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Influence of Halide Ligands on the Energetics of the Reversible Loss of Hydrogen from the Iridium Nonclassical Polyhydride Complexes $IrXH_2(H_2)(PPr^i_3)_2$ (X = Cl, Br, I)

Trang Le-Husebo and Craig M. Jensen*

Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

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Recently there has been a great deal of interest in nonclassical polyhydride complexes.[1-21] Early studies of these complexes were primarily concerned with the determination of the dihydrogen versus hydride character of the metal-bound hydrogen.[1-18] More recent studies have focused on the influence of the ligand environment on the metal–dihydrogen interaction.[19-22] Crabtree[20] and Kubas[22] have shown that the activation of dihydrogen ligands increases with increasing basicity of ancillary phosphine ligands.[20] We have demonstrated[19] a threshold to the steric sensitivity of the energetics of the reversible binding of H_2 by the complexes $IrClH_2(PR_3)_2$ (R = Pr^i (**1a**), Cy (**1b**), Bu^t (**1c**)). Our results also suggest that the presence of the chloride ligand in **1a** is responsible for the arrested activation of dihydrogen in $IrClH_2(H_2)(PPr^i_3)_2$ (**2**) relative to $IrH_5(PPr^i_3)_2$.[23] In order to understand the influence of halide ligands on the activation of dihydrogen, we have prepared the complexes $IrXH_2(PPr^i_3)_2$ (X = Br (**3**), I (**4**)) and compared their hydrogen binding behavior to that previously observed[19] for $IrClH_2(PPr^i_3)_2$ (**1a**).

A procedure similar to Werner's method[24] of preparing $IrClH_2(PPr^i_3)_2$ (**1a**) was used to synthesize $IrBrH_2(PPr^i_3)_2$ (**3**). A solution of $[IrBr(C_8H_{14})_2]_2$[25] (100 mg, 0.102 mmol) in 15 mL of pentane was treated with PPr^i_3 (80 μL, 0.408 mmol). After 5 min of stirring, hydrogen was bubbled through the solution for 5 min. Removal of solvent by vacuum followed by recrystallization in pentane gave purified, yellow-orange **3**[26] (0.151 mg, 74% yield). Reaction of a solution of $[IrCl(C_8H_{14})_2]_2$[27] (100 mg, 0.110 mmol) and NaI (40 mg, 0.246 mmol) in 20 mL of methylene chloride with PPr^i_3 (89 μL, 0.440 mmol) followed by the same synthetic procedure gave purified, orange $IrIH_2(PPr^i_3)_2$ (**4**)[28] (100 mg, 71% yield).

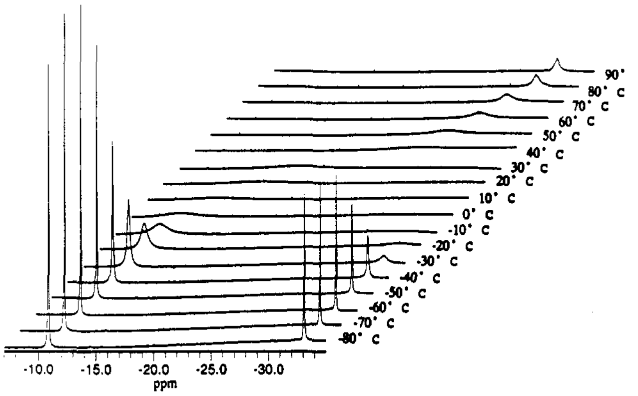

Figure 1. Variable-temperature ^1H NMR spectra (500 MHz) of the hydride region of $IrBrH_2(PPr^i_3)_2$ (**3**) dissolved in toluene-d_8 under 0.5 atm of H_2 (total pressure).

Variable-temperature ^1H and ^{31}P NMR spectroscopic studies have demonstrated[19] that, in the presence of H_2, the chloro complex, **1a**, establishes an equilibrium with the dihydrogen complex, **2**. The hydride regions of variable-temperature ^1H NMR spectra at 500 MHz of a sample of **3** dissolved in toluene and placed under 0.5 atm of hydrogen are seen in Figure 1. These spectra are similar to those obtained in our study of **1a** and indicate that **3** establishes a rapid equilibrium with the dihydrogen complex $IrBrH_2(H_2)(PPr^i_3)_2$ (**5**). Below −10 °C separate resonances are observed for the metal-bound hydrogens of **3** at −33.1 ppm and those of **5** at −10.9 ppm. In a parallel spectroscopic study of **4**, separate resonances are observed below −10 °C for the metal-bound hydrogens of **4** and $IrIH_2(H_2)(PPr^i_3)_2$ (**6**). The minimum T_1 values found for the resonances of **5** (54 ms, −60 °C) and **6** (43 ms, −60 °C) at 500 MHz are consistent[9,29,30] with the presence of rapidly exchanging hydride and dihydrogen ligands in these complexes.[31] A notable shift in the equilibrium position between

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(26) ^1H NMR (300 MHz, toluene-d_8), δ: 2.32, m, 6H, C*H*(CH_3)$_2$; 1.16, dvt, J_{H-H} = 13.7 Hz, J_{H-H} = 7.1 Hz, 36H, CH(C*H*$_3$)$_2$; −33.1, t, J_{H-P} = 12.9 Hz, 2H, Ir–*H*. $^{31}P\{^1H\}$ NMR (121.7 MHz, toluene-d_8), δ: 56.4, br s. $^{31}P\{^1H$ aliphatic only$\}$ NMR: t, J_{P-H} = 13.0 Hz. IR (KBr): ν_{M-H} 2256 cm^{-1}. Anal. Calcd: C, 36.36; H, 7.46. Found: C, 36.52; H, 7.16.
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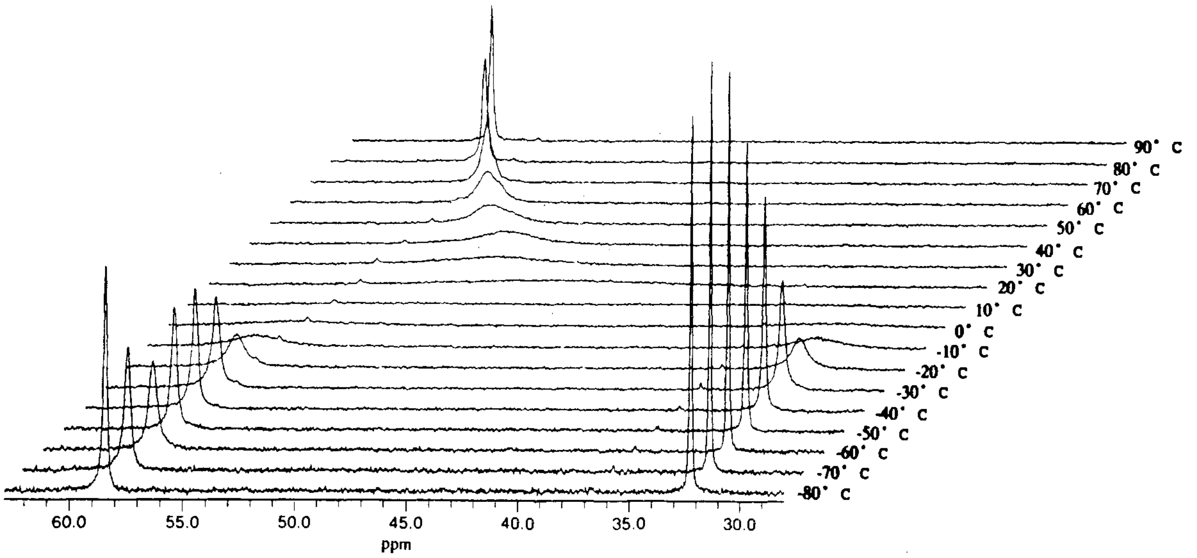

Figure 2. Variable-temperature ^1H NMR spectra (500 MHz) of the hydride region of $IrIH_2(PPr^i_3)_2$ (**4**) dissolved in toluene-d_8 under 0.5 atm of H_2 (total pressure).

the dihydrogen and unsaturated complexes can also be seen by comparison of the spectra obtained at −80 °C. Considering **5** and **6** contain twice the number of metal-bound hydrogens as **3** and **4**, the ratios of the integrated intensities of the equilibrating complexes at −80 °C show the equilibria to consist of the unsaturated and dihydrogen complexes in 1.1:1 and 0.6:1 ratios for bromo and iodo complexes, respectively. This difference in equilibrium position reflects a greater thermodynamic stabilization of the dihydrogen ligand in the case of the iodo complex. The dihydrogen ligand in both complexes is stabilized in comparison to that in the chloro analog for which the ratio of **1a** to **2** is observed to be 1.7 at 0.5 atm of hydrogen.

We have also studied the equilibrating solutions of **3**/**5** and **4**/**6** by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy (202.46 MHz). These spectra show temperature-dependent dynamic effects and trends in the equilibrium position similar to those observed in the ^1H NMR studies. Spectra of a sample of **4** under 0.5 atm of H_2 in toluene-d_8 are displayed in Figure 2. Below −10 °C, separate resonances are observed for **4** at 58.2 ppm and **6** at 32.4 ppm. A similar pair of resonances were observed for a sample of **3** under 0.5 atm of H_2 in toluene-d_8 at 56.4 and 35.6 ppm for **3** and **5**, respectively. Rate constants for the reversible release of H_2 from **2**, **5**, and **6** were approximated from line shape analysis[32] of variable-temperature spectra of the equilibrating solutions of **3**/**5** and **4**/**6** which were obtained at 10 °C increments over the temperature range −60 to −10 °C. Additionally, rate constants were also determined for equilibrating solutions of **1a**/**2** from variable-temperature $^{31}P\{^1H\}$ NMR spectra (202.46 Hz) of a sample of **1a** under 0.5 atm of H_2 in toluene-d_8 which were obtained at 10 °C increments over the temperature range −70 to −20 °C. From the activation parameters obtained from Eyring plots of the estimated rate constants, ΔG^* values for the reversible elimination of H_2 from **2**, **5**, and **6** at 0 °C were calculated to be 10.1 ± 0.6, 10.9 ± 0.8, and 11.4 ± 0.6 kcal/mol, respectively.

The thermodynamic stability of our dihydrogen complexes follows the $I^- > Br^- > Cl^-$ trend in σ-donor strengths.[33] Increasing halide σ-donation results in increased electron density at the metal center and thus enhancement of the d–σ* metal–dihydrogen interaction. This explanation is consistent with the lack of dihydrogen character found for the metal-bound hydrogen in $IrH_5(PPr^i_3)_2$,[22] where a strong σ-donating hydride replaces the halide ligand in our complexes. The $I^- > Br^- > Cl^-$ trend also appears to hold for the kinetic barrier to the elmination of H_2 from our dihydrogen complexes, although only the barriers determined for the chloro and iodo complexes differ within experimental error. This trend is also accounted for by the stabilization of the dihydrogen ligand by increased halide σ-donor strength. Our conclusions are potentially complicated by the possibility of stabilization of the unsaturated complexes **1a**, **3**, and **4** through lone-pair donation from the halide ligands to the iridium center. Such an effect was recently observed in the closely related complex $IrH_2(OCH_2CF_3)(PCy_3)_2$.[34] However, an X-ray structure determination[35] has shown the Ir–Cl distance of **1a** to be identical to the 2.427(2) Å found[19] for **2**. Additionally, the 2.728(3) Å Ir–I distance determined[36] for **4** indicates that there is no significant π-internificant between the halide lone pair and the iridium center of the unsaturated complex. We conclude that, in addition to the established influences of π-donor abilities[20,22] and steric constraints,[19] the σ-donor abilities of ancillary ligands contribute to the kinetic and thermodynamic stabilities of dihydrogen complexes.

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Supplementary Material Available: Figures of variable-temperature ^1H NMR spectra (500 MHz) of samples of $IrClH_2(PPr^i_3)_2$ and $IrIH_2(PPr^i_3)_2$ dissolved in toluene-d_8 under 0.5 atm of hydrogen, variable-temperature $^{31}P\{^1H\}$ NMR spectra of samples of $IrClH_2(PPr^i_3)_2$ and $IrBrH_2(PPr^i_3)_2$ dissolved in toluene-d_8 under 0.5 atm of hydrogen, and simulated variable-temperature $^{31}P\{^1H\}$ NMR spectra of equilibrating solutions $IrClH_2(PPr^i_3)_2/IrClH_2(H_2)(PPr^i_3)_2$, $IrBrH_2(PPr^i_3)_2/IrBrH_2(H_2)(PPr^i_3)_2$, and $IrIH_2(PPr^i_3)_2/IrIH_2(H_2)(PPr^i_3)_2$ (7 pages). Ordering information is given on any current masthead page.

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