J. Am. Chem. Soc. **1994**, *116*, 3137–3138 3137

Preparation and Properties of [TpIr(PMe$_3$)(H$_2$)H]BF$_4$: Observation of Novel Isotopic Perturbation

D. M. Heinekey* and Warren J. Oldham, Jr.

Department of Chemistry BG-10
University of Washington
Seattle, Washington 98195

Received December 21, 1993

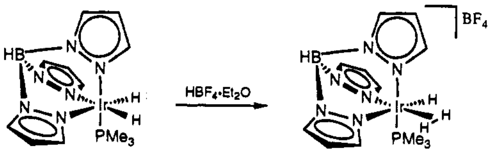
There is currently great interest in the structure and reactivity of transition metal polyhydride complexes. Many polyhydrides are stereochemically nonrigid (fluxional) with very low barriers to rearrangements which render all the hydride ligands equivalent on the NMR time scale. Since the first report of a molecular hydrogen complex by Kubas and co-workers,[1] the possibility that a fluxional polyhydride complex may also contain a dihydrogen ligand has been investigated by a number of workers, primarily using T_1 measurements to detect short H–H contacts.[2] In general, the most definitive solution-state indicator for the presence of a dihydrogen ligand is the observation of H–D coupling upon partial deuteration. A wide range of values for J_{HD} have been reported, but most of the reported H–D complexes have H–D coupling constants of 15–35 Hz.[3,4] Fluxional polyhydride complexes, $L_mM(H_2)H_n$ ($n \geq 1$), suspected to contain a dihydrogen ligand should also display J_{HD} couplings in the ^1H NMR spectrum upon partial deuteration, albeit reduced in magnitude due to statistical averaging. There is also the possibility of large isotope effects on the ^1H NMR chemical shifts due to isotopic perturbation of resonance (IPR).[5] Surprisingly, retention of H–D coupling in the high-temperature limiting spectrum of metal polyhydrides has rarely been observed.[6] IPR effects have never been conclusively observed in a polyhydride complex.

Following our observation of large proton–proton exchange couplings in *trihydride* complexes of the type $[(C_5H_5)Ir(L)H_3]BF_4$ (L = various PR$_3$),[7] Chaudret, Limbach, and co-workers have postulated the existence of a thermally accessible dihydrogen/hydride tautomer to explain the observed large couplings in these and related polyhydride complexes.[8] In order to explore the effect of an increase in the steric demand of the coligands which might be expected to stabilize a dihydrogen/hydride structure, we have investigated substitution of the cyclopentadienyl moiety for the sterically more demanding hydridotris(pyrazolyl)borate ligand (Tp).[9] This communication addresses the synthesis and characterization of TpIr(PMe$_3$)H$_2$ (**1**) and its reaction with HBF$_4$·Et$_2$O to yield [TpIr(PMe$_3$)(H$_2$)H]BF$_4$ (**2**). Unusual temperature dependent IPR and IPC data is presented for **2**-d_1 and **2**-d_2 which indicates that deuterium favors the terminal hydride site over the dihydrogen ligand in this complex.

Complex **1** was prepared in a one-pot reaction from $[(\eta\text{-}C_5Me_5)Ir(PMe_3)H_3]SO_3CF_3$.[10] Following the recent report by Pedersen and Tilset for the PPh$_3$ analog,[11] we find that dissolution of the trihydride complex in acetonitrile generates $[(MeCN)_3Ir(PMe_3)H_2]SO_3CF_3$. Subsequent addition of NaTp affords **1** in 55% yield as an air-stable colorless solid (eq 1).[12]

$$[(C_5Me_5)Ir(PMe_3)H_3]SO_3CF_3 \xrightarrow[(2)\ NaTp]{(1)\ MeCN} \underset{\mathbf{1}}{(Tp)Ir(PMe_3)H_2} \qquad (1)$$

Complex **2** can be generated by reaction of HBF$_4$·Et$_2$O with **1** in CD$_2$Cl$_2$ at room temperature or can be isolated from Et$_2$O at 0 °C (eq 2). Room temperature ^1H and ^{13}C NMR spectra of **2** exhibit appropriate resonances for the Tp and PMe$_3$ ligands,[13] but only a single hydride resonance was observed in the ^1H NMR spectrum at −10.4 ppm ($^2J_{PH}$ = 11 Hz).[14] A quartet ($^2J_{PH}$ = 11 Hz) at −42.7 ppm is observed in the ^{31}P NMR spectrum when the methyl protons are decoupled. These observations are very similar to those that we have previously made for the cyclopentadienyl analog of **2** (which is a *trihydride*). In contrast, the T_1 (min, 300 MHz) for the hydride resonance of **2** is found to be 21 ms at 182 K, suggestive of a dihydrogen/hydride structure.[15]



1 2 (2)

Deuteration of the hydride positions is observed over the course of several hours at room temperature upon exposure of solutions of **2** to an atmosphere of D$_2$. The ^1H NMR spectra of mixtures of **2**, **2**-d_1, and **2**-d_2 show large, temperature dependent *downfield*

---

(1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 451–452.

(2) (a) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133. (b) Luo, X. L.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 2788–2791. (c) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173–4184.

(3) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913–926.

(4) Exceptionally low J_{HD} coupling constants have been observed in a series of osmium dihydrogen complexes: (a) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1990**, *112*, 2261–2263. (b) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946–8947.

(5) This effect results from nonstatistical occupation of two chemically distinct proton sites by deuterium. Similar effects in agostic alkyl complexes were first noted by Calvert and Shapley: Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726–7727. Similarly, isotopic perturbation of coupling (IPC) could also be observed. In this case, the J_{HD} values observed for various isotopomers of a polyhydride complex need not be the same.

(6) H–D coupling in polyhydrides: (a) Baird, G. J.; Davies, S. G.; Moon, S. D.; Simpson, S. J.; Jones, R. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1479–1486. (b) Paciello, R.; Manriquez, J. M.; Bercaw, J. E. *Organometallics* **1990**, *9*, 260–265. In dihydrogen/hydride complexes: (c) Bampos, N.; Field, L. D. *Inorg. Chem.* **1990**, *29*, 587–588. (d) Earl, K. A.; Guochen, J.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027–3039. In general, retention of H–D coupling at high temperature should be commonly observed in dihydrogen-containing polyhydride species. The general lack of such reports in the literature can presumably be attributed to the relatively small values of the H–D coupling.

(7) (a) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909–919. (b) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Neshyba, S. P.; Duchamp, J. C.; Szcyrba, J. *J. Am. Chem. Soc.* **1990**, *112*, 920–929.

(8) Limbach, H. H.; Schere, G.; Maurer, M.; Chaudret, B. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1369–1370.

(9) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943–980.

(10) This trihydride complex was previously obtained by reaction of $(\eta\text{-}C_5Me_5)Ir(PMe_3)H_2$ with HBF$_4$ by Bergman and Gilbert: Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3502–3507. We find that a more efficient synthesis can be achieved using the reaction of $(\eta\text{-}C_5Me_5)Ir(PMe_3)Cl_2$ with AgSO$_3$CF$_3$ under an atmosphere of hydrogen.

(11) Pedersen, A.; Tilset, M. *Organometallics* **1993**, *12*, 3064–3068.

(12) Data for **1** are as follows. ^1H NMR (CD$_2$Cl$_2$, 298 K): δ (ppm) 7.70, 7.63 (d, J_{HH} = 2 Hz, 2 H, 3,5-pz$_{eq}$); 7.67, 7.59 (m, 1 H, 3,5-pz$_{ax}$); 6.18 (t, J_{HH} = 2 Hz, 2 H, 4-pz$_{eq}$); 6.08 (m, 1 H, 4-pz$_{ax}$); 1.63 (d, $^2J_{PH}$ = 10.0 Hz, 9 H, P*Me*$_3$); −21.3 (d, $^2J_{PH}$ = 25.0 Hz, 2 H, Ir–*H*). $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$, 298 K): δ (ppm) 146.2, 134.0 (s, 1 C, 3,5-pz$_{ax}$); 144.0, 138.8 (s, 2 C, 3,5-pz$_{eq}$); 105.8 (s, 1 C, 4-pz$_{ax}$); 105.6 (s, 2 C, 4-pz$_{eq}$); 21.7 (d, $^1J_{PC}$ = 39.4 Hz). ^{31}P NMR (CD$_2$Cl$_2$, 298 K): δ (ppm) −45.6 (t, $^2J_{PH}$ = 25 Hz). IR (Nujol): ν(B–H) = 2482 cm^{-1}; ν(Ir–H) = 2143 cm^{-1}. MS: *m/z* 484 (M$^+$), 482 (M − 2H)$^+$. Anal. Calcd (found) for $C_{12}H_{21}BIrN_6P$: C, 29.83 (29.51); H, 4.38 (4.83); N, 17.39 (17.26).

(13) Data for **2** are as follows. ^1H NMR (CD$_2$Cl$_2$, 298 K): δ (ppm) 7.87, 7.85 (d, J_{HH} = 2 Hz, 2 H, 3,5-pz$_{eq}$); 7.69, 7.67 (br s, 1 H, 3,5-pz$_{ax}$); 6.43 (t, J_{HH} = 2 Hz, 2 H, 4-pz$_{eq}$); 6.32 (br m, 1 H, 4-pz$_{ax}$); 1.78 (d, $^2J_{PH}$ = 11 Hz, 9 H, P*Me*$_3$); −10.4 (d, $^2J_{PH}$ = 11 Hz, 3 H, Ir–*H*). $^{13}C\{^1H\}$ NMR (CD$_2$Cl$_2$, 298 K): δ (ppm) 146.1, 135.8 (s, 1 C, 3,5-pz$_{ax}$); 144.9, 136.8 (s, 2 C, 3,5-pz$_{eq}$); 107.8 (s, 2 C, 4-pz$_{eq}$); 107.3 (s, 1 C, 4-pz$_{ax}$); 17.9 (d, $^1J_{PC}$ = 42.9 Hz, P*Me*$_3$). ^{31}P NMR (CD$_2$Cl$_2$, 298 K): δ (ppm) −42.7 (q, $^2J_{PH}$ = 11 Hz). IR (Nujol): ν(B–H) = 2499 cm^{-1}; ν(Ir–H) = 2199 cm^{-1}. Anal. Calcd (found) for $C_{12}H_{22}B_2F_4IrPN_6$: C, 25.24 (25.45); H, 3.88 (4.03); N, 14.72 (14.40).

(14) ^1H NMR spectra obtained for a Freon-21 solution composed principally of **2**-d_2 show no evidence for decoalescence of the hydride resonance at temperatures down to 127 K.

(15) The T_1 observed for the hydride protons in $[(\eta\text{-}C_5H_5)Ir(PMe_3)H_3]^+$ is 300 ms: Heinekey, D. M.; Payne, N. G.; Schulte, G. K. *J. Am. Chem. Soc.* **1988**, *110*, 203–205.

0002-7863/94/1516-3137$04.50/0

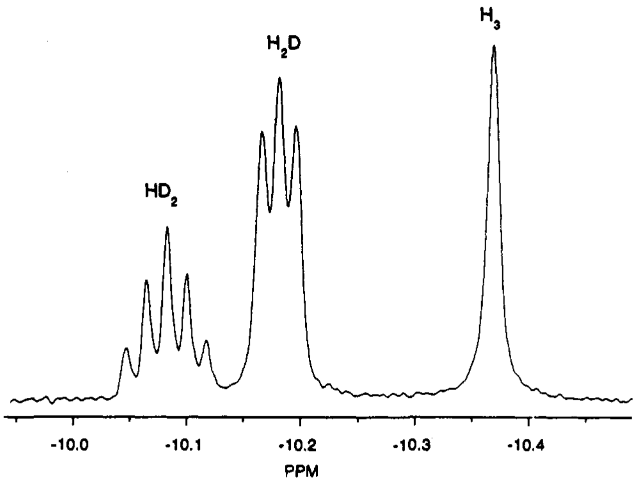
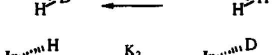
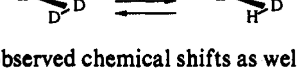


Figure 1. High-field region of the $^1H\{^{31}P\}$ NMR spectrum (CD_2Cl_2, 500 MHz, 240 K) of a partially deuterated sample of $[TpIr(PMe_3)(H_2)H]BF_4$ (**2**). Signals due to **2**-d_1 and **2**-d_2 exhibit H–D coupling of 7.5 and 8.8 Hz, respectively.

isotope shifts for the hydride resonances attributed to **2**-d_1 and **2**-d_2 (see Figure 1). The isotope shifts, $\Delta_1 = \delta(H_2D) - \delta(H_3)$ and $\Delta_2 = \delta(HD_2) - \delta(H_2D)$, vary from 228 and 122 ppb at 215 K to 149 and 72 ppb at 281 K, respectively. Over the same temperature range, J_{HD} coupling varies from 6.87 to 7.63 Hz for **2**-d_1. In this temperature range J_{HD} = 8.75 Hz for **2**-d_2 and is essentially independent of temperature. These observations are rationalized by proposing a nonstatistical site preference for the deuterium isotope (eqs 3 and 4; Ir = $TpIrPMe_3$).



(3)



(4)

The observed chemical shifts as well as the J_{HD} coupling data can be analyzed quantitatively at various temperatures (eqs 5–9) to obtain the limiting chemical shifts of the dihydrogen ligand (δ_{H_2}) and the terminal hydride (δ_H), J_{HD} coupling for the dihydrogen ligand, and K_1 and K_2, the equilibrium constants for eqs 3 and 4.

$$\delta(H_3) = (2\delta_{H_2} + \delta_H)/3 \tag{5}$$

$$\delta(H_2D) = (K_1\delta_{H_2} + \delta_{H_2} + \delta_H)/(2 + K_1) \tag{6}$$

$$\delta(HD_2) = (2K_2\delta_{H_2} + \delta_H)/(2K_2 + 1) \tag{7}$$

$$J(H_2D) = J_{HD}/(2 + K_1) \tag{8}$$

$$J(HD_2) = (J_{HD}K_2)/(2K_2 + 1) \tag{9}$$

This analysis indicates that J_{HD} = 24.6 Hz, δ_{H_2} = −8.4 ppm, and δ_H = −14.4 ppm. These values for the chemical shift and the H–D coupling can most profitably be compared with the iridium benzoquinolinate (bq) complex $[IrH(H_2)(PPh_3)_2(bq)]^+$ in which Crabtree and Lavin reported similar low-temperature limiting chemical shifts and J_{HD} = 29.5 Hz.[16]

Of greater interest is the observation that both K_1 and K_2 are greater than unity (*ca.* 1.32 and 1.26, respectively, at 240 K[17]), indicating a tendency for deuterium to concentrate in the hydride site, rather than the dihydrogen ligand. Since the chemical shift of the dihydrogen ligand is downfield of the hydride signal, this leads to the significant downfield isotope shift upon deuteration.[18] Although we are not able to attempt a full analysis due to the lack of complete vibrational data for **2**, since only a weak Ir–H stretch at 2199 cm^{-1} was observed, it is a valid approximation to assume that the H–H stretching mode in **2** will have a frequency of *ca.* 2600–2700 cm^{-1} and will be reduced by *ca.* 300 cm^{-1} upon deuteration. This approximation is based on data reported by Kubas for a tungsten dihydrogen complex.[19] Thus the energy change upon deuterium substitution can be estimated to slightly favor the concentration of deuterium in the terminal site since deuteration will shift the terminal metal hydride stretching mode by 644 cm^{-1}.

It should be noted that there are several examples of *cis* dihydrogen/hydride complexes in the literature. Partial deuteration has been generally employed to establish the presence of the H_2 ligand, but large isotope effects such as those observed here have not been previously reported. A modest *upfield* isotope shift has been reported by Field and co-workers in $[Fe\{P(CH_2CH_2CH_2PMe_2)_3\}(H_2)H]BPh_4$. The fact that $J_{HD}(H_2D) > J_{HD}(HD_2)$ in this iron complex is consistent with some concentration of deuterium in the dihydrogen ligand.[6c]

The observations reported here demonstrate that alteration of the ligand set from Cp (or Cp*) to Tp in this iridium complex alters the ground-state structure from a trihydride to a very dynamic dihydrogen/hydride.[20] Partial deuteration and the observation of IPR allow the limiting chemical shifts δ_{H_2} and δ_H to be determined. From this data and the observation of a single hydride resonance at 127 K, the activation energy for the hydride site exchange can be calculated as $\Delta G^‡ \le 5$ kcal mol^{-1}. The slight preference of deuterium for the terminal hydride site in **2** has potentially important implications for the interpretation of any molecular property which is thought to represent a population-weighted average of more than one rapidly equilibrating structure.

We are continuing to explore the preparation and properties of complexes related to **2**.

Acknowledgment. We thank the National Science Foundation for support of this research. We are grateful for fellowship support (W.J.O.) from the Chevron Research and Technology Company.

---

[16] (16) (a) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794–795. (b) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032–4037.

[17] (17) Note that this analysis does not require that $K_1 = K_2$; however, we find that they are indistinguishable within experimental error (±7%).

[18] (18) This analysis does not take into account the possible existence of *intrinsic* isotope effects, which are usually upfield and relatively small. *Cf.*: Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813–4821.

[19] (19) Kubas, G. J.; Ryan, R. R. *Polyhedron* **1986**, *5*, 473–485.

[20] (20) Similar observations have been recently reported by Chaudret and co-workers for a ruthenium complex: Halcrow, M. A.; Chaudret, B.; Trofimenko, S. *J. Chem. Soc., Chem. Commun.* **1993**, 465–467.