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Spectroscopic Detection of a Hydrogen Fluoride Complex of Iridium

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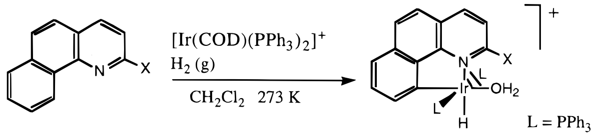
The work described here was performed to study the effect of introducing a non-ligating hydrogen-bonding functionality into the ligand sphere of a metal complex. We report the incorporation of an amino group into the benzoquinoline ligand of an iridium(III) complex and its effect on the stabilization of an HF ligand. Although there are examples[1] of M−F···H hydrogen-bonding interactions, and more recently, of bifluoride complexes,[2] we report here spectroscopic evidence at 183 K for what appears to be the first M−F−H···N interaction in which a molecule of HF is bound to the metal, stabilized by an intramolecular hydrogen bond.

The new ligand, 2-amino-7,8-benzoquinoline (**1a**), was readily synthesized by a Chichibabin reaction between $NaNH_2$ and 7.8-benzoquinoline.[3] Following the procedure previously reported for **2b**,[4] **1a** reacts smoothly with the complex $[Ir(COD)(PPh_3)_2]BF_4$ and hydrogen (1 atm) in moist CH_2Cl_2 to give the new cyclometallated complex, **2a** (88% yield). The spectral data for **2a** show that it is a direct analog of the crystallographically characterized[4] species, **2b**.



(1)

1, X = NH_2, **a**
X = H, **b**

2, X = NH_2, **a**
X = H, **b**

The fluoride complex **3a** is easily prepared by stirring **2a** with 1 equiv of $[n\text{-}Bu_4N]F$ in acetone for 1 h under N_2. The identity of the complex follows from its elemental analysis and spectral data. As for the closely related complex $[IrH_2F(2\text{-aminopyridine})(PPh_3)_2]$ (**4**), previously studied by us,[5] we find that **3a** has an intramolecular N−H···F−Ir hydrogen bond, as shown by the $^1J_{HF}$ coupling constant of 52 Hz observed for the N−H_a proton resonance in the ^1H NMR spectrum at 183 K, and the shift of the ν(N−H) band in the IR spectrum to low energy (free **1a** 3411 cm^{-1}; **3a** 3175 cm^{-1}). These values are similar to those previously observed ($^1J_{HF}$ = 65 Hz; $\Delta\nu$ = 230 cm^{-1}) for **4**. The $\Delta G^\ddagger$ barrier at 193 K for H_a/H_b exchange in the ^1H NMR spectrum of **3a** is 12.4 ± 0.5 kcal/mol by line shape analysis,[6] which allows us to estimate the strength of the hydrogen bond as 6.6 ± 0.5 kcal/mol by the method previously described.[7]

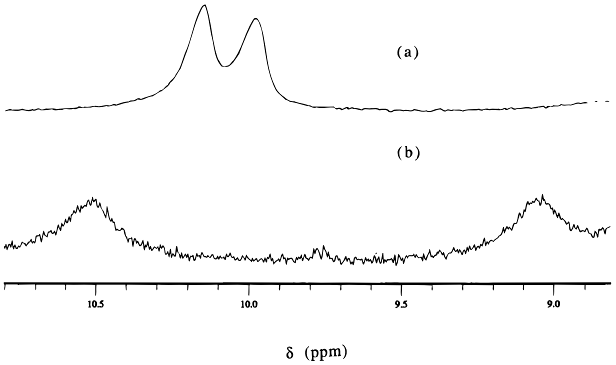


Figure 1. The N−*H*···F−Ir and N···*H*−F−Ir proton resonances in the 300 MHz ^1H NMR spectra of **3a** (a) and **5a** (b) at 183 K.

On protonating the fluoro complex **3a** with $HBF_4−Et_2O$ at 183 K in CD_2Cl_2, we find a new complex is formed (**5a**) that shows a ^1H NMR spectrum similar to that found for **3a** but having a new doublet at 9.78 ppm with a coupling constant of 440 ± 5 Hz which, for reasons discussed below, we assign to the Ir−F−*H*···NH_2 proton of a molecule of HF which is bound to the iridium center and intramolecularly hydrogen bonded to the amino nitrogen (Figure 1). A broad resonance at 6.84 ppm is assigned to the nonhydrogen bonded NH_2 hydrogens. The identification of the 440 ± 5 Hz splitting as a true coupling was confirmed by performing the experiment at both 300 and 500 MHz and by observing the same $^1J_{HF}$ coupling in the ^{19}F NMR spectrum ($\delta = -178$ ppm);[8,9] the origin of the coupling in the ^{19}F NMR spectrum is further confirmed by its collapse to a broad singlet when proton decoupled. Selective decoupling of the NH_2 signal led to a narrowing of the HF resonance, suggesting they are coupled, as required by structure **5a**. The assignment of the resonances at 9.78 and 6.84 ppm to exchangeable H−F or N−H protons is also supported by their deuteration with CD_3OD, which causes these ^1H resonances to disappear after mixing.

$^1J_{HF}$ coupling constants measured for HF in Lewis base solvents have been shown[10] to decrease from experimental gas phase values (530 Hz)[10−12] by as much as 10−20%, as a result of hydrogen bonding. Furthermore, the δ and $^1J_{HF}$ values for F−H···base systems are related,[10] as shown in Figure 2. Comparison with our values supports our belief that we are dealing with an F−H···base hydrogen-bonded system. In contrast, the $^1J_{HF}$ value for the $[F\cdots H\cdots F]^-$ ion (120 Hz)[10,13] is much smaller than for F−H···base, suggesting the presence of an Ir−F−H···N rather than an Ir−F···H−N arrangement.

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[7] (a) Lee, J. C., Jr.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014−9. (b) The method assigns a value of 5.8 kcal/mol to the intrinsic barrier for Ar-NH_2 rotation in the absence of H-bonding, based on theoretical studies and NMR studies of the free ligands.

[8] ^{19}F NMR chemical shifts are reported relative to external $CFCl_3$ in CD_2Cl_2.

[9] No other ^{19}F NMR signals were found over a 400 ppm range. For ^{19}F NMR chemical shifts of neutral Ir(III) fluoro complexes, see: Cockman, R. W.; Ebsworth, E. A. V.; Holloway, J. H.; Murdoch, H.; Robertson, N.; Watson, P. G. *ACS Symp. Ser. 555*, Thrasher, J. S., Strauss, S. H., Eds.; Chapter 20.

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[12] A $^1J_{HF}$ value of 615 ± 50 Hz has been reported for the HF coupling constant measured in neat HF. Solomon, I.; Bloembergen, N. *J. Chem. Phys.* **1956**, *25*, 261−6.

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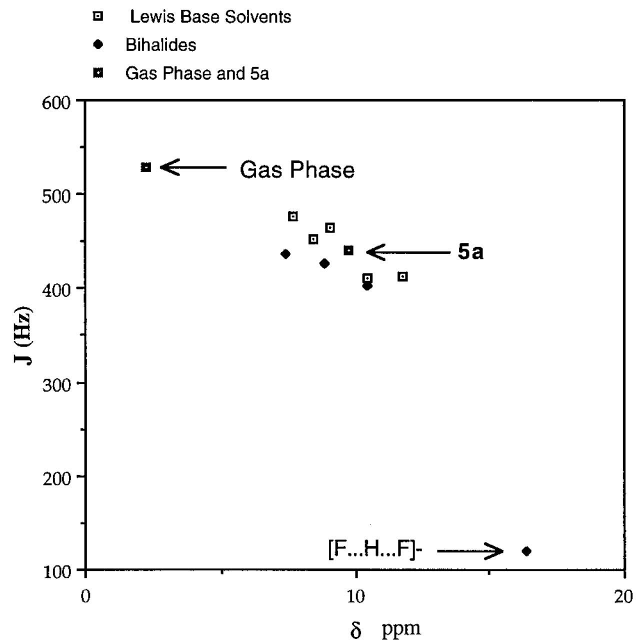


Figure 2. $^1J_{HF}$ vs δ correlation plot of data taken from ref 10, showing close agreement with the data point for **5a**.

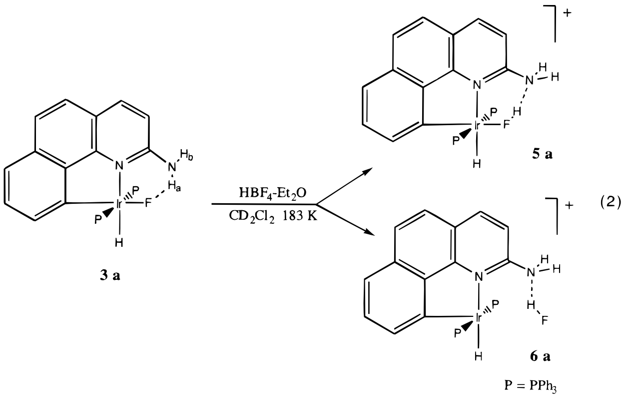
In order to show that the F of this HF is still bound to Ir, as shown in **5a**, and not dissociated from the metal center and merely hydrogen-bonded to the amino functionality, shown as **6a**, we turned to the $^{31}P\{^1H\}$ NMR, where the unprotonated species **3a** has a doublet at 16.8 ppm with a *cis* $^2J_{PF}$ of 21 Hz. Protonation at 183 K to give the HF complex **5a** causes the ^{31}P resonance to move to 21.5 ppm, but a *cis* $^2J_{PF}$ coupling of 12 Hz is retained, showing that F is still bound to iridium.[14]

This new HF complex is analogous to our previously reported halocarbon complexes.[15] The bent R−X−M arrangement always found for halocarbon complexes (∠RXM = ca. 100−120°)[15] implies that H−F−M in **5a** might also be bent, allowing for a hydrogen bond with the adjacent amine as shown. This prior work[15] also shows that the NMR properties of RX are little affected by coordination for R = alkyl; in this work, we see the same is true for HF.

Warming the sample above 210 K leads to the irreversible loss of HF. The ^1H NMR resonance at 9.78 ppm assigned to coordinated HF and the $^2J_{HF}$ coupling of the hydride resonance at −16.1 ppm are both lost, while in the ^{19}F NMR spectrum the HF resonance at −178 ppm is lost, and in the $^{31}P\{^1H\}$ NMR spectrum the $^2J_{PF}$ coupling is lost. Free HF was never observed in the spectrum, possibly due to rapid proton exchange with trace amounts of basic materials present or reaction with the glass of the NMR tube.[16]

In a control experiment on the fluoro complex lacking the NH_2 group, $[Ir(7,8\text{-benzoquinoline})(PPh_3)_2(H)F]$ (**3b**), protonation under the same conditions described above for **3a** leads to immediate and irreversible loss of the fluoride ligand as determined by ^1H, $^{31}P\{1H\}$, and ^{19}F NMR spectroscopies; free HF is not seen.

The NMR evidence of Figure 2 supports the idea that the coordinated HF is hydrogen bonded as F−H···base and the NH_2 lone pair of the benzoquinoline group in **5a** is the most likely candidate for the base. We therefore believe the HF ligand is stabilized by an intramolecular hydrogen bond, showing the utility of this strategy.



(2)

We conclude that the presence of reactive nonligating hydrogen-bonding groups in the ligand sphere of a metal complex can play an important role in modifying the chemistry observed, and this strategy may prove generally useful.

Acknowledgment. We thank Professor J. W. Faller for several helpful suggestions and the NSF for support.

Supporting Information Available: Spectroscopic and analytical data, as well as experimental details for the preparation of **1a**, **2a**, **3a**, and **5a** (2 pages). See any current masthead for ordering and Internet access instructions.

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[14] No $^2J_{FP}$ coupling was observed in the ^{19}F NMR of **5a** because the peaks for the H*F* ligand were very broad ($W_{1/2}$ = 190 Hz).

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[16] Nor could HF be observed in attempts to introduce small quantities of authentic HF into the same solvent under the conditions of the NMR experiments.