

Complexation of an Amide to Iridium *via* an Iminol Tautomer and Evidence for an Ir–H⋯H–O Hydrogen Bond

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The OH group of the iminol complex [IrH₂L'(PPh₃)₂]SbF₆·2H₂O where L' is the iminol tautomer of quinolin-8-acetamide, takes part in an O–H⋯H–Ir hydrogen bond.

Neutral amides, normally poor ligands for platinum metals, can bind *via* O or N.¹ We thought that the reaction of [IrH₂(Me₂CO)₂(PPh₃)₂][SbF₆]² with the amide quinolin-8-acetamide (L) would be of interest since it seemed unlikely that L could bind *via* O and might therefore act in a bidentate fashion to give an N–H⋯Ir system.³ Instead, the amide tautomerises to the iminol form L' 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⁺ (dien = diethylenetriamine) have so far only been detected spectroscopically.⁴

Complex 1 (760 mg) was treated with amide L (110 mg) in CH₂Cl₂ for 0.5 h to give a solution from which pale yellow microcrystals of [IrH₂L'(PPh₃)₂]SbF₆·2H₂O (2, 560 mg, 71%) were isolated. ¹H NMR resonances (in CD₂Cl₂ at 293 K) are observed for PPh₃, L' and Ir–H with the appropriate integral ratio. Two inequivalent Ir–H hydrides appear at δ –19.09 and –19.19, consistent with the presence of different ligands *trans* to each hydride. A range of complexes of the [IrH₂(L¹)L²(PPh₃)₂]⁺ type are known,² where L¹ and L² represent different ligands, and show similar spectra. The hydrides show the expected ²J(H_aH_b) value of 6 Hz corresponding to a *cis* IrH₂ group and a ²J(HP) of 16 Hz due to coupling to the *cis* PPh₃ groups.

Suitable crystals were grown from CH₂Cl₂–hexanes under H₂ and studied by X-ray diffraction.† The results (Fig. 1) show that the amide group of L has tautomerized to the iminol form L' and that the essentially planar iminol now binds *via* the imine nitrogen [Ir–N(1) 2.186(13) Å]. The short iminol C=N bond length of 1.260(22) Å is close to an ideal C=N double bond (1.24 Å)⁵ and much shorter than C–N bonds in amides (1.31–1.38 Å)⁵ while the C–O at 1.321(23) Å is much longer than the value in amides (1.19–1.28 Å).⁵ There are no unusual intermolecular contacts. The O–H hydrogen, although not detected in the X-ray structure, gives a feature at a position (δ + 9.54, intensity 1H) in the ¹H NMR expected⁴ for an iminol OH; it slowly exchanges with D₂O. From ¹⁵N–¹H correlation experiments, this resonance has no ¹J(¹⁵NH) coupling under conditions in which complexes of Pt containing the amide form do show coupling.⁶ The Ir–H hydrogens were not detected in the X-ray crystal structure, but the *cis* ²J(PH) coupling shows that they complete the octahedron expected for Ir^{III}.

Decoupling and COSY studies show that the OH proton is coupled [*J*(HH) = 3 Hz] to one of the Ir–H resonances, assigned as H_a. The X-ray crystal structure shows that the OH oxygen is located close to the position occupied by the Ir–H_a hydride. The data are most easily accommodated if the OH group of the iminol is hydrogen bonded to the Ir–H_a hydride. The calculated H⋯H distance in the hydrogen bond is 1.58 Å from the Ir–H_a and O–H positions [calculated on the basis of an octahedral geometry, *d*(Ir–H) = 1.65 Å and a planar ligand with *d*(O–H) = 1.00 Å]. The H-bonded protons also show somewhat short *T*₁ values (Ir–H_a, 262 ms at 300 MHz and 183 K; O–H, 220 ms) which are most consistent 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. A much weaker O–H⋯H–Ir interaction [*d*(H⋯H) = 2.4 Å] was reported by Milstein and co-workers⁷ and an N–H⋯H–Ir example [*d*(H⋯H) = 1.8 Å] of similar strength to our own has been found very recently by Ramachandran and Morris.⁸ In forming the hydrogen bond, the hydride acts as a weak base and the –OH group as a weak acid. 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. Such coupling was not reported in either of the two other examples.‡ The broad ν(O–H) peak at 3310 cm^{–1} in the IR spectrum (Nujol) is also consistent with a hydrogen-bonded OH. The broad ν(Ir–H) peak at 2152 cm^{–1} is found at somewhat lower energy than in 1 (2252 cm^{–1}).

The C–O bond in 2 is *syn* to the N–Ir group, in sharp

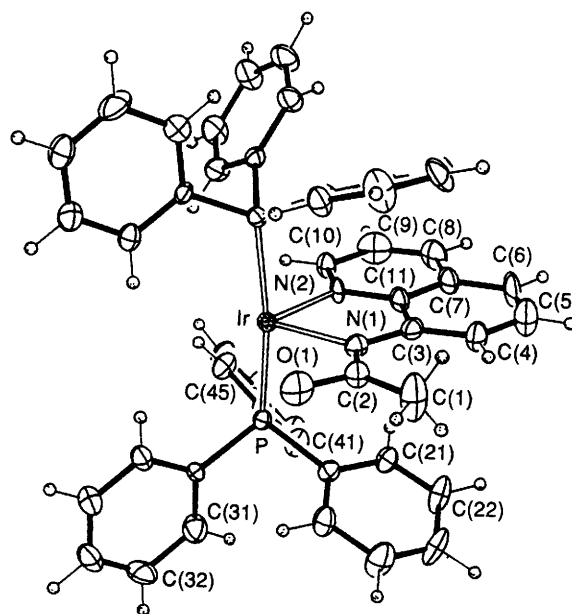
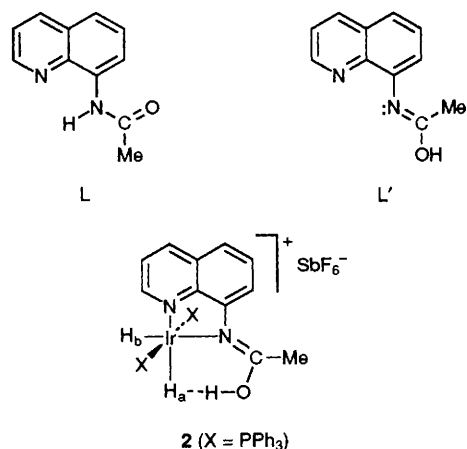


Fig. 1 An ORTEP diagram of the cation of 2, showing the iminol tautomeric form and the *syn* conformation of the C–OH and N lone pair. The Ir–H and O–H hydrogens were not located. Some bond lengths (Å) and angles (°) are: Ir–P 2.312(3), Ir–N(2) 2.124(12), Ir–N(1) 2.186(13), N(1)–C(2) 1.260(22), C(2)–O(1) 1.321(23), P–Ir–P' 171.4(1), N(1)–Ir–N(2) 77.8(5).

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, but it may also indicate that iminols, unlike amides, do not show a strong preference for an *anti* conformation.

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Footnotes

† *Crystal Data* for **3**: $M = 1188.7$, orthorhombic, space group $Pnma$, $a = 14.844(2)$, $b = 14.842(2)$, $c = 21.778(2)$ Å, $V = 4854.7(11)$ Å³, $Z = 4$, $D_c = 1.646$ g cm⁻³, $F(000) = 2328$; absorption coefficient = 3.467 mm⁻¹, $\mu = 3.467$ mm⁻¹, $\lambda = 0.71073$ Å, crystal dimensions $0.12 \times 0.32 \times 0.40$ mm, 3279 Reflections with $I > 3\sigma(I)$ converged at $R = 0.0532$ after a semiempirical absorption correction. Despite $a \approx b$, the diffraction symmetry ($hkl \neq khl$) revealed only *mmm* Laue symmetry and the statistical distribution of *E*-values strongly indicated the centrosymmetric space group $Pnma$, with the quinoline system lying on the mirror plane. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge

Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Attempts to grow crystals suitable for neutron diffraction have not yet been successful.

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