Switching On and Off a New Intramolecular Hydrogen–Hydrogen Interaction and the Heterolytic Splitting of Dihydrogen. Crystal and Molecular Structure of $[Ir\{H(\eta^1\text{-}SC_5H_4NH)\}_2(PCy_3)_2]BF_4\cdot 2.7CH_2Cl_2$

Alan J. Lough, Sunghan Park,
Ravindranath Ramachandran, and Robert H. Morris*

Department of Chemistry and
Scarborough Campus
University of Toronto
80 St. George Street
Toronto, Ontario M5S 1A1, Canada

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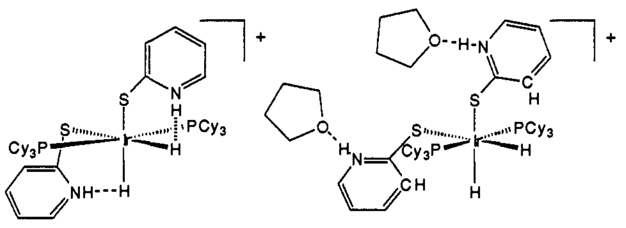
In the course of studying the intra- and intermolecular proton transfer reactions of acidic dihydrogen complexes,[1,2] we have discovered a new type of interaction between an iridium hydride and the protonated nitrogen of a sulfur-bonded thiopyridine ligand, $Ir—H^{\delta-}\cdots H^{\delta+}–N$. Thus far, two complexes containing this structural unit have been isolated: the mononuclear complex, $[Ir\{H(\eta^1\text{-}SC_5H_4NH\}_2(PCy_3)_2]BF_4$ (**1**), reported here and a dinuclear iridium complex, $[\{IrH(\eta^1\text{-}SC_5H_4NH)(PCy_3)\}_2(\mu\text{-}SC_5H_4N)_2](BF_4)_2$, which will be described elsewhere. We also show here that this unit exists when **1** is in CD_2Cl_2 but not when it is in the presence of good hydrogen-bond acceptors and that the H···H interaction is essential for rapid H/D exchange with D_2 gas.


1 in CH_2Cl_2 1 in THF

The addition of a CH_2Cl_2 solution of protonated 2-pyridinethiol (2 equiv of $[HSC_5H_4NH]BF_4$) to a suspension of $IrH_5(PCy_3)_2$[3] in methanol at −80 °C under Ar produces complex **1** as a yellow precipitate after partial evaporation of the solvent under vacuum. The analytical and spectroscopic data are consistent with the structure labeled as **1** in CH_2Cl_2.[4]

The structure from X-ray analysis[5] of a crystal at 226 K reveals an iridium complex with trans PCy_3 groups and cis $\eta^1\text{-}SC_5H_4NH$ ligands coordinated via the sulfur atoms and protonated at the nitrogens (Figure 1).[6] The hydrogens on N1 and N2 are well-defined in electron difference maps, but the hydride positions are obscured by residual electron density near the iridium. The Ir–S–C–N–H units are planar. Hydride ligands can be positioned at 1.61 Å[7] from Ir and about 1.75 ± 0.05 Å from the H on N in these planes and at reasonable positions on the distorted octahedron around iridium.

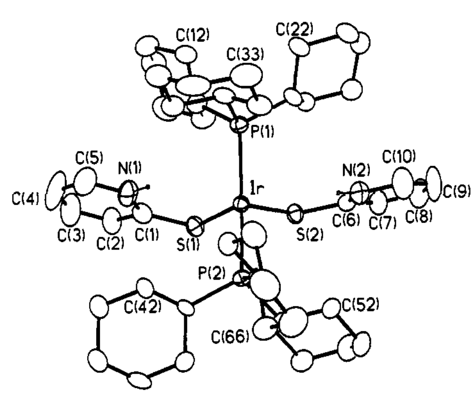


Figure 1. ORTEP plot of **1**. Selected bond distances (angstroms) and bond angles (deg): Ir—P(1) 2.371(2), Ir—P(2) 2.358(2), Ir—S(1) 2.451(2), Ir—S(2) 2.434(2), S(1)—C(1) 1.718(8), S(2)—C(6) 1.707(7), C(1)—N(1) 1.355(10), C(6)—N(2) 1.355(10), Ir···N(1) 3.49(1), Ir···N(2) 3.55(1), S(1)—Ir—S(2) 80.88(6), P(1)—Ir—P(2) 159.69(6), S(1)—Ir—P(1) 102.17(6), S(1)—Ir—P(2) 92.73(6), S(2)—Ir—P(1) 96.18(6), S(2)—Ir—P(2) 99.78(6), Ir—S(1)—C(1) 111.7(3), Ir—S(2)—C(6) 113.5(2), S(1)—C(1)—N(1) 120.4(6), S(2)—C(6)—N(2) 121.4(5).

The ^1H NMR data provide the evidence for the IrH···HN interactions in solution. The hydrogen-bonded pyridinium proton of **1** in CD_2Cl_2 appears at 12.18 ppm as a broad singlet with a short minimum T_1 of 0.178 s (relaxation rate 5.6 s^{-1}) at 400 MHz, 233 K. This proton is near to only two dipolar nuclei: the ^{14}N nucleus at about 0.90 Å (relaxation rate contribution of about 2.5 s^{-1}) and the hydride which must therefore be at 1.77 ± 0.05 Å (relaxation rate contribution of 3.1 s^{-1}).[8] Similarly, the hydride resonance centered at −18.28 ppm is a broad triplet with a minimum T_1 of 0.168 s at 233 K. When the total relaxation contributions (2.2 s^{-1}) of the cis hydride at about 2.4 Å and two cyclohexyl protons at about 2.2 Å are subtracted from the hydride relaxation rate (5.95 s^{-1}), the calculated hydride to HN distance is 1.72 ± 0.05 Å. Therefore, the H···H distance in the IrH···HN unit of **1** in CD_2Cl_2 is about 1.75 ± 0.05 Å, consistent with the value of 1.75 ± 0.05 Å obtained by placing the hydrides into the X-ray-derived structure. An NOE difference experiment has also confirmed the presence of this short contact; irradiation at the hydride resonance resulted in an 11% enhancement of the NH peak. The widths of the IrH and NH peaks indicate that the $J(H\cdots H)$ coupling constant is 2 Hz or less.

When **1** is dissolved in THF-d_8, the THF forms a hydrogen bond with the pyridinium units and disrupts the IrH···HN

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(4) Preparation of **1**: $IrH_5(PCy_3)_2$ (50 mg, 0.066 mmol) was suspended in MeOH (6 mL) in a Schlenk flask, fitted with a stirring bar under argon. To this was slowly added a CH_2Cl_2 solution of ca. 2 equiv of $HSC_5H_4NHBF_4$ (26 mg, 0.13 mmol) while the flask was cooled in a dry ice/ethanol bath. After completion of addition, the solution was stirred for a further 20 min at −20 °C. The solvent was then partially removed *in vacuo* at this temperature. The resulting yellow powder was filtered and washed with *n*-hexane several times and dried *in vacuo*. The yield obtained was 74% (52 mg). NMR (CD_2Cl_2, δ): $^{31}P\{^1H\}$ 8.21 (s); ^1H −18.28 (t, 2H, $^2J_{PH}$ = 15.3 Hz, Ir*H*), 0.7–2.2 (m, 66H, $P(C_6H_{11})_3$), 6.88 (t, 2H, *para* to S of $SC_5H_4NH^+$), 7.43 (t, 2H, *para* to N of $SC_5H_4NH^+$), 7.73 (m, 4H, *ortho* to S and N of $SC_5H_4NH^+$), 12.18 (br s, 2H, $SC_5H_4NH^+$). IR (CH_2Cl_2, 20 °C): 2120, ν(Ir–H) (w). IR (KBr): 3184, 3111 $\nu(NH^+)$ (br); 2137, ν(Ir—H) (s br). Anal. Calcd for $C_{46}H_{78}BF_4IrN_2P_2S_2$: C, 51.86; H, 7.38; N, 2.63. Found: C, 51.43; H, 6.94; N, 2.44.

(5) Compound **1** of formula $C_{46}H_{78}IrN_2P_2S_2^+BF_4^-\cdot 2.7CH_2Cl_2$ crystallizes from CH_2Cl_2/pentane in the triclinic space group $P\bar{1}$ with a = 13.593(2), b = 14.179(3), and c = 17.067(3) Å, α = 111.60(1)°, β = 101.58(1)°, γ = 96.15(1)°, V = 2936.4(9) $Å^3$, Z = 2, T = 226 K. There was no decay in standards during data collection. Full-matrix least-squares refinement on F^2 for 8815 independent reflections; $R[F^2 > 2\sigma(F^2)] = 0.046$, $wR(F^2) = 0.109$. All non-hydrogen atoms in the cation and anion were refined anisotropically. The hydrogens on the nitrogens were located in an electron difference map but were placed in calculated positions. The hydrogens in the Ir–H bonds were not located. Interchanging N(1) with C(2) and N(2) with C(7) gave inappropriate thermal parameters in the refinements. Calculations were done using SHELXTL-PC and SHELXL-93.

(6) A somewhat related structure is $[Rh(\eta^2\text{-}SC_5H_4N)_2(\eta^1\text{-}SC_5H_4NH)_2]Cl$, where the chloride is hydrogen bonded to the protonated nitrogens. Deeming, A. J.; Hardcastle, K. I.; Meah, M. N.; Bates, P. A.; Dawes, H. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1988**, 227–233.

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(8) H–H distances were calculated using standard equations which apply to dipolar relaxation; the dipolar contribution of ^{14}N must be included for the NH proton. See ref 7 and the following: Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027–3039.

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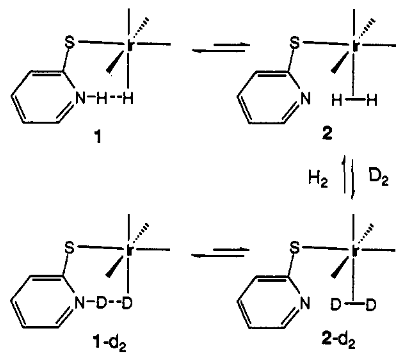
interaction. The chemical shifts of the IrH and NH hydrogens change from their positions in **1** in CD_2Cl_2.[9] Exciting the hydride resonance in an NOE difference experiment no longer gives an enhancement of the NH resonance. Instead, resonances at 7.65 ppm due to the hydrogens on the ortho carbons (C2 and C7 of Figure 1) of the pyridinium group are enhanced by 5%. Therefore, the pyridinium rings have flipped approximately 180° about the C–S bonds so that the THF can hydrogen-bond without interference from the cyclohexyl groups which shield the hydride site.[10] The T_1 values of the NH (0.29 s) and IrH (0.21 s) hydrogens at 253 K[11] are now longer than those for **1** in CD_2Cl_2 at 253 K (0.19 and 0.18 s, respectively) because there is no short IrH···HN interaction. Cooling this THF-d_8 solution results in broadening and then decoalescence (at 193 K) of the NH and IrH resonances into several peaks; this indicates the presence of different H-bonded conformers which are not observed in CD_2Cl_2 solution.[9] Very similar spectral changes to those in THF-d_8 are generated by a solution of **1** and $OPPh_3$ in a 1:2 ratio in CD_2Cl_2. The minimum T_1 values for this solution which occur at approximately 250 K are 0.23 s for the NH singlet at 12.66 ppm and 0.19 s for the IrH singlet at −18.26 ppm, again longer than the minimum values for **1**. Therefore, only 2 equiv of $OPPh_3$, a strong H-bond acceptor, are required to "turn off" the IrH···HN interaction.

When a solution of complex **1** in CD_2Cl_2 is exposed to D_2 (1 atm) for 5 min, the intensities of the NH and IrH resonances in the ^1H NMR decrease by approximately 75%. ^2H NMR experiments confirm that there is deuteration of these two sites as well as, to a lesser degree, at the ortho carbons of the pyridinium group and some carbons of the cyclohexyl rings. A solution of **1** in THF-d_8 under similar conditions does not react with D_2. We propose that the H/D exchange takes place in CD_2Cl_2 via initial intramolecular proton transfer from NH to IrH to give the dihydrogen tautomer **2** which can then exchange readily with D_2 gas (Scheme 1). This H/D exchange is switched off in THF because the NH is not positioned correctly for the intramolecular proton transfer step. This work implies that the pK_a of the η^2-H_2 ligand in **2** is less than that of $C_5H_5NH^+$ (pK_a(aq) = 5.2). In other words, the dihydrogen tautomer of **1** in CD_2Cl_2 is quite acidic.

The first report in the literature of a possible attractive intramolecular hydrogen interaction between an acidic hydrogen on a cis ligand and a hydride ligand was the X-ray and neutron diffraction study of $[Ir(H)(OH)(PMe_3)_4](BF_4)$ (**3**).[12,13] Complex **3** has an octahedral Ir(III) center containing cis hydride and the hydroxyl ligands. However, the H···H distance in the Ir—H···H—O unit is long at 2.40(1) Å. Recently Lee et al. reported evidence for a much shorter distance of ≈1.7 Å in an Ir—H···HO grouping in an iminol complex.[14] Somewhat related is the intermolecular interaction between a dihydrogen ligand and a chloride ligand Ir(η^2-HH)···(Cl)Ir with an H···Cl distance of 2.64 Å and an H—H distance of 1.11(3) Å.[15] These structural studies thus serve to map out the reaction trajectory for the deprotonation of the dihydrogen ligand—the heterolytic splitting of dihydrogen.[16,17]

Scheme 1



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Supplementary Material Available: Structure determination summary, two difference electron density maps around the Ir and N centers, and tables of fractional atomic coordinates, thermal parameters, bond distances and angles (14 pages); listing of observed and calculated structure factors (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(9) **1** in THF-d_8: ^1H NMR (293 K) δ −19.1 (t, 2H, $^2J_{PH}$ = 15.3 Hz, Ir*H*), 0.8–2.1 (m, 66H, $P(C_6H_{11})_3$), 6.92 (br t, 2H, *para* to S of $SC_5H_4NH^+$), 7.53 (br t, 2H, *para* to N of $SC_5H_4NH^+$), 7.65 (br d, 2H, *ortho* to S of $SC_5H_4NH^+$), 8.22 (br t, 2H, *ortho* to N of $SC_5H_4NH^+$), 13.0 (br s, 2H, $SC_5H_4NH^+$); ^1H NMR (193 K, all broad singlets) δ 13.8, 12.3, 12.8, 12.15, 11.7 (NH), −17.5, −17.7, −18.15, −19.1 (IrH); ^{31}P NMR (253 K) δ 10 ppm (br s).

(10) A reviewer suggested that the complex might isomerize in THF to the trans hydride form where dihydrogen elimination might be impossible. We consider this unlikely because of the small change in the ^{31}P NMR spectrum of **1** on going from CD_2Cl_2 to THF-d_8 and because of the fact that trans dihydride complexes are usually much higher in energy than cis dihydride ones.

(11) These T_1 values are near the minimum but this could not be verified due to broadening of the peaks below 250 K.

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