# Deuteration Studies of $Tp^*IrH_4$ ($Tp^*$ = $HB(3,5\text{-}Me_2pz)_3$): Observation of Very Unusual $^1H$ NMR Chemical Shift Effects

Margarita Paneque, Manuel L. Poveda,* and
Soraya Taboada

*Departamento de Química Inorgânica*
*Instituto de Ciencia de Materiales*
*Universidad de Sevilla-CSIC*
*Apdo. 553, 41071 Sevilla, Spain*

*Received October 15, 1993*
*Revised Manuscript Received January 25, 1994*

Transition metal polyhydrides continue to attract broad general interest mainly with respect to their formulation as classical hydrides or dihydrogen complexes.[1] Following our recent studies on Ir complexes containing the $Tp^*$ ligand ($Tp^*$ = $HB(3,5\text{-}Me_2pz)_3$),[2] we now show that the high-temperature hydrogenation of a variety of $Tp^*Ir(R)(R')L$ species (R, R′ = hydride, alkyl, or aryl, L = labile 2e⁻ donor ligand, e.g., $Tp^*Ir(C_6H_5)_2(N_2)$,[2b] 60 °C, $C_6H_{12}$, 2–3 atm, 3 h) affords the very stable $Tp^*IrH_4$ (**1**) as a white microcrystalline solid.[3] $^1H$ NMR spectroscopy indicates that **1** is a highly fluxional molecule with the three pyrazolate arms of the $Tp^*$ ligand and the four hydrides remaining equivalent on the NMR time scale even at −70 °C. Similarly to the closely related species $Cp^*IrH_4$, reported[4] by Bergman in 1983, complex **1** behaves chemically as a classical Ir(V) polyhydride and reacts with donor ligands, like CO and $PMe_3$, only under rather forcing conditions (90–130 °C, 24 h) to produce the expected $Tp^*Ir(H)_2L$ products.[2c] Variable temperature $T_1$ measurements[1,5] are also more in accord with the description of **1** as an Ir(V) tetrahydride ($T_1$(min) ca. 400 ms, flat region, −50 to −70 °C, 500 MHz, $CD_2Cl_2$).[6] This contrasts with the recently reported Rh analogue $Tp^*Rh(H)_2(H_2)$, which has been shown to contain a dihydrogen ligand.[7]

Upon deuteration, complex **1** shows remarkable spectroscopic behavior. A $C_6D_6$ (or $C_6D_5CD_3$) solution of **1**, at room temperature, gradually incorporates (days) deuterium exclusively into the hydride sites (Figure 1) to produce a mixture of all possible isotopomers $Tp^*IrH_{4-n}D_n$ ($n$ = 0–4). As it can be observed, $J_{HD}$ couplings are clearly resolved and their values slightly increase with the deuterium content . These $J_{HD}$ seem to be somewhat larger than expected for a classical polyhydride,[1] and this may suggest the presence of an elongated (H···H) dihydrogen ligand or, alternatively, the establishment of a fast tautomeric equilibrium with an unobserved $Ir(H)_2(H_2)$ species.[1a,b,8,9] However, it is important to note that truly authenticated Ir(V) classical polyhydrides such as $[(C_5H_5)Ir(H)_3L]^+$ exhibit similar $T_1$ and $J_{HD}$ values (e.g., 3.7 Hz for L = $AsPh_3$; computed from the reported[10] $J_{HT}$ couplings). Accordingly, we favor formulation of **1** as a classical Ir(V) polyhydride with a four-legged piano-stool structure, a proposal which is also in accord with the substitution chemistry mentioned above.

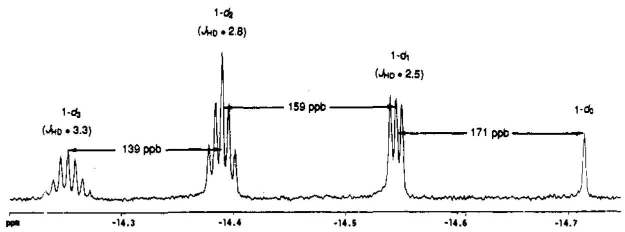


**Figure 1.** High-field region of the $^1H$ NMR spectrum ($C_6D_6$, 25 °C) of a mixture of the isotopomers $Tp^*IrH_{4-n}D_n$ (**1**-$d_n$, $n$ = 0–3).

While this matter remains open to discussion, a most remarkable variation of the chemical shift of the hydride ligands is observed upon deuteration. Very small shifts to *higher fields* are usually observed upon deuteration of an $AH_n$ species ($\Delta\delta_n = \delta d_n - \delta d_{n-1}$ = −10 to −20 ppb),[11] but in some cases enhanced $^1H$ chemical shifts are detected and explained on the basis of isotopic perturbation of resonance[12] phenomena (IPR), such as the existence of fast equilibria between tautomeric $AH_n$ species or isotope fractionation between unequivalent H sites. Theoretically, the IPR shifts can be to either higher or lower field with respect to the reference isotopomer,[13] and in transition metal agostic alkyls and related systems they can be as large as −1 ppm, particularly at low temperatures.[1b,14,15] In transition metal polyhydrides, $\Delta\delta_1$ is normally in the range ~0 to ~−50 ppb,[10,16,17] although some abnormal *low-field* shifts ($\Delta\delta_1$ = 10–80 ppb) have been observed recently.[5a,7b,8a,16c,18] For complex **1**, $\Delta\delta_1$ *amounts to 170 ppb*, and other $\Delta\delta_n$ values decrease slightly upon further deuteration. The spectrum shown in Figure 1 is essentially field, concentration, and solvent independent (aromatic solvents or

---

(1) (a) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789. (c) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120.

(2) (a) Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288. (b) Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Carmona, E. *J. Am. Chem. Soc.* **1994**, *116*, 791. (c) Unpublished work from this laboratory. (d) For a general reference on Tp–Ir complexes, see: Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943.

(3) Selected spectroscopic data for **1**: IR (Nujol mull) 2155 (s) cm$^{-1}$; $^1H$ NMR ($C_6D_6$, 25 °C) $\delta$ −14.71 (s, 4 H, IrH), 2.15 (s, 9 H, 3 Me), 2.19 (s, 9 H, 3 Me), 5.57 (s, 3 H, 3 CH); $^{13}C$ NMR ($C_6D_6$, 25 °C) $\delta$ 12.0, 16.8 (Me), 105.1 (CH). Anal. Calcd for **1**: C, 36.50; H, 5.32; N, 17.03. Found: C, 36.64; H, 5.13; N, 16.51.

(4) Gilbert, T. M.; Bergman, R. G. *Organometallics* **1983**, *2*, 1458.

(5) (a) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173. (b) Gusev, D. G.; Nietlispach, D.; Vymenits, A. B.; Bakhmutov, V. I.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3270 and references therein.

(6) For comparison, the dihydride $Tp^*Ir(H)_2$(thiophene)[2c] shows a $T_1$(min) of 670 ms at −40 °C (500 MHz, $CD_2Cl_2$).

(7) (a) Bucher, U. E.; Lengweiler, T.; Nanz, D.; von Philipsborn, W.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 548. (b) Nanz, D.; von Philipsborn, W.; Bucher, U. E.; Venanzi, L. M. *Magn. Reson. Chem.* **1991**, *29*, S38.

(8) (a) Earl, K. A.; Jia, G.; Maltby, P.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027. (b) Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241. (c) Kim, Y.; Deng, H.; Meek, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 2798. (d) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1991**, *113*, 8946. (e) Hasegawa, T.; Koetzle, T. J.; Li, Z.; Parkin, S.; McMullan, R.; Taube, H. *Abstracts of the 29th International Conference on Coordination Chemistry*; Lausanne, Switzerland, 1992; p 575. (f) Michos, D.; Luo, X.-L.; Howard, J. A. K.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 3914.

(9) From the observed $J_{HD}$ a value of ca. 17 Hz can be computed[1a] for the coupling within the elongated H···D ligand in a hypothetical $Tp^*Ir(H\cdots D)(H)_{2-n}(D)_n$ species ($n$ = 0–2). It is important, however, to note that this calculation assumes zero value for all the $^2J_{HD}$ couplings, and this may not be a good approximation, at least for third-row transition metal complexes. In fact, $^2J_{HD}$ values of 3.7 and 2.0 Hz have been found in Ir and Re classical polyhydrides, respectively. See ref 10b and the following: Casey, C. P.; Tanke, R. S.; Hazin, P. N.; Kemnitz, C. R.; McMahon, R. J. *Inorg. Chem.* **1992**, *31*, 5474.

(10) (a) Heinekey, D. M.; Payne, N. G.; Schulte, G. K. *J. Am. Chem. Soc.* **1988**, *110*, 2303. (b) Heinekey, D. M.; Millar, J. M.; Koetzle, T. F.; Payne, N. G.; Zilm, K. W. *J. Am. Chem. Soc.* **1990**, *112*, 909.

(11) (a) Batiz-Hernandez, H.; Bernheim, R. A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1967**, *3*, 63. (b) Lambert, J. B.; Greifenstein, L. G. *J. Am. Chem. Soc.* **1974**, *96*, 5120. (c) Hanson, P. E. *Annu. Rep. NMR Spectrosc.* **1983**, *15*, 105.

(12) (a) Saunders, M.; Jaffe, M. H.; Vogel, P. *J. Am. Chem. Soc.* **1971**, *93*, 2558. (b) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070.

(13) (a) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912. (b) Hamilton, D. G.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3198.

(14) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

(15) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(16) (a) Heinekey, D. M.; Chinn, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (b) Bianchini, C.; Pérez, P. J.; Peruzzini, M.; Zanobini, F.; Vacca, A. *Inorg. Chem.* **1991**, *30*, 279. (c) Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876 and references cited in these papers.

(17) For comparison, in free $H_2$, $\Delta\delta_1$ = −36 ppb. Evans, D. F. *Chem. Ind. (London)* **1961**, 1960.

0002-7863/94/1516-4519$04.50/0

acetone-$d_6$), but it is temperature dependent: while the $J_{HD}$ values remain almost unchanged, *all the* $\Delta\delta_n$ experience similar behavior, with lower temperatures enhancing $\Delta\delta_n$. Thus, in the proximity of -50 °C $\Delta\Delta\delta_n$ is on the order of 3 ppb/deg while near 50 °C $\Delta\Delta\delta_n$ is only about 1 ppb/deg. Hence, at -60 °C the four observable **1**-$d_0$–$d_3$ isotopomers span over a 1 ppm range.

The observed $\delta$ values for **1**-$d_n$ may be explained with reference to a Tp*Ir(H)$_2$(H$_2$) species with very anomalous $\delta_H$ and $\delta_{H_2}$ values,[1a] but the almost insignificant variation of $\Delta\Delta\delta_n$ with $n$, in the temperature range studied (toluene-$d_8$, -50 °C: $\Delta\delta_1 = 339$, $\Delta\delta_2 = 324$, $\Delta\delta_3 = 285$ ppb, hence $\Delta\delta_1 - \Delta\delta_2 = 15$ and $\Delta\delta_2 - \Delta\delta_3 = 39$ ppb; at 25 °C (Figure 1) $\Delta\delta_1 - \Delta\delta_2 = 12$ and $\Delta\delta_2 - \Delta\delta_3 = 20$ ppb), seems to argue against this possibility, since only under very special circumstances could IPR considerations predict such a variation.[13,19] Since, on the other hand, the related complex TpIrH$_4$[20] (Tp = HBpz$_3$) exhibits similar behavior, it is clear that this phenomenon cannot be associated with the sterically demanding Tp* ligand. A plausible, although somewhat speculative, explanation is to invoke the higher transoid (and perhaps cisoid[21]) influence of $^2$H as compared to $^1$H, which can give rise, in certain transition metal systems, to low-field chemical shifts upon deuteration. This effect, first evidenced by Crabtree[22] employing $^{13}$C NMR spectroscopy, was subsequently invoked by Morris[8a,16c] and Luo[18a] in $^1$H NMR studies of dihydrogen complexes. In fact, a simple model of this kind predicts[23] equal values of $\Delta\delta_n$ for **1**-$d_n$, i.e., in good agreement with our experimental data.[24] In any case, irrespective of the origin of the spectroscopic behavior,[25] it seems clear that the observation of remarkably large $^1$H low-field shifts upon deuteration of the type herein reported requires a precise combination of metal and ligands since no such shifts are observed, for example, for Cp*IrH$_4$[4] and TpReH$_6$.[13b]

**Acknowledgment.** We thank Prof. Ernesto Carmona for his encouragement and support and the Dirección General de Investigación Científica y Técnica for financial support (Grant No. PB90-0890). We also thank the University of Sevilla for the use of NMR and analytical facilities.

**Supplementary Material Available:** A plot of the $\Delta\delta_n$ values in the **1**-$d_n$ species as a function of temperature (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(18) (a) Michos, D.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 4245. (b) Miller, R. L.; Toreki, R.; LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D.; Roe, D. C. *J. Am. Chem. Soc.* **1993**, *115*, 5570. (c) Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.; McMullan, R. K.; O'Loughlin, T. J.; Pélissier, M.; Ricci, J. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300. (d) Antoniutti, B.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1989**, 229.

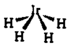
(19) At present, we are unable to find a reasonable chemical and spectroscopic model that predicts an IPR effect of this kind. A more detailed discussion will be presented in the full paper.

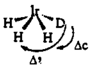
(20) So far, this complex has not been obtained in an analytically pure form. $\delta_{IrH}$ (C$_6$D$_6$, 25 °C) -14.8; $\Delta\delta_1 = 164$ ppb; $\Delta\delta_2 = 151$ ppb; $\Delta\delta_3 = 134$ ppb; $J_{HD} = 2.5, 2.8$, and 3.2 Hz for the $d_1$, $d_2$, and $d_3$ isotopomers, respectively.

(21) Interestingly, the hydride resonance of Tp*Ir(H)$_2$(thiophene)[2c] exhibits a small shift to *lower field* upon deuteration ($\Delta\delta_1 = 20$ ppb).

(22) Crabtree, R. H.; Habib, A. *Inorg. Chem.* **1986**, *25*, 3698. The same effect may be responsible for the downfield drift of the phosphorus resonance in the complex (C$_5$Me$_5$)Rh(PMe$_3$)(H)$_2$ upon deuteration of the hydride sites. See: Jones, W. D.; Kuykendall, V. L.; Selmeczy, A. D. *Organometallics* **1991**, *10*, 1577.

(23) If $\Delta_{transoid}$ and $\Delta_{cisoid}$ are the corresponding additive deuteride effects in a four-legged piano-stool structure, then $\Delta\delta_n = (\Delta_{transoid} + 2\Delta_{cisoid})/3$. This is exemplified below for the $d_1$ species (for the $d_2$ isotopomer both interchangeable cisoid and transoid ground-state stereochemistries with their 2:1 statistical populations must be taken into account). This effect needs to be temperature dependent.





$\delta_0$

$\delta_1 = [(\delta_0+\Delta_t)+2(\delta_0+\Delta_c)]/3 = \delta_0+(\Delta_t+2\Delta_c)/3$

(24) The deviations from ideal behavior may be caused by a coexistent IPR effect that shifts the resonances to higher field, with this effect being enhanced upon progressive deuteration.[7b] Alternatively, and more consistent with the properties of **1**, these deviations may be attributed to the normal upfield shifts (ca. 10–30 ppb) expected upon deuteration.[11]

(25) A recent report dealing with mercury hydrides shows a distinct lower field shift of the $^{199}$Hg NMR signal in the deuterated species, RHgD, as compared with RHgH. Thus, it seems that, contrary to the expectations, deuterium attached to very heavy metal atoms can, under certain circumstances, induce anomalous downfield chemical shift effects. See: Kwetkat, K.; Kitching, W. *J. Chem. Soc., Chem. Commun.* **1994**, 345.