

## Intramolecular N-H...X-Ir (X = H, F) Hydrogen Bonding in Metal Complexes

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Intramolecular N-H...X-Ir (X = H, F) hydrogen bonds are found in a series of metal hydrides.

In a recent study of amide complexation, we found an unexpected example of O-H...H-Ir hydrogen bonding, where the role of weak base partner was taken by an Ir-H bond.<sup>1</sup> This interaction was confirmed by structural and spectroscopic data, including the  $J(\text{H}, \text{H}')$  of 3 Hz in the  $^1\text{H}$  NMR spectrum. Morris<sup>2a</sup> has recently found a similar N-H...H-M species. We wanted to know the generality and strength of this type of bond, to see how it compares with conventional H-bonds.<sup>3</sup>

The pyridines **1a,b** react with  $[\text{IrH}_5(\text{PPh}_3)_2]^4$  at 80 °C in benzene to give **2a,b** as colourless complexes in 70–80% yield [eqn. (1)]. The identity of **2a,b** follows from the microanalytical and spectral data. In particular, at 253 K in  $\text{CD}_2\text{Cl}_2$  (**2a**), or at 293 K in  $\text{C}_6\text{D}_6$  (**2b**),  $\text{H}_b$ ,  $\text{H}_c$  and  $\text{H}_d$  are all inequivalent and show *cis*  $J(\text{H}, \text{P})$  couplings of ca. 16 Hz and mutual H,H couplings of ca. 4 Hz. In both cases H-bonds are present, based on the following data: (i)  $\text{H}_a$  and  $\text{H}_b$  show the expected<sup>1</sup> coupling (ca. 2.5 Hz, **1a**; 2.8 Hz, **1b**) in the  $^1\text{H}$  NMR spectrum; (ii) the  $\text{H}_b$  resonance shows a large excess  $T_1$  relaxation relative to  $\text{H}_c$  and  $\text{H}_d$  [excess rate =  $4.0 \text{ s}^{-1}$  (**2b**) at the  $T_1$  (min)], which corresponds to an  $\text{H}_a\cdots\text{H}_b$  distance of 1.80 Å.<sup>‡</sup> Morris<sup>2a</sup> estimated a very similar distance in his complex by the same method;<sup>2b-d</sup> (iii) the N-H proton resonance at  $\delta$  7.2–7.8 shows a 3 ppm low-field shift from the free ligand value expected<sup>3</sup> for a H-bonded ligand. The  $\nu(\text{N-H})$  stretch at 3403 (**2a**) or 3409  $\text{cm}^{-1}$  (**2b**) also shows the expected low-energy shift in the IR spectrum relative to free N-H.

Complex **2a** gave information about the hydrogen-bond strength. The variable-temperature NMR data shows that the signals for the two inequivalent  $\text{NH}_2$  protons coalesce at 253 K, leading to a  $\Delta G^\ddagger$  of  $10.8 \pm 0.2 \text{ kcal mol}^{-1}$  (1 cal = 4.184 J) for rotation about the C-NH<sub>2</sub> bond. This barrier represents the sum of the intrinsic rotation barrier, known<sup>6</sup> to be about 6–7  $\text{kcal mol}^{-1}$ , and the H-bond strength, which must therefore be ca. 4.3  $\text{kcal mol}^{-1}$ . The hydrogen-bond in **2** could only be broken with  $\text{Ph}_3\text{P}=\text{O}$  (0.2 mol  $\text{dm}^{-3}$ ) as an intermolecular hydrogen-bond acceptor (B component), as judged by disappearance of the  $J(\text{H}_a, \text{H}_b)$  coupling, but not by addition of the weaker acceptors acetone or ethanol.

Do conventional intramolecular hydrogen-bonds<sup>5</sup> also form in this system? When  $[\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2]\text{BF}_4^7$  is treated

with  $\text{NBu}_4\text{F}$  and pyridine **1a**, the new complex formed, **3a**, shows N-H...F-Ir hydrogen bonding. The clearest evidence is the large  $\text{H}_a\cdots\text{F}$  coupling of 63 Hz at 253 K. Low-energy shifts of  $\nu(\text{N-H})$  are also observed as well as the expected 3 ppm low-field shift of the N-H proton resonance. Variable-temperature NMR data show that Ar-NH<sub>2</sub> bond rotation has a barrier of  $11.0 \pm 0.2 \text{ kcal mol}^{-1}$  which we associate with an hydrogen-bond strength of ca. 4.5  $\text{kcal mol}^{-1}$ . An N-H...H-Ir hydrogen bonded tautomer, in principle possible in **3a**, was not observed (<2%). This means the F substitution must lower the basicity of the *trans* hydride.

The same type of  $\text{H}_a\cdots\text{F}$  interaction is observed when we use the phenylaminopyridine complex **1b**, eqn. (2). The compound obtained, **3b**, shows a large  $\text{H}_a\cdots\text{F}$  coupling of 65.1 Hz at room temperature. Once again, no N-H...H-Ir tautomer was observed in this new compound.

Conventional hydrogen-bonds of the type A-H...B are strong only when B is N, O or F.<sup>3</sup> Here we have a case where B = Ir-H and we see a bond strength in the range of conventional hydrogen-bonds. We ascribe this to the following special factors: (i)  $\text{H}_a$  and  $\text{H}_b$  can approach comparatively close (1.8 Å in **2** versus a typical range of 1.5–2.1 Å for H...B in A-H...B complexes because both  $\text{H}_a$  and  $\text{H}_b$  are small atoms); (ii) unlike the B component in a conventional hydrogen-bond, Ir-H has no lone pairs, repulsion involving which is known to weaken A-H...B; (iii) Ir-H<sub>b</sub> is a polarizable bond and so  $\text{H}_b$  may become more  $\delta^-$  in character on the approach of the  $-\text{NH}_a$  group.

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## Footnotes

† This signal is broad but decoupling reveals  $^1J(\text{H}_a, \text{H}_b)$  is present.

‡ We make the usual<sup>2a-d</sup> assumptions and that the  $\text{H}_a\cdots\text{H}_b$  vector rotates with the complex and so  $C = 1$ ; field = 300 MHz.

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