of an amino group bound to an aromatic ring. This rotation barrier is known[17] to be 6−7 kcal/mol, so the H-bond strength must be about 4.3 kcal/mol. We regard this value as tentative because it depends so strongly on the value taken for the intrinsic rotation barrier in the ligand. Further studies are currently being carried out to better define this intrinsic barrier.

**Reactions of 6 and 7.** On warming, the H-bonded species **6** and **7** lose $H_2$ to form chelate complexes of type **8**. At 20 °C, this takes 24 h for **6** and 3 days for **7**.




The kinetics of this reaction have been measured for the fastest process (**6** → **8**) by monitoring the disappearance of the $^{31}P$ NMR signal at 30.8 ppm (due to **6**) and the appearance of the signal at 22.1 ppm (due to **8**) in toluene solutions between 298 and 353 K. The reaction was first order in **6**. Table 3 shows the $k_{obs}$ and the activation parameters for this process as calculated from the NMR data (see Experimental Section).

From the highly negative $\Delta S^{\ddagger}$, an associative process with a highly ordered transition state seems likely. The formation of an Ir−$H_2$−N intermediate prior to the loss of $H_2$, similar to that proposed for the $H_a-H_b$ exchange, is a possibility.

**Origin of H-Bond Strength.** In conventional H-bonds of the type A−H···B, A−H interacts with a lone pair of B, where B is an electronegative atom, most commonly O, N, or F. More

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**Table 3:** Values of $k_{obs}$ at Different Temperatures for the Reaction 6 → 8. Activation Parameters

| $T$ (K) | $10^5 k_{obs}$ ($s^{-1}$) |
|---|---|
| 298 | 2.1 |
| 313 | 6.3 |
| 333 | 30.8 |
| 353 | 122.1 |

Activation Parameters from Eyring Plot

$\Delta H^{\ddagger} = 14 \pm 2$ kcal/mol $\Delta S^{\ddagger} = -32 \pm 6$ eu

rarely, A−H interacts with a $\pi$-bond; in this case the H-bond acceptor is usually an arene, as in the case of phenol or pyrrole H-bonding with $C_6Me_6$.[18] H-bonding with a $\sigma$-bonding pair—in this case the Ir−H bonding pair—does not seem to have been previously proposed before our work and that of Morris et al. and Milstein et al.

Why is the H-bond so strong in a case where B is not an electronegative element? One of the factors that is believed[19] to contribute to the strength of a conventional H-bond is the close approach of H to B, possible because of the small size of H. Extending this idea to the case of $X-H_a\cdots H_b-Ir$, we propose that the approach in this case ($d\{H\cdots H\} = 1.8$ Å) is even closer than is possible in a conventional H-bond, so enhancing the interaction. A factor thought[18] to limit the strength of a conventional H-bond is the repulsion between the lone pairs of A and B. In our case the base $H_b$ has no lone pairs, and so we suggest that the repulsion term is reduced in magnitude. Finally, a new factor not normally present in conventional H bonds is the high polarizability of the Ir−H bond. We believe that the approach of the positively charged $X-H_a$ proton may induce a polarization of the $Ir-H_b$ bond so as to give $H_b$ a higher negative charge than it has in the free case. These three factors help explain why the interaction strength for $X-H_a\cdots H_b-Ir$ is in the range of conventional H-bonds. A theoretical study in collaboration with Odile Eisenstein (Orsay) is planned to help elucidate the nature of the bonding in greater detail.

## Conclusions

We and others[3,20] have investigated attractive interactions between ligands that lead to the formation of $H_2$ complexes in di- and polyhydrides. Now we see an unusual type of attractive interligand interaction in these $M-H\cdots H-X$ hydrogen bonds (X = O or N). By proton transfer, these species provide probable intermediates in $\sigma$-bond metathesis reactions, such as those of eqs 3 and 4. H-bonded intermediates of this type are likely to be involved in protonation of metal hydrides by acids. The work also raises questions about what other types of interligand interactions might be possible if $H_b$ were replaced by other ligands and how these interactions might affect the chemistry of the complexes concerned.

## Experimental Section

**General Procedures and Materials.** $[IrH_2(acetone)_2(PPh_3)_2]SbF_6$ and $IrH_5(PPh_3)_2$ were obtained according to literature methods.[6,21] All solvents were of analytical grade and were degassed before use. Ligands, such as 8-aminoquinoline, 2-hydroxypyridine, 7-azaindole, 2-(phenylamino)pyridine and 2-aminopyridine (Aldrich) were used as received. NMR measurements were recorded on a GE Omega-300 or QE300-plus spectrometer. IR spectra were recorded on a MIDAC M1200 FTIR.

**Synthesis of Ligands.** General procedure for **3**: To a solution of acyl chloride (e.g., acetyl chloride in the case of **3a**) (3.82 mmol) in $CH_2Cl_2$ (15 mL) at room temperature were added 8-aminoquinoline (551 mg, 3.82 mmol) and a 1.5−fold excess of pyridine (453 mg, 5.73 mmol) over 5 min. After being stirred for 20 min, the mixture was filtered over Celite, and the volatiles were removed under reduced pressure. Chromatography (silica gel 60, $CH_2Cl_2$) yielded **3** in 72−86% yield as pale yellow solids of liquids. The identities of the products were confirmed by comparison (NMR, melting point) with literature data.[23]

**Synthesis of Complexes of Type 1: Dihydrido(quinoline-8-acyliminol)bis(triphenylphosphine)iridium(III) Hexafluoroantimonates. Preparation of $[Ir(H)_2\{(C_9H_6N)N{=}C(OH)Me\}(PPh_3)_2]SbF_6$ (1a).** A solution of $[IrH_2(acetone)_2(PPh_3)_2]SbF_6$ (760 mg, 0.71 mmol) in $CH_2Cl_2$ (20 mL) was treated with amide **3a** (110 mg, 0.71 mmol) at room temperature for 0.5 h. The solution was concentrated and ether (6 mL) added. The resulting yellow powder was collected by filtration and dried under vacuum to give **1a** (71%, 560 mg). The material can be recrystallized from $CH_2Cl_2/Et_2O$. $^1H$ NMR ($CD_2Cl_2$) in ppm: −19.09, −19.19 [2H, m, Ir−H], 6.63 [1H, dd, $J$(H,H) = 7.2, 10.0 Hz, aromatic], 6.78 [1H, dd, $J$(H,H) = 4.8, 8.4 Hz, aromatic], 7.04 [1H, d, $J$(H,H) = 7.2 Hz, aromatic], 7.63 [1H, d, $J$(H,H) = 8.4 Hz, aromatic], 7.83 [1H, d, $J$(H,H) = 4.8 Hz, aromatic], 8.09 [1H, d, $J$(H,H) = 8.7 Hz, aromatic], 7.09−7.56 [30H, m, $PPh_3$], 9.54 [1H, d, $J$(H,H) = 3.0 Hz, OH]. $^{31}P\{$partially $^1H$ decoupled$\}$ NMR ($CD_2Cl_2$) in ppm: 19.77 [t, $^2J(P,H_{cis})$ = 16.5 Hz]. IR (film) in $cm^{-1}$: 2152 (br, Ir−H), 1611 (s, C=N). Elemental anal. Calcd for $IrP_2N_2OC_{47}H_{42}SbF_6 + 0.3(CH_2Cl_2)$: C, 48.63; H, 3.68; N, 2.40. Found: C, 48.78; H, 3.79; N, 2.35.

The same procedure was followed for the preparation of compounds **1b−1f** using ligands **3b−f**. $\{Ir(H)_2[(C_9H_6N)N{=}C(OH)^nBu](PPh_3)_2\}SbF_6$ (**1b**): 68%. $^1H$ NMR ($CD_2Cl_2$) in ppm: −19.11, −19.23 [2H, m, Ir−H], 6.72 [1H, dd, $J$(H,H) = 5.1, 8.4 Hz, aromatic], 6.99 [1H, d, $J$(H,H) = 7.8 Hz, aromatic], 7.52 [1H, t, $J$(H,H) = 7.8 Hz, aromatic], 7.64 [1H, d, $J$(H,H) = 7.8 Hz, aromatic], 7.70 [1H, d, $J$(H,H) = 5.1 Hz, aromatic], 8.07 [1H, d, $J$(H,H) = 7.8 Hz, aromatic], 7.18−7.41 [30 H, m, $PPh_3$], 9.70 [1H, d, $J$(H,H) = 3.6 Hz, OH]. $^{31}P\{$partially $^1H$ decoupled$\}$ NMR ($CD_2Cl_2$) in ppm: 19.63 [t, $^2J(P,H_{cis})$ = 15.2 Hz]. IR (film) in $cm^{-1}$: 2165, 2118 (br, Ir−H), 1603 (s, C=N). Elemental Anal. Calcd for $IrP_2N_2OC_{50}H_{48}SbF_6 + (CH_2Cl_2)$: C, 48.32; H, 3.98; N, 2.21. Found: C, 48.21; H, 4.06; N, 2.20.

**$[Ir(H)_2\{(C_9H_6N)N{=}C(OH)(p\text{-tolyl})\}(PPh_3)_2]SbF_6$ (1c)**: 64%. $^1H$ NMR ($CD_2Cl_2$) in ppm: −18.94, −19.12 [2H, m, Ir−H], 6.37 [1H, d, $J$(H,H) = 7.5 Hz, aromatic], 6.61 [1H, d, $J$(H,H) = 8.4 Hz, aromatic], 6.74 [1H, dd, $J$(H,H) = 5.1, 8.4 Hz, aromatic], 7.69 [1H, t, $J$(H,H) = 10.1 Hz, aromatic], 7.88 [1H, d, $J$(H,H) = 10.8 Hz, aromatic], 8.05 [1H, d, $J$(H,H) = 8.4 Hz, aromatic], 6.82−7.63 [30H, m, $PPh_3$], 9.93 [1H, d, $J$(H,H) = 3.0 Hz, OH]. $^{31}P\{$partially $^1H$ decoupled$\}$ NMR ($CD_2Cl_2$) in ppm: 19.13 [br, s]. IR (film) in $cm^{-1}$: 2181, 2122 (br, Ir−H), 1608 (s, C=N). Elemental anal. Calcd for $IrP_2N_2OC_{53}H_{46}SbF_6 + 0.5(CH_2Cl_2)$: C, 51.03; H, 3.76; N, 2.22. Found: C, 51.21; H, 3.69; N, 2.19.

**$[Ir(H)_2\{(C_9H_6N)N{=}C(OH)(Ph)\}(PPh_3)_2]SbF_6$ (1d)**: 51%. $^1H$ NMR ($CD_2Cl_2$) in ppm: −18.94, −19.05 [2H, m, Ir−H], 6.44 [1H, dd, $J$(H,H) = 6.9, 1.5 Hz, aromatic], 6.54 [1H, d, $J$(H,H) = 7.2 Hz, aromatic], 6.73 [1H, dd, $J$(H,H) = 4.8, 8.4 Hz, aromatic], 7.80 [1H, d, $J$(H,H) = 4.8 Hz, aromatic], 8.06 [1H, d, $J$(H,H) = 7.8 Hz, aromatic], 7.03−7.62 [31H, m, $PPh_3$ and one aromatic proton from **3'd**], 10.03 [1H, br, OH]. $^{31}P\{$partially $^1H$ decoupled$\}$ NMR ($CD_2Cl_2$) in ppm: 19.20 [br, s]. IR (film) in $cm^{-1}$: 2175, 2116 (br, Ir−H), 1613 (s, C=N). Elemental anal. Calcd for $IrP_2N_2OC_{52}H_{45}SbF_6 + 1.5(CH_2Cl_2)$: C, 48.27; H, 3.63; N, 2.10. Found: C, 48.32; H, 3.69; N, 2.14.

**$[Ir(H)_2\{(C_9H_6N)N{=}C(OH)(p\text{-}FC_6H_4)\}(PPh_3)_2]SbF_6$ (1e)**: 62%. $^1H$ NMR ($CD_2Cl_2$) in ppm: −18.98, −19.09 [2H, m, Ir−H], 6.48 [1H,

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dd, $J$(H,H) = 5.4, 8.4 Hz, aromatic], 6.57 [1H, d, $J$(H,H) = 7.8 Hz, aromatic], 6.72 [1H, dd, $J$(H,H) = 5.4, 8.4 Hz, aromatic], 7.56 [1H, d, $J$(H,H) = 7.8 Hz, aromatic], 7.81 [1H, d, $J$(H,H) = 4.5 Hz, aromatic], 8.08 [1H, d, $J$(H,H) = 8.4 Hz, aromatic], 6.95−7.42 [30H, m, $PPh_3$], 9.97 [1H, br, OH]. $^{31}P\{$partially $^1H$ decoupled$\}$ NMR ($CD_2Cl_2$) in ppm: 19.18 [br, s]. IR (film) in $cm^{-1}$: 2177, 2121 (br, Ir−H), 1611 (s, C=N). Elemental anal. Calcd for $IrP_2N_2OC_{52}H_{43}SbF_7 + (CH_2Cl_2)$: C, 48.75; H, 3.47; N, 2.15. Found: C, 48.70; H, 3.41; N, 2.17.

**$[Ir(H)_2\{(C_9H_6N)N{=}C(OH)(3,4\text{-}F_2C_6H_3)\}(PPh_3)_2]SbF_6$ (1f)**: 70%. $^1H$ NMR ($CD_2Cl_2$) in ppm: −19.02 [2H, br t, $^2J(P,H_{cis})$ = 15.6 Hz, Ir−H], 6.22 [1H, br d, $J$(H,H) = 6.0 Hz, aromatic], 6.45 [1H, d, $J$(H,H) = 7.5 Hz, aromatic], 6.76 [1H, dd, $J$(H,H) = 5.4, 8.4 Hz, aromatic], 7.56 [1H, d, $J$(H,H) = 7.8 Hz, aromatic], 7.79 [1H, d, $J$(H,H) = 4.5 Hz, aromatic], 8.08 [1H, d, $J$(H,H) = 8.7 Hz, aromatic], 7.10−7.43 [30H, m, $PPh_3$], 10.02 [1H, br, OH]. $^{31}P\{$partially $^1H$ decoupled$\}$ NMR ($CD_2Cl_2$) in ppm: 19.12 [br, s]. IR (film) in $cm^{-1}$: 2182, 2123 (br, Ir−H), 1601 (s, C=N). Elemental anal. Calcd for $IrP_2N_2OC_{52}H_{42}SbF_8 + (CH_2Cl_2)$: C, 48.09; H, 3.35; N, 2.12. Found: C, 48.13; H, 3.38; N, 2.10.

**Trihydrido(2-(phenylamino)pyridine)bis(triphenylphosphine)-iridium(III) (6).** $IrH_5(PPh_3)_2$ (100 mg, 0.14 mmol) and 2-(phenylamino)pyridine (23.8 mg, 0.14 mmol) were suspended in benzene (20 mL). The white suspension was warmed to 80 °C, and a clear pale yellow solution was formed in 10 min. The solvent was removed under vacuum, and the crude solid was precipitated with $CH_2Cl_2$−hexane (1:1, 5 mL), yielding a pale yellow powder of $IrH_2(pyNHPh)(PPh_3)_2$, **6** (75% yield). $^1H$ NMR ($CD_2Cl_2$) in ppm: −22.3 [1H, tt, $^2J(H,H)$ = 4.2 Hz, $^2J(P,H)$ = 17.1 Hz, Ir−H], −10.0 [1H, tt, $^2J(H,H)$ = 4.2 Hz, $2J(P,H)$ = 17.1 Hz, $J(H,H)$ = 2.6 Hz, Ir−H], −9.8 [1H, ttd, $^2J(H,H)$ = 4.2 Hz, $^2J(P,H)$ = 14.4 Hz, $^1J(H,H)$ = 2.6 Hz, Ir−H], 6.6−7.4 (30H, m, aromatics, 9H, m, pyNHPh), 10.5 [1H, $J$(H,H) = 2.6 Hz, N−H]. $^{31}P$ NMR ($CD_2Cl_2$) in ppm: 30.8 [$^2J(P,H)$ = 17 Hz]. IR (film) in $cm^{-1}$: 2170 (br), 3409 (w). Elemental anal. Calcd for $IrP_2N_2OC_{47}H_{44}$: C, 64.36; H, 5.02; N, 3.19. Found: C, 64.27; H, 4.97; N, 3.12.

The same procedure with the 2-aminopyridine ($pyNH_2$) leads to compound **7**.

**$IrH_3(pyNH_2)(PPh_3)_2$ (7)**: 81%. $^1H$ NMR ($CD_2Cl_2$) in ppm at 293 K: −22.55 [1H, tt, $^2J(H,H_{cis})$ = 4.2 Hz, $^2J(P,H_{cis})$ = 17.1 Hz, Ir−H], −10.4 [1H, tt, $^2J(H,H_{cis})$ = 4.2 Hz, $^2J(H,H_{trans})$ = 4.2 Hz, $^2J(P,H_{cis})$ = 15.1 Hz, Ir−H], −9.8 [1H, tt, $^2J(H,H_{cis})$ = 4.2 Hz, $^2J(H,H_{trans})$ = 4.2 Hz, $^2J(P,H)$ = 16.4 Hz, Ir−H], 6.5 [2H, br singlet, N−H; at 183 K it decoalesces to two peaks (7.8 and 4.4 ppm) in a 1:1 ratio], 5.2−6.5 (3H, py), 6.4−7.4 (30H, m, aromatics). $^{31}P$ NMR ($CD_2Cl_2$) in ppm at 293 K: 29.8 [$^2J(P,H)$ = 16 Hz)]. IR (film) in $cm^{-1}$: 2141 (br), 3403 (br). Elemental anal. Calcd for $IrP_2N_2OC_{41}H_{39} + (CH_2Cl_2)$: C, 56.11; H, 4.56; N, 3.12 Found: C, 56.27; H, 4.63; N, 3.28.

**$H_a$−$H_b$ Exchange in Compounds of Type 1.** In a typical $^1H$ NMR experiment, a 0.5 mL $CD_2Cl_2$ solution of **2** (27.4 mg, 0.026 mmol) and amide **3** (4 mg, 0.026 mmol) was sealed under vacuum in a 5 mm NMR tube equipped with a PTFE valve (Aldrich) and then introduced into the probe of the NMR spectrometer preheated or cooled to a fixed temperature. The exchange rate is determined from the line-broadening of the OH signal, and the activation parameters are determined from the corresponding Eyring plot.

**Reaction of Benzonitrile with Compounds of Type 1.** PhCN (2.5 mg, 0.024 mmol) was added to a 0.6 mL $CD_2Cl_2$ solution of **1** (0.022 mmol) at room temperature. The reaction was monitored at 20 °C by $^1H$ NMR every 30 min for 4 h. The rate of reaction is determined from the intensity of the monohydride product, which shows a characteristic triplet at −17.6 ppm.

**$T_1$ (min) Determination.** Determination of $T_1$ (min) values for compound **6** was performed using a conventional inversion−recovery pulse sequence at temperatures in the range 293−193 K.[21]

**Kinetic Measurements for Reaction 6.** Compound **6** (10 mg, 0.011 mmol) was introduced in an NMR tube and dissolved in toluene-$d_8$ (0.5 mL). The NMR probe was equilibrated at 298, 313, 333, and 353 K, and a series of $^{31}P$ NMR spectra were recorded every 10 min. The course of the reaction was followed from the disappearance of the signal at 30.8 ppm and the appearance of the new signal for **8** at 22.2 ppm. No other intermediates were detected. The $k_{obs}$ values were obtained from the slopes of the function $\ln[I(\mathbf{6})/\{I(\mathbf{6}) + I(\mathbf{8})\}]$, which showed correlation factors over 0.993. The activation parameters were obtained from the corresponding Eyring plots.

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