

# Synthesis and Properties of $\text{Tp}^{\text{Me}_2}\text{IrH}_4$ and $\text{Tp}^{\text{Me}_2}\text{IrH}_3(\text{SiEt}_3)$ : Ir(V) Polyhydride Species with $C_{3v}$ Geometry

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**Abstract:** The hydrogenation of  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$  under forcing conditions ( $\text{C}_6\text{H}_{12}$ , 90 °C, 2 atm, 3 days) affords the tetrahydride  $\text{Tp}^{\text{Me}_2}\text{IrH}_4$  (**1\***) in very high yield.  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{R})(\text{R}')(\text{L})$  complexes ( $\text{R} = \text{R}' = \text{H}$ , alkyl, aryl;  $\text{L} =$  labile ligand) can also be used for the synthesis of **1\***, but their hydrogenation is not as clean as that of the bis(ethylene) complex.  $\text{TpIrH}_4$  (**1**) has also been obtained from  $\text{TpIr}(\text{C}_2\text{H}_4)_2$  by a similar procedure but only in  $\leq 10\%$  yield.  $\text{Tp}^{\text{Me}_2}\text{IrH}_4$  is a very stable molecule, and both its chemical behavior and  $T_1$  relaxation studies are in accord with a classical, highly fluxional, tetrahydride structure.  $^1\text{H}$  and  $^2\text{H}$  NMR spectroscopic studies carried out with mixtures of  $\text{Tp}^{\text{Me}_2}\text{IrH}_{4-n}\text{D}_n$  ( $n = 0-4$ ) species reveal the existence of a very unusual isotopic perturbation of resonance (IPR) effect that is best reconciled with **1\*** (and, by extension, with **1**), possessing in solution a ground-state  $C_{3v}$  structure in which a hydride ligand caps the face of the remaining hydrides in an otherwise distorted octahedral structure. Due to the existence of two kinds of Ir–H bonds, a nonstatistical fractionation of D in the two types of hydride sites available is observed upon deuteration, and this constitutes a very rare example of an IPR effect on a classical polyhydride. It is also the first one that shows in addition resolved  $J_{\text{HD}}$  couplings. Complex **1\*** exchanges easily its hydrides with deuteriums not only in deuterated protolytic solvents but also in  $\text{C}_6\text{D}_6$  and other substrates, albeit under somewhat more forcing condition. This behavior has been exploited in a somewhat limited catalytic deuteration of THF by  $\text{D}_2\text{O}$ . The very stable compound  $\text{Tp}^{\text{Me}_2}\text{IrH}_3(\text{SiEt}_3)$  (**2\***) can be easily obtained from  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{C}_2\text{H}_4)$  or  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$  and neat  $\text{HSiEt}_3$  at 80 °C. Spectroscopic studies, including those of the deuterated species  $\text{Tp}^{\text{Me}_2}\text{IrH}_{3-n}\text{D}_n(\text{SiEt}_3)$  ( $n = 1-3$ ) (which show no IPR effect), are in accord with **2\*** being an Ir(V) species with a similar  $C_{3v}$  geometry in which the  $\text{SiEt}_3$  group acts as the capping ligand. This assumption is supported by a single-crystal X-ray study.

## Introduction

Transition metal polyhydrides continue to attract the general interest of the chemical community.<sup>1</sup> After the seminal discovery of Kubas et al. of the first dihydrogen complex,<sup>2</sup> much work has been devoted to understanding fully the factors that promote the dihydrogen structure ( $\text{M}(\text{H}-\text{H})$  or elongated  $\text{M}(\text{H}\cdots\text{H})$  ligands) vs the so-called classical dihydride formulation ( $\text{MH}_2$ ).<sup>3</sup> From recent studies, it seems apparent that the presence of  $\text{Tp}'$  ligands ( $\text{Tp}' =$  any hydrotris(1-pyrazolyl)borate)<sup>4</sup> favors the adoption of the dihydrogen form when compared with the related  $\text{Cp}'$  system; the following examples illustrate this point:  $[\text{TpIrH}(\text{H}_2)(\text{PR}_3)]^+$  vs  $[\text{CpIrH}_3(\text{PR}_3)]^+$ ;<sup>5</sup>  $\text{Tp}'\text{RuH}(\text{H}_2)(\text{PR}_3)$  vs  $\text{Cp}'\text{RuH}_3(\text{PR}_3)$ ,<sup>6</sup> and  $[\text{TpRu}(\text{H}_2)(\text{PPh}_3)_2]^+$  vs  $[\text{CpRuH}_2(\text{PPh}_3)_2]^+$ .<sup>7</sup> In all

these cases, the formation of the  $\text{H}_2$  ligand allows the corresponding complex to adopt an octahedral configuration, a geometry very stable for  $\text{Tp}'\text{M}$  systems, particularly those of the middle and late transition metals.<sup>8,9</sup> In accord with this trend, even some  $\text{Tp}'\text{RuH}(\text{H}_2)_2$  species that possess a very rare combination of two dihydrogen ligands have been described.<sup>6a</sup> By contrast, both  $\text{TpReH}_6$ <sup>10</sup> and  $(\text{C}_5\text{Me}_5)\text{ReH}_6$ <sup>11</sup> appear to exist as classical Re(VII) complexes. Thus, it is evident that the presence of a  $\text{Tp}'$  ligand is not a sufficient condition for  $\text{M}(\text{H}_2)$  stabilization. In this contribution, we report on the synthesis,

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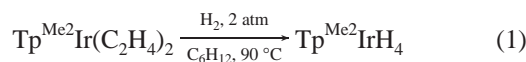
(3) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155. (b) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913. (c) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

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spectroscopic characterization, and some chemical properties of  $\text{Tp}^{\text{Me}_2}\text{IrH}_4$ . Our preliminary report<sup>12</sup> described this complex as an Ir(V) species with a pseudo- $C_{4v}$  "piano stool" geometry. However, the peculiarities observed in the  $^1\text{H}$  NMR spectra upon partial deuteration of the hydride sites and other new data obtained are best reconciled with a seven-coordinate formulation derived from a capped-octahedron in which one of the hydrides caps the face comprising the other hydride ligands, i.e.,  $C_{3v}$  geometry. To seek further evidence for this hypothesis, we have investigated the somewhat related compound  $\text{Tp}^{\text{Me}_2}\text{IrH}_3(\text{SiEt}_3)$ , for which X-ray studies are in agreement with the above proposal: the  $\text{SiEt}_3$  group now acts as the capping fragment.

## Results and Discussion

**Synthesis and Chemical Properties of  $\text{Tp}^{\text{Me}_2}\text{IrH}_4$  (**1\***).** Complex **1\*** was first observed in our study of the hydrogenolysis of  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{2-thienyl})_2(\text{thiophene})$  in  $\text{C}_6\text{H}_{12}$ .<sup>13</sup> This reaction afforded (2 atm, 60 °C, 6 h)  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{SC}_4\text{H}_4)$  as the main product, but a minor hydride species was also detected in the upfield region of the  $^1\text{H}$  NMR spectrum recorded in  $\text{C}_6\text{D}_6$ . The characteristic resonance of product **1\***, a singlet at  $-14.71$  ppm, slowly disappeared with time in that solvent with concomitant appearance of closely spaced multiplets characteristic of HD couplings in a partially deuterated polyhydride. By forcing the conditions of the reaction (2 atm, 90 °C, 6 h), complex **1\*** was obtained as the main product in very high yield. Other Ir(III) species can be used as starting materials for the synthesis of **1\***, and thus, for example,  $\text{Tp}^{\text{Me}_2}\text{IrH}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$ <sup>9,14</sup> and  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_6\text{H}_5)_2(\text{N}_2)$ <sup>15</sup> react with  $\text{H}_2$  at 70–90 °C with ultimate formation of **1\***. While in the first case the known<sup>14</sup>  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{C}_2\text{H}_4)$  can be detected as an active intermediate, in the hydrogenation of the bis(phenyl) derivative no intermediates are observed (NMR monitoring). The simplest preparative route, and the only one described in the Experimental Section, however, involves the Ir(I) complex  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$ <sup>9</sup> as the starting material, thus avoiding the preparation of the above-mentioned Ir(III) species that, after all, need be synthesized from the same bis(ethylene) derivative. In that case, the intermediates  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{C}_2\text{H}_4)$  and  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$  are formed under  $\text{H}_2$ , even at room temperature,<sup>14</sup> and further hydrogenation under more forcing conditions ( $\text{C}_6\text{H}_{12}$ , 2 atm, 90 °C, 3 days) is needed to transform this mixture into **1\*** (eq 1). Quite recently, Venanzi et al.<sup>16</sup> have also observed the formation of **1\*** in the hydrogenation of other  $\text{Tp}^{\text{Me}_2}\text{Ir}$  substrates.



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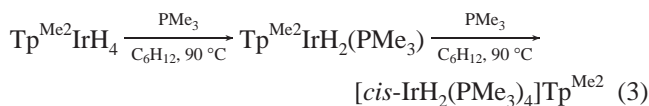
Although the related  $\text{TpIr}(\text{C}_2\text{H}_4)_2$ <sup>17</sup> complex can be easily hydrogenated at 25 °C to give  $\text{TpIrH}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$ ,<sup>14</sup> further reaction with  $\text{H}_2$  at higher temperatures gives only small yields (~10%) of the corresponding  $\text{TpIrH}_4$  (**1**), along with a mixture of uncharacterized products. This is not a surprising result since, in general,  $\text{TpIr}$  compounds exhibit poorer thermal stability and more complex decomposition routes than the  $\text{Tp}^{\text{Me}_2}$  analogues.<sup>9,14</sup> For this reason, **1** has only been characterized by high-field  $^1\text{H}$  NMR spectroscopy without attempted purification.

Crude **1\***, as it results from the evaporation of  $\text{C}_6\text{H}_{12}$  after the hydrogenation reaction, can be easily purified by washing with a little cold methanol, and in that way it is isolated as a white microcrystalline powder. It is only slightly soluble in  $\text{C}_6\text{H}_{12}$  and  $\text{C}_6\text{H}_6$  but appreciably more so in  $\text{CH}_2\text{Cl}_2$ ; the solubility increases with temperature. It is also quite soluble in  $\text{CDCl}_3$ , but its solutions in this solvent are less stable due to a slow chlorination reaction. In the solid state, in an open atmosphere, complex **1\*** remains unaltered for long periods of time. It is also a remarkably thermally stable compound, which decomposes only slightly upon heating in  $\text{C}_6\text{H}_{12}$  at 100 °C (Ar or  $\text{N}_2$ , 2–3 h).

$\text{Tp}^{\text{Me}_2}\text{IrH}_4$  is a rather inert molecule. Heating at 60 °C with carbon monoxide ( $\text{C}_6\text{H}_{12}$ , 3 atm, 24 h) causes only a small conversion to the known<sup>14</sup>  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{CO})$ ; higher temperatures are required for the complete transformation to be achieved at a practical rate (eq 2). Significantly, under the same thermal



treatment, complex **1\*** does not transform into  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{SC}_4\text{H}_4)$ ,<sup>13</sup> even when a very large excess of thiophene is used as substrate.  $\text{PMe}_3$  is also a very poor trapping reagent. When **1\*** is heated in  $\text{C}_6\text{H}_{12}$  at 130 °C with >100 equiv of  $\text{PMe}_3$ , clean conversion to an ionic species that contains the cation  $[\text{cis-IrH}_2(\text{PMe}_3)_4]^+$  is achieved. Based on spectroscopic data, we formulate this product with  $\text{Tp}^{\text{Me}_2-}$  acting as the counterion. The complex  $[\text{IrH}_2(\text{PMe}_3)_4]\text{PF}_6$  was mentioned in a preliminary form by Thorn,<sup>18</sup> but, to our knowledge, no spectroscopic data of the cation have been published in the open literature. In an attempt to detect some intermediates in this interesting transformation (eq 3), the reaction was repeated with ca. 1 equiv of  $\text{PMe}_3$ . In this case, and at low conversions, the dihydride  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{PMe}_3)$ <sup>5b,14</sup> was detected in the mixture.

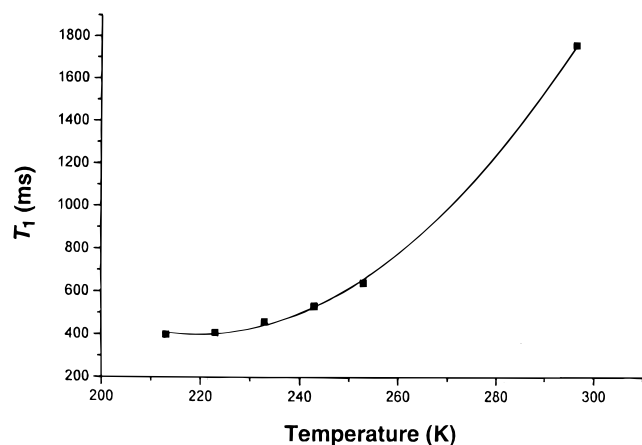


It is tempting to speculate that the substitution reactions mentioned above require the formation of " $\text{Tp}^{\text{Me}_2}\text{IrH}_2$ " as the active intermediate, which thereafter coordinates the Lewis base present in solution. This unsaturated  $16e^-$  species has been postulated in recent studies on the photochemistry of  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{COE})$  (COE = cyclooctene),<sup>19</sup> but the apparent dependence of the reactivity of **1\*** on the nature of the incoming ligand may indicate an associative mechanism with concomitant change in the hapticity of the  $\text{Tp}^{\text{Me}_2}$  ligand. Further kinetic studies are clearly needed to clarify this point.

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**Figure 1.**  $T_1$  relaxation time of the hydride nuclei of complex **1\*** as a function of temperature ( $\text{CD}_2\text{Cl}_2$ , 500 MHz). The curve has been drawn only as a guide for the eye.

In 1983, Gilbert and Bergman<sup>20</sup> reported the synthesis of  $(\text{C}_5\text{Me}_5)\text{IrH}_4$  and described it as a polyhydride of Ir(V) with a pseudo- $C_{4v}$  “piano stool” geometry, a formulation that found later additional support in the theoretical studies of Lin and Hall.<sup>21</sup> Quite interestingly, the reactivity of this  $\text{C}_5\text{Me}_5$  complex closely resembles that found for **1\*** and therefore supports the formulation of the latter as an Ir(V) species.<sup>22</sup>

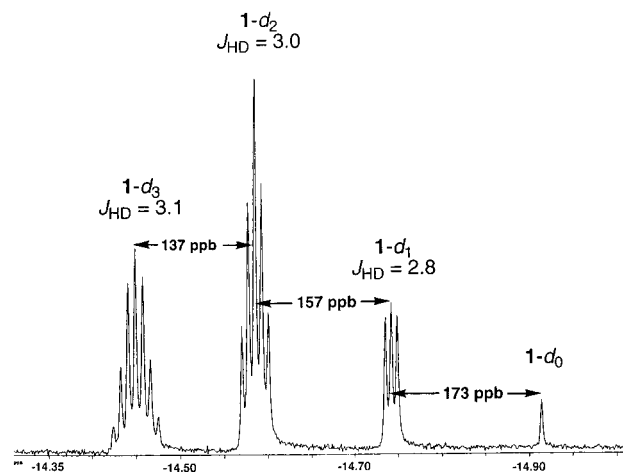
**Spectroscopic Characterization of  $\text{Tp}^{\text{Me}_2}\text{IrH}_4$  (**1\***).**  $^1\text{H}$  NMR spectroscopy indicates that **1\*** is a highly fluxional molecule with the three pyrazolate arms of the  $\text{Tp}^{\text{Me}_2}$  ligand and the four hydrides remaining equivalent on the NMR time scale even at  $-70^\circ\text{C}$ . As mentioned above, the hydride resonance appears as a singlet at ca.  $-15$  ppm ( $-14.71$ ,  $\text{C}_6\text{D}_6$ ;  $-14.92$ ,  $\text{CD}_2\text{Cl}_2$ , both at  $25^\circ\text{C}$ ). Variable-temperature  $T_1$  studies are also in accord with **1\*** being a classical tetrahydride. Figure 1 shows the experimental  $T_1$  values vs temperature ( $\text{CD}_2\text{Cl}_2$ , 500 MHz), and, although a clear minimum is not observed, a safe  $T_1(\text{min})$  of ca. 400 ms can be deduced from the graph. For comparison, the Rh and Ir hydrides  $\text{Tp}^{\text{Me}_2}\text{MH}_2(\text{PMe}_3)$  show  $T_1(\text{min})$  of 390 (M = Ir) and 360 ms (M = Rh) at  $-70^\circ\text{C}$  ( $\text{CD}_2\text{Cl}_2$ , 400 MHz). For the related Ir complex  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{thiophene})$ , the  $T_1(\text{min})$  is greater, being 670 ms at  $-40^\circ\text{C}$  ( $\text{CD}_2\text{Cl}_2$ , 500 MHz). If we assume that the major contribution to the relaxation of an Ir–H nucleus in the thiophene complex is the dipole–dipole interaction with the remaining *cisoid* hydride, a crude estimate of the  $T_1(\text{min})$  of **1\***, which may have, at most, three H,H interactions, is  $670/3 = 223$  ms. Consideration of other relaxation sources, such as the interaction with the Me groups of the  $\text{Tp}^{\text{Me}_2}$  ligand, will approach the experimental and grossly calculated  $T_1(\text{min})$  values. Recent  $\text{MH}_4$  species of late third-row transition metals are available for comparison: the  $T_1(\text{min})$  (average) of  $[(\text{C}_5\text{Me}_5)\text{OsH}_2(\text{H}_2)(\text{PPh}_3)]^+$ , which possesses an elongated dihydrogen ligand, as demonstrated by neutron diffraction studies, is 99 ms at 500 MHz;<sup>23</sup> that of  $\text{OsH}_2(\text{H}_2)(\text{CO})(\text{PBUt}_2\text{Me})_2$  is ca. 24 ms (average, 300 MHz),<sup>24</sup> and finally  $[\text{IrH}_2(\text{H}_2)(\text{triphos})]^+$  exhibits  $T_1(\text{min})$  values of 36 and  $<13$  ms

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

(21) Lin, Z.; Hall, M. B. *Organometallics* **1992**, *11*, 3801.

(22) Other stable Ir(V) complexes include the following. (a)  $(\text{C}_5\text{Me}_5)\text{IrMe}_3$ : Isobe, K.; Vázquez de Miguel, A.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 929. (b)  $\text{IrH}_4(\text{SiR}_3)(\text{PPh}_3)_2$ : Loza, M.; Faller, J. W.; Crabtree, R. H. *Inorg. Chem.* **1995**, *34*, 2937. (c)  $\text{IrH}_4(\text{C}_6\text{H}_3-2,6-(\text{CH}_2\text{PBUt}_2)_2)$ : Gupta, M.; Hagen, C.; Kaska, W. C.; Cramer, R. E.; Jensen, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 840. (d)  $\text{Ir}(\text{=O})(\text{mesityl})_3$ : Hay-Motherwell, R. S.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1993**, *12*, 2009.

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**Figure 2.** High-field region of the  $^1\text{H}$  NMR spectrum ( $\text{CD}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ , 400 MHz) of a mixture of the isotopomers  $\text{Tp}^{\text{Me}_2}\text{IrH}_{4-n}\text{D}_n$  (**1\***- $d_n$ ,  $n = 0-4$ ).

(300 MHz) for the hydride and dihydrogen ligands, respectively.<sup>25</sup> Although the use of the  $T_1$  criterion for the establishment of a dihydrogen structure may lead to ambiguous or incorrect conclusions,<sup>3,24,26,27</sup> and keeping in mind that some dihydrogen complexes are relatively stable molecules,<sup>3</sup> both the chemical behavior and the  $T_1(\text{min})$  value of **1\*** strongly support a classical formulation. By contrast,  $\text{Tp}^{\text{Me}_2}\text{RhH}_2(\text{H}_2)$  is stable only at low temperatures and has a  $T_1(\text{min})$  of 42 ms at  $-107^\circ\text{C}$  (400 MHz).<sup>28</sup>

Further insight into the nature of complex **1\*** comes from deuteration studies. Despite its remarkable inertness against Lewis bases, solutions of **1\*** in  $\text{C}_6\text{D}_6$  at  $25^\circ\text{C}$  slowly evolve to the deuterated species  $\text{Tp}^{\text{Me}_2}\text{IrH}_{4-n}\text{D}_n$  ( $n = 1-4$ ), i.e., with the deuteration being specific to the hydride sites. More practical deuteration rates for spectroscopic studies are achieved by heating at  $60^\circ\text{C}$ , the deuteration content being readily monitored by  $^1\text{H}$  NMR spectroscopy. Both the  $k_{\text{H}\rightarrow\text{D}}$  qualitative values and the fact that these rates decrease only very slightly in the presence of 2 atm of  $\text{H}_2$  indicate that the mechanism of the **1\***- $\text{C}_6\text{D}_6$  deuterium exchange does not involve the above-mentioned “ $\text{Tp}^{\text{Me}_2}\text{IrH}_2$ ” intermediate. In fact, recent work by Sostero et al.<sup>19</sup> is in accord with this unsaturated species evolving in  $\text{C}_6\text{H}_6$  first with formation of “ $\text{Tp}^{\text{Me}_2}\text{IrH}(\text{C}_6\text{H}_5)$ ” and then with subsequent reaction. A radical mechanism for the deuteration can also be excluded as the isotope exchange is not inhibited by the presence of hydroquinone. We will return to this topic later on in this manuscript. Complex **1** experiences the same sequence of events and at a similar rate in  $\text{C}_6\text{D}_6$ .

Figure 2 contains a representative  $^1\text{H}$  NMR spectrum (high-field region) of a mixture of the isotopomers  $\text{Tp}^{\text{Me}_2}\text{IrH}_{4-n}\text{D}_n$ . It clearly shows separated resonances for all the **1\***- $d_n$  ( $n = 0-3$ ) species and also that  $J_{\text{HD}}$  are clearly resolved. Further deuteration does not result in any new resonance, and therefore the  $\text{IrH}_4$  formulation is secured. The  $J_{\text{HD}}$  values increase slightly with the deuteration content (2.8, **1\***- $d_1$ ; 3.0, **1\***- $d_2$ ; and 3.1 Hz, **1\***-

(24) Gusev, D. G.; Kuhlman, R. L.; Renkema, K. B.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 6775.

(25) Bianchini, C.; Moneti, S.; Peruzzini, M.; Viza, F. *Inorg. Chem.* **1997**, *36*, 5818.

(26) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173.

(27) Gusev, D. G.; Hübener, R.; Burger, P.; Orama, O.; Berke, H. *J. Am. Chem. Soc.* **1997**, *119*, 3716.

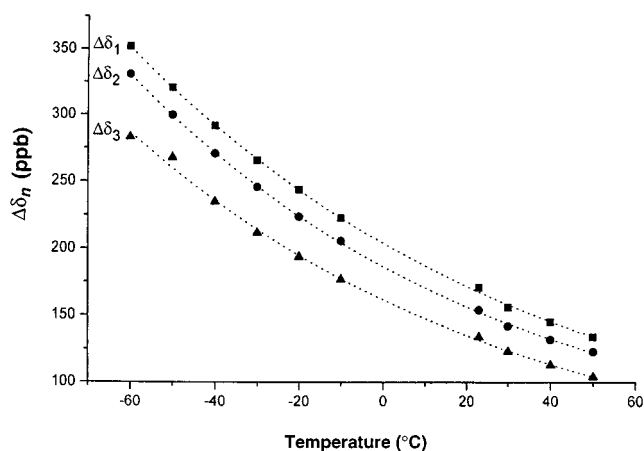
(28) (a) Bucher, U. E.; Lengweiler, T.; Nanz, D.; von Philipsborn, W.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 548. (b) Nanz, D.; von Philipsborn, W.; Bucher, U. E.; Venanzi, L. M. *Magn. Reson. Chem.* **1991**, *29*, S38.



$d_3$ ).<sup>29</sup> Almost the same figures are computed for  $1-d_n$ . While these values seem, at first, somewhat high for a true tetrahydride species, we will try to demonstrate that this is not the case. In a hypothetical  $\text{Tp}^{\text{Me}_2}\text{IrHD}(\text{H}\cdots\text{D})$  species, values in the range 18–13 Hz can be computed for the coupling within the elongated  $\text{H}\cdots\text{D}$  ligand.<sup>3a,30</sup> This is done on the assumption that all the  ${}^2J_{\text{HD}}$  couplings vary between 0 and 1 Hz, and whereas this appears to be a general, widely accepted approximation, it may not be a sufficiently good one. In fact, there is an increasing number of classical hydrides that exhibit much larger  ${}^2J_{\text{HD}}$  coupling. These include  $[\text{OsH}_3(\text{PMe}_3)_4]^+-d_1$  (3.8 Hz),<sup>27</sup>  $[(\text{C}_5\text{H}_5)\text{IrH}_3(\text{AsPh}_3)]^+-d_1$  (3.7 Hz, computed from the reported  $J_{\text{HT}}$ ),<sup>5d</sup>  $[\text{OsH}_3(\text{CH}_3\text{CN})_2(\text{PPr}_3)_2]^+-d_1$  (2.8 Hz),<sup>31</sup> and  $[\text{Pd}(\text{dipp})]_2(\mu\text{-H})_2-d_1$  (2.4 Hz).<sup>32,33</sup> Particularly interesting in our context are the above-mentioned  $\text{MH}_4$  species  $[\text{IrH}_2(\text{H}_2)(\text{triphos})]^+-d_1$  (4.6 Hz),<sup>25</sup>  $\text{OsH}_2(\text{H}_2)(\text{CO})(\text{PBU}'_2\text{Me})_2-d_1$  (4.2 Hz),<sup>24</sup> and  $[(\text{C}_5\text{Me}_5)\text{OsH}_2(\text{H}\cdots\text{H})(\text{PPh}_3)]^+-d_1$  (3.6 Hz),<sup>23</sup> with this last species having an elongated dihydrogen ligand. From this sequence of average  $J_{\text{HD}}$  couplings, our experimental value of 2.8 Hz (for  $1^*-d_1$ ) is clearly in accord with a classical tetrahydride structure. Of course, there are classical tetrahydrides of the third-row transition elements that do not show resolved  $J_{\text{HD}}$  couplings ( $<1$  Hz?), for example,  $[\text{ReHD}_3(\text{CO})(\text{PR}_3)_3]^+$  ( $T_1(\text{min})$  for the  $\text{H}_4$  species:  $\text{PR}_3 = \text{PMe}_2\text{Ph}$ , 101 ms at 250 MHz;  $\text{PMe}_3$ , 130 ms at 300 MHz)<sup>34</sup> and the already mentioned  $(\text{C}_5\text{Me}_5)\text{IrH}_4$ .<sup>20,35</sup> From all the literature data, we have to conclude that, at least in the polyhydrides  $\text{MH}_n$  with  $n \geq 4$ , the assignment of  $\text{M}(\text{H}-\text{H})$  or  $\text{M}(\text{H}\cdots\text{H})$  structures on the basis of the average  $J_{\text{HD}}$  couplings can be seriously misleading, mostly because of the uncertainty that accompanies the usually unknown  ${}^2J_{\text{HD}}$  values. This conclusion has also been reached by other authors.<sup>24,27</sup>

#### Evidence for the Existence of an IPR Effect in $\text{Tp}^*\text{IrH}_4$ .

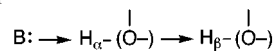
The most interesting feature of the  ${}^1\text{H}$  NMR spectra of both  $1-d_n$  and  $1^*-d_n$  ( $n = 0-3$ ) is the remarkable variation of the chemical shift of the hydride ligands upon deuteration. For the species  $1^*-d_n$ ,  $\Delta\delta_n = \delta_{d_n} - \delta_{d_{n-1}}$  are all positive, i.e. to lower field with respect to the reference isotopomer, and  $\Delta\delta_1$  is as large as 170 ppb at 25 °C (Figure 2). Other  $\Delta\delta_n$  values decrease slightly upon further deuteration, and for **1** the  $\Delta\delta_n$  values are quite similar:  $\Delta\delta_1 = 164$ ,  $\Delta\delta_2 = 151$ ,  $\Delta\delta_3 = 134$  ppb. The spectrum shown is essentially field, concentration, and solvent independent (aromatic solvents or acetone- $d_6$ ). It is, however, temperature dependent: while the  $J_{\text{HD}}$  values remain almost unchanged, all the  $\Delta\delta_n$  experience similar behavior, with lower temperatures enhancing  $\Delta\delta_n$ . Thus, in the proximity of  $-50$



**Figure 3.** Variation of  $\Delta\delta_n$  values in the  $1^*-d_n$  species as a function of temperature (acetone- $d_6$ ). The dotted lines have been drawn only as a guide for the eye.

°C,  $\Delta\Delta\delta_n$  is of the order of 3 ppb/deg, while near 50 °C  $\Delta\Delta\delta_n$  is only about 1 ppb/deg (Figure 3). Hence, at  $-60$  °C, the four observable  $1-d_0-d_3$  isotopomers span a 1-ppm range. Very small shifts to higher fields are usually observed upon deuteration of an  $\text{AH}_n$  species ( $\Delta\delta_n = -10$  to  $-20$  ppb),<sup>36</sup> but in some cases enhanced  ${}^1\text{H}$  chemical shifts are detected and explained on the basis of isotopic perturbation of resonance phenomena (IPR),<sup>37</sup> such as the existence of fast equilibria between tautomeric  $\text{AH}_n$  species or isotope fractionation between nonequivalent H sites. Theoretically, the IPR shifts can be to either higher or lower field with respect to the reference isotopomer,<sup>34a,37c,38</sup> and in transition metal agostic alkyls and related systems they can be as large as  $-1$  ppm,<sup>3c,39</sup> particularly at low temperatures (IPR effects are normally very sensitive to temperature<sup>37c</sup>). In transition metals, polyhydrides'  $\Delta\delta_1$  is normally in the approximate range from 0 to  $-50$  ppb,<sup>40,41</sup> although some abnormal low-field shifts ( $\Delta\delta_1 = 10-230$  ppb) have been observed,<sup>40c,42</sup> the

(36) (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. Some interesting exceptions to this rule are found in the cations  $\text{NH}_{4-n}\text{D}_n^+$  and  $\text{OH}_{3-n}\text{D}_n^+$ , in the sense that  $\Delta\delta_n$  is positive; see: (d) Sanders, J. K. M.; Hunter, B. K.; Jameson, C. J.; Romeo, G. *Chem. Phys. Lett.* **1988**, *143*, 471. (e) Gold, V.; Grant, J. L.; Morris, K. P. *J. Chem. Soc., Chem. Commun.* **1976**, 397. This is also the case in some hydrogen-bonded aggregates of the type



when the  $\text{H}_\beta$  atom is substituted by D, see: (f) Lemieux, R. U.; Bock, K. *Jpn. J. Antibiot.* **1979**, *32* (Suppl.), S-163. (g) Christopides, J. C.; Davies, D. B.; Martin, J. A.; Rathbone, E. B. *J. Am. Chem. Soc.* **1986**, *108*, 5738. For some interesting down- and high-field deuterium effects in the  ${}^1\text{H}$  chemical shift of the OH group of stabilized enols, see: (h) Biali, S. E.; Rappoport, Z.; Hull, W. E. *J. Am. Chem. Soc.* **1985**, *107*, 5450.

(37) (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. (c) Siehl, H.-U. *Adv. Phys. Org. Chem.* **1987**, *23*, 63.

(38) Hamilton, D. G.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3198.

(39) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726. (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(40) (a) Heinekey, D. M.; Chinn, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (b) Bianchini, C.; Pérez, P. J.; Peruzzini, M.; Zanolini, 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. (d) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3, 875. (e) Ruiz, J.; Mann, B. E.; Spencer, C.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 1963 and references cited in these papers. For  $\text{M}(\text{H}_2)$  complexes, see: Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1998**, *37*, 127 and references therein.

(41) For comparison, in free  $\text{H}_2$ ,  $\Delta\delta_1 = -36$  ppb. Evans, D. F. *Chem. Ind. (London)* **1961**, 1960.

(29) These values are slightly different from those reported in ref 12. The data reported in Figure 2 have been obtained under higher digital resolution.

(30) For example, and taking into account statistical weighting,  ${}^1J_{\text{H}\cdots\text{D}} = 6J_{\text{HD}}(\text{aver}) - 5J_{\text{HD}} = 6(3) - 5 = 13$  Hz when all the  ${}^2J_{\text{HD}}$  values are taken as 1 Hz.

(31) Smith, K.-T.; Tilset, M.; Kuhlman, R.; Caulton, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 9473.

(32) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 3804.

(33) Early transition metal classical polyhydrides can also show high  ${}^2J_{\text{HD}}$  values. Recent examples, computed from the reported  ${}^2J_{\text{HH}}$  couplings, include the following. (a)  $[(\text{C}_5\text{Me}_5)\text{ZrH}_3]^-$ , 2.6 Hz: Etkin, N.; Hoskin, A. J.; Stephan, D. W. *J. Am. Chem. Soc.* **1997**, *119*, 11420. (b)  $(\text{C}_5\text{Me}_5)(\text{C}_5\text{H}_4\text{-SiMe}_3)\text{TaH}_3$ , 1.8 Hz: Castro, A.; Gómez, M.; Gómez-Sal, P.; Manzanero, A.; Royo, P. *J. Organomet. Chem.* **1996**, *518*, 37.

(34) (a) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912. (b) Gusev, D. G.; Nietispach, D.; Evemenko, I. L.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3628.

(35) The hydride resonance of  $\text{Tp}^{\text{Me}_2}\text{IrHD}(\text{thiophene})$  is broader than the corresponding signal of the dihydride, but the  ${}^2J_{\text{HD}}$  coupling cannot be resolved. From the width of the resonance, we estimate  ${}^2J_{\text{HD}} \approx 1$  Hz.  $\text{Tp}^{\text{Me}_2}\text{-IrH}_2(\text{CH}_2=\text{CHCOOBu}')$  (ref 19) shows  ${}^2J_{\text{HH}} = 7.3$  Hz, and hence  ${}^2J_{\text{HD}} = 1.1$  Hz.

first example being apparently that reported by Harrod et al. in 1979.<sup>43,44</sup> Some of them, particularly those of the  $[\text{Tp}^{\text{Me}_2}\text{IrH}(\text{H}_2)]$ - $(\text{PR}_3)^+$  system of Heinekey et al.,<sup>5a,b</sup> are clearly derived from an IPR effect, but others have been explained on the basis of the higher *transoid* influence of D as compared with <sup>1</sup>H, which can give rise, in certain H(H<sub>2</sub>) systems, to low-field chemical shifts upon deuteration.<sup>40c,42a,b</sup> Although in some cases this last explanation may be open to discussion, we believe that, in special instances, there are examples of small, low-field shifts that cannot be explained by IPR; i.e.,  $\Delta\delta_1$  for  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{thiophene})$  is +20 ppb, and this may be a *cisoid* influence of the D or an intrinsic deuterium effect of anomalous sign.<sup>45,46</sup>

In our original report,<sup>12</sup> we suggested that, for **1\***, a very high *transoid* and perhaps *cisoid* influence of the D in a pseudo- $C_{4v}$  “piano stool” structure was a possible explanation for the unusual  $\Delta\delta_n$  values, as this model predicts equal values for  $\Delta\delta_n$  for **1\***- $d_n$ , i.e., in good agreement with the experimental data.<sup>47</sup> Why this effect would be temperature dependent is, however, difficult to rationalize; no literature data are available on this aspect. At the same time, both the very high values of  $\Delta\delta_n$  and, above all, their strong temperature dependence pointed toward some kind of IPR. Despite our conviction that **1** and **1\*** were classical polyhydrides and the fact that IPR effects due to the interchange of similar M–H functionalities are very rare,<sup>48</sup> we analyzed  $A_2B_2$  and  $AB_3$  spin model systems such as those exemplified by structures **A** and **B**, i.e., an elongated  $\text{H}_2(\text{H}\cdots\text{H})$  complex and a  $C_{3v}$  tetrahydride, respectively, and concluded that these models were unable to reproduce satisfactorily the graphs shown in Figure 3. Subsequent reports by Heinekey et al.<sup>5a,b</sup> on  $[\text{Tp}^{\text{Me}_2}\text{IrH}(\text{H}_2)(\text{PR}_3)]^+$  showed conclusively, for the first

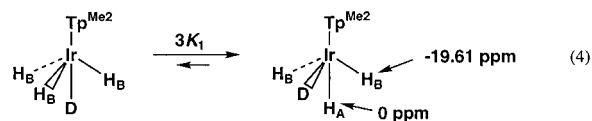


time, an example of an IPR effect in a  $\text{MH}_n(\text{H}_2)$  structure and, more importantly in the context of this contribution, that the isotope fractionation factor can vary with the degree of deuteration. This last circumstance had been addressed theoretically previously,<sup>10</sup> but we considered it at that time so improbable that we did not test it. However, we have now found that the experimental  $\Delta\delta_n$  can be fitted nicely to an  $AB_3$  spin system with an IPR effect. The corresponding equations for the averaged  $\delta d_n$  in such a situation are as follows, where  $\delta_A$  and

$$\delta d_0 = \frac{\delta_A + 3\delta_B}{4} \quad \delta d_2 = \frac{K_2\delta_A + 2\delta_B + K_2\delta_B}{2 + 2K_2}$$

$$\delta d_1 = \frac{K_1\delta_A + \delta_B + 2K_1\delta_B}{1 + 3K_1} \quad \delta d_3 = \frac{K_3\delta_A + 3\delta_B}{3 + K_3}$$

$\delta_B$  are the chemical shifts of the anisochronous hydrides in the static all-protio molecule and  $K_1$ ,  $K_2$ , and  $K_3$  the corresponding fractionation factors that are temperature dependent. From the experimental data, it can be concluded that  $\delta_A = 0$  and  $\delta_B = -19.61$  ppm, and that at 25 °C  $K_1 = 1.15$ ,  $K_2 = 1.14$ , and  $K_3 = 1.13$ , i.e., the D atoms prefer the B sites. A chemically reasonable model is, as suggested above, a  $C_{3v}$  geometry with  $\text{H}_A$  capping the hydride face of an otherwise distorted octahedral  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{H}_B)_3$  structure. These are shown schematically for **1\***- $d_1$  in eq 4. This structural proposal is in contrast with that



theoretically found for  $(\text{C}_5\text{Me}_5)\text{IrH}_4$ ,<sup>21</sup> but it is in accord with the ability of  $\text{Tp}'$  ligands to enforce octahedral structures. We can speculate that, in this proposed geometry, the  $\text{Tp}'$  is causing the lengthening and weakening of  $\text{Ir}-\text{H}_A$  bond, and this would explain the anomalous chemical shift of this nucleus and also the relative strength of the  $\text{Ir}-\text{H}_A$  bond as compared with the  $\text{Ir}-\text{H}_B$ , readily inferred from the calculated  $K_n$  values, somewhat larger than 1.

All the  $K_n$  values follow the expected behavior<sup>37</sup> with temperature, and the plots of  $\ln K_1$ ,  $\ln K_2$ , and  $\ln K_3$  vs  $1/T$  are shown in Figure 4. From these graphs, the corresponding  $\Delta E_n$  values can be extracted:  $\Delta E_1 = 260$ ,  $\Delta E_2 = 240$ , and  $\Delta E_3 = 200$  cal/mol.

The experimental values of the average H–D couplings should also be sensitive to the IPR effect, but their small magnitude makes them rather insensitive to the also small  $K_n$ , and therefore they are subject to large errors. Experimentally we have found very little variation with temperature (up to 0.5 Hz). Interestingly, and since there is evidence (see the following

(48) This is because the difference in bond energies is close to zero. Nevertheless, very small energy differences will cause an IPR if, for any reason, the intrinsic  $\delta$  of the involved nuclei have very disparate values. See, for example: (a) Saunders, M.; Faller, J. W.; Murray, H. H. *J. Am. Chem. Soc.* **1980**, *102*, 2306. For some interesting exceptions, see: (b) Saunders, M.; Siehl, H.-U. *J. Am. Chem. Soc.* **1980**, *102*, 6868. (c) Anet, F. A. L.; Kopelevich, M. *J. Am. Chem. Soc.* **1989**, *111*, 3429. (d) Heinekey, D. M.; Liegeois, A.; van Room, M. *J. Am. Chem. Soc.* **1994**, *116*, 8388. (e) Heinekey, D. M.; van Room, M. *J. Am. Chem. Soc.* **1996**, *118*, 12134.

(42) (a) Earl, K. A.; Jia, G.; Maltby, P.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027. (b) Michos, D.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 4245. (c) 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. (d) 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. (e) Antonietti, B.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1989**, 229. (f) Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E.; Lewis, N. S.; López, M. A.; Guillard, R.; L'Her, M.; Bothner-By, A. A.; Mishra, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 5654. (g) Sola, E.; Bakhmutov, V. I.; Torres, F.; Elduque, A.; López, J. A.; Lahoz, F. J.; Werner, H.; Oro, L. *Organometallics* **1998**, *17*, 683.

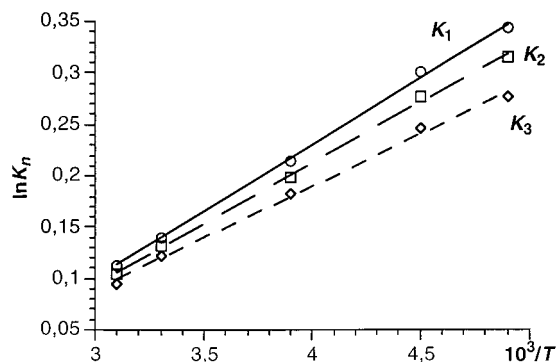
(43) Up to +100 ppb in an Ir(III) polyhydride, see: Harrod, J. F.; Hamer, G.; Yorke, W. *J. Am. Chem. Soc.* **1979**, *101*, 3987.

(44) In  $[\text{FeH}(\text{H}_2)(\text{PP}_3)]^+$ ,  $\Delta\delta_n$  changes in sign upon increasing deuteration: Bampos, N.; Field, L. D. *Inorg. Chem.* **1990**, *29*, 587. For a more complex behavior, see: Field, L. D.; Hambley, T. W.; Yau, B. C. K. *Inorg. Chem.* **1994**, *33*, 2009.

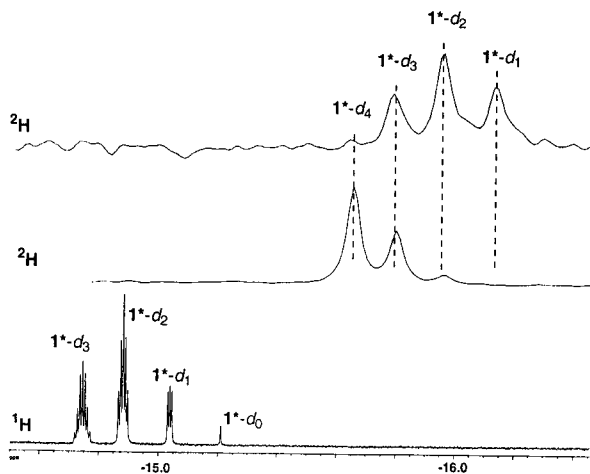
(45) In  $[(\text{silox})_2\text{TaH}_2]_2$ , the *down-field* shift of the hydrides upon deuteration is not easily explained by IPR: (a) Miller, R. L.; Toreki, R.; LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D.; Roe, D. C. *J. Am. Chem. Soc.* **1993**, *115*, 5570. The same is true for  $[(\text{C}_5\text{H}_5)\text{RuH}_2(\text{PMe}_3)_2]^+$  with  $\Delta\delta_1 = +20$  ppb: (b) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980. For other examples of positive  $\Delta\delta_1$  in  $[(\text{C}_5\text{H}_5)\text{RuH}_2(\text{P}-\text{P})]^+$ , see ref 40d.

(46) D–M–X nuclei (M = transition metal, X = <sup>13</sup>C, <sup>31</sup>P, etc.) sometimes resonate at lower frequencies than the H–M–X isotopomer: (a) Crabtree, R. H.; Habib, A. *Inorg. Chem.* **1986**, *25*, 3698. (b) Jones, W. D.; Kuykendall, V. L.; Selmezy, A. D. *Organometallics* **1991**, *10*, 1577. (c) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647. (d) References 19 and 42g. For other shorter and longer range *low-field* D effects on <sup>13</sup>C, <sup>31</sup>P, or other heteronuclei in organic, inorganic, and organometallic systems, see: (e) Aydin, R.; Günther, H. *J. Am. Chem. Soc.* **1981**, *103*, 1301. (f) Jarret, R. M.; Saunders, M. *J. Am. Chem. Soc.* **1986**, *108*, 7549. (g) Kwetkat, K.; Kitching, W. *J. Chem. Soc., Chem. Commun.* **1994**, 345. (h) DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601. (i) Lee, J. B.; Gadja, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Strauss, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358.

(47) See footnote 23 of ref 12 for a diagram of the model and the deduced relevant equations.



**Figure 4.** Fractionation factors ( $K_n$ ) of the species  $1^*-d_n$  as a function of temperature.



**Figure 5.**  $^1\text{H}$  and  $^2\text{H}$  NMR spectra of a mixture of  $1^*-d_n$  species ( $\text{CD}_2\text{-Cl}_2$  and  $\text{CH}_2\text{Cl}_2$ , respectively,  $25^\circ\text{C}$ ). The degree of deuteration is different for all the spectra.

section) that the coupling constants,  $J_{\text{HD}}$ , among the B sites is  $\leq 1$  Hz, we can estimate a  $J_{\text{HD}}$  value of  $(2.8(1 + 3K_1) - 2K_1)/(1 + K_1) = 4.7$  Hz for the corresponding coupling between the A and B sites. This could be the highest reported value for a classical polyhydride, but because it is a calculated datum and not an experimental one, the above value should be taken with due caution.

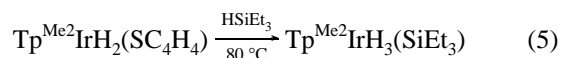
Infrared spectroscopy could, in principle, be used to confirm the above structural proposal for the  $\text{Tp}'\text{IrH}_4$  species. However, this kind of analysis has often proved unreliable for  $\text{Cp}'\text{MH}_n$  species,<sup>49</sup> and in accord with these expectations, the IR spectrum of partially deuterated  $1^*$  does not help in that respect. The Ir–H stretches are identified as a relatively broad absorption centered at  $2163\text{ cm}^{-1}$ , while the corresponding Ir–D frequencies are ca.  $1564\text{ cm}^{-1}$  (i.e., close to the expected value of  $1534\text{ cm}^{-1}$ ), but we cannot be confident about the fact that the Ir– $\text{H}_\text{B}$  stretch is being observed.

The proposed IPR effect in  $1^*$  can also be detected by comparing the  $^1\text{H}$  and  $^2\text{H}$  NMR spectra of  $1^*-d_n$  samples, a technique which is specially useful for the structural characterization of transition metal polyhydrides.<sup>5b,50</sup> The spectra corresponding to the  $1^*-d_n$  samples are shown in Figure 5. Both the magnitude and the sign of the isotope shifts in the  $^2\text{H}$  NMR spectra are in perfect agreement with the structural model described above. However, the fact that the  $^1\text{H}$  resonance of

$1^*-d_0$  and the  $^2\text{H}$  signal of  $1^*-d_4$  are not coincident escapes our understanding. This primary isotope effect,<sup>51</sup>  $\Delta\delta(^1\text{H},^2\text{H}) = \delta(^1\text{H}) - \delta(^2\text{H})$ , is normally very small, and whereas some exceptions ( $\Delta\delta$  up to  $+0.6$  ppm) have been found in systems with strong hydrogen bonds, this circumstance is clearly not at work in our case. For comparison,  $\Delta\delta(^1\text{H},^3\text{H})$  for  $[\text{Tp}'\text{IrH}(\text{H}_2)(\text{PR}_3)]^+$  complexes is zero in all cases,<sup>5b</sup> but appreciable  $\Delta\delta(^1\text{H},^2\text{H})$  values are inferred for some  $\text{H}_2\text{BR}_2$  complexes of Nb.<sup>50a</sup> We will maintain this question open until more data of this kind are available for polyhydride complexes.

Finally, and in connection with the deuteration studies described above, it is interesting to note the ability of  $1^*$  to exchange its hydrides with deuterium when  $\text{CD}_3\text{OD}$  or  $\text{D}_2\text{O}$  is present in its solutions. This exchange is so easy, particularly with water, that the manipulation of  $1^*-d_n$  ( $n \geq 1$ ) under not very strict conditions always results in washing out the label. We propose that the Ir– $\text{H}_\text{A}$  is acidic enough that the exchange with protolytic solvents is an acid–base process. We speculate that the  $[\text{Tp}'\text{IrH}_3]^-$  species may be a relatively stable anion due to the already mentioned ability of the  $\text{Tp}'$  group to stabilize octahedral structures, and work to confirm this hypothesis is now in progress in our laboratory. Perhaps the deuteration of  $1^*$  and  $1$  by  $\text{C}_6\text{D}_6$  is also heterolytic<sup>52</sup> in nature, but further work is needed to clarify this point. Other substrates, including THF, can interchange their hydrogens with the hydrides of  $1^*$ . This allows for the catalytic deuteration of THF by  $\text{D}_2\text{O}$  by  $1^*$  at  $90^\circ\text{C}$  ( $\text{D}_2\text{O}$ –THF, 1:4 volume ratio, 0.8 mL, 2–3 mg of  $1^*$ ), with the deuteration of THF being monitored by  $^2\text{H}$  NMR. Both  $\alpha$ - and  $\beta$ -H are deuterated at the same rate, but unfortunately the catalyst is slowly decomposed under these conditions, and only a maximum of a 4-fold increase over the natural  $^2\text{H}$  abundance of the substrate is achieved after 7 days. Other easier and more effective catalytic exchanges, such as the transfer of  $^2\text{H}$  from  $\text{C}_6\text{D}_6$  to thiophene, will be reported in due course.

**Synthesis and Chemical and Spectroscopic Properties of  $\text{Tp}^*\text{Ir}(\text{H}_3)(\text{SiEt}_3)$  ( $2^*$ ).** The title compound can be obtained, in virtually quantitative yield, by the reaction of  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{thiophene})^{13}$  with neat  $\text{HSiEt}_3$  ( $80^\circ\text{C}$ , 24 h) (eq 5).  $\text{Tp}^{\text{Me}_2}\text{Ir}$ –



( $\text{C}_2\text{H}_4$ )<sub>2</sub> also furnishes complex  $2^*$  in ca. 90% yield when treated with  $\text{HSiEt}_3$  under the same experimental conditions, but separation from the accompanying byproducts is difficult, and the yield of isolated  $2^*$  only amounts to ca. 50%. In the infrared, the Ir–H stretches appear at ca.  $2168\text{ cm}^{-1}$ , i.e., very close to those observed in  $1^*$ .

Compound  $2^*$  is also a very stable and rather inert molecule. No reaction is observed when it is heated with an excess of  $\text{PMe}_3$  or  $\text{CH}_3\text{CN}$  ( $60$ – $80^\circ\text{C}$ , 2 days). In addition, no H–D exchange is detected upon thermal treatment with  $\text{DSiEt}_3$ ,  $\text{C}_6\text{D}_6$ ,  $\text{C}_6\text{D}_6$ – $\text{CD}_3\text{OD}$ , or  $\text{CD}_3\text{COCD}_3$ – $\text{D}_2\text{O}$  for days at  $80^\circ\text{C}$ . Obviously, no elimination of  $\text{HSiEt}_3$  takes place under these conditions, and also the “acidity” of  $2^*$  is considerably reduced as compared with that of  $1^*$ .  $^1\text{H}$  NMR spectroscopy indicates that, even at  $-80^\circ\text{C}$ , the three hydrides are equivalent, as are the three pyrazolate arms of the  $\text{Tp}^{\text{Me}_2}$  ligand. The Ir–H nuclei appear as a sharp singlet at  $-18.30$  ( $\text{C}_6\text{D}_6$ ) or at  $-18.71$  ppm

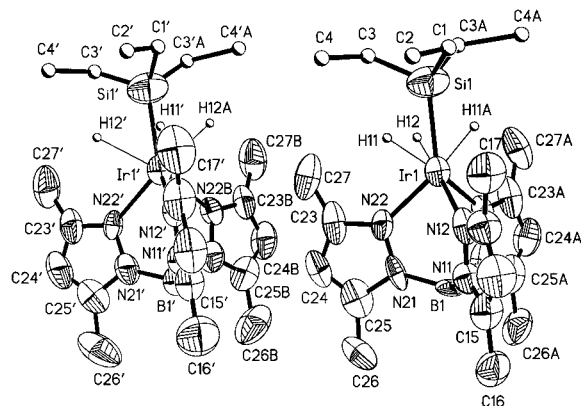
(49) Gross, C. L.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1994**, *116*, 10294.

(50) (a) Hartwig, J. F.; De Gala, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 3661. (b) Lantero, D. R.; Ward, D. L.; Smith, M. R., III. *J. Am. Chem. Soc.* **1997**, *119*, 9699.

(51) Gunnarson, G.; Wennerström, H.; Forsén, S. *J. Am. Chem. Soc.* **1978**, *100*, 8264.

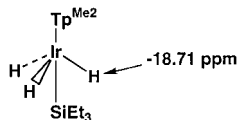
(52) (a) Arndsten, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. (b) Shilov, A. E.; Shulpin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (c) Junk, T.; Catalo, W. *J. Chem. Soc. Rev.* **1997**, *26*, 401.





**Figure 6.** ORTEP views of the two crystallographically independent molecules of **2\***.

( $\text{CD}_2\text{Cl}_2$ ), and since no substantial  $^1\text{H}(\text{hydrides})\text{--}^{29}\text{Si}$  coupling is detected (this is also inferred from  $^{29}\text{Si}$  NMR studies), any important interaction between the hydrides and the Si atom can, therefore, be excluded.<sup>3c,22b,53a</sup> Variable-temperature  $T_1$  measurements were also carried out. The  $T_1(\text{min})$  for the Ir–H nuclei of ca. 360 ms ( $-70^\circ\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ , 400 MHz) is clearly in accord with it being  $\text{IrH}_3(\text{SiEt}_3)$ , an Ir(V) species. Interestingly, the hydrides resonate at a chemical shift fairly close to that calculated for the B sites in **1\***, and this observation led us to propose for **2\*** a similar,  $C_{3v}$  formulation in which the bulky  $\text{SiEt}_3$  ligand caps the hydride face of an otherwise distorted octahedral structure. This is supported by a single-crystal X-ray



diffraction study, whose results will be presented below. It may, therefore, be concluded that, in compounds **1\*** and **2\***, the  $\text{Tp}^{\text{Me}_2}$  ligand, instead of favoring the “piano stool” geometry found by neutron diffraction studies for the Ir(V) species  $(\text{C}_5\text{Me}_5)\text{--}\text{IrH}_2(\text{SiEt}_3)_2$ <sup>53b,c</sup> and proposed for  $(\text{C}_5\text{Me}_5)\text{IrH}_4$  on the basis of theoretical calculations,<sup>21,54</sup> imposes an octahedron-derived structure, namely a capped octahedron with the hydride and the silyl groups respectively for **1\*** and **2\*** as the capping ligands.

Figure 6 shows an ORTEP view of the molecules of **2\***; selected bond distances and angles can be found in Table 1. The structure derived from the crystallographic study clearly shows that the molecules of **2\*** do not have  $C_{3v}$  symmetry in the solid state; instead, the compound crystallizes in the space group  $Pmc2_1$ . There is, however, a plane of symmetry that contains one of the pyrazolyl rings as well as the Ir, Si, and H(12) atoms. As expected, the two nonequivalent Ir–H bond distances (1.88(4) Å average) are equal within the experimental

(53) (a) On the basis of NMR data ( $J_{\text{HSi}} = 29$  Hz) and ab initio calculations, the complex  $\text{Os}(\text{PPh}_3)_3\text{H}_3(\text{SiR}_3)$  ( $\text{R} = 1\text{-NC}_4\text{H}_9$ ) has been formulated as having three  $\text{Os}\text{--}\text{H}\cdots\text{Si}$  interactions. Hübler, K.; Hübler, U.; Roper, W. R.; Schwedtfeger, P.; Wright, L. *J. Chem. Eur. J.* **1997**, *3*, 1608. (b) Fernández, M.-J.; Maitlis, P. M. *Organometallics* **1983**, *2*, 164. (c) Ricci, J. S., Jr.; Koetzle, T. F.; Fernández, M.-J.; Maitlis, P. M.; Green, J. C. *J. Organomet. Chem.* **1986**, *299*, 383. For the synthesis and characterization of the related  $(\text{C}_5\text{Me}_5)\text{IrH}_3(\text{SiMe}_3)$ , see: (d) Gilbert, T. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3500.

(54) In fact,  $(\text{C}_5\text{R}_5)\text{ML}_4$  complexes ( $\text{L} = \text{simple ligand}$ ) possess almost invariably four-legged piano stool geometry. An exception to this rule is the trigonal bipyramidal W(VI) cation  $[(\text{C}_5\text{Me}_5)\text{WMe}_4]^+$ . See: Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.

**Table 1.** Selected Bond Lengths (Å) and Angles (deg) for  $\text{Tp}^{\text{Me}_2}\text{IrH}_3(\text{SiEt}_3)$  (**2\***)

Bond Lengths (Å)			
Ir(1)–H(11)	1.89(4)	Ir(1)–H(12)	1.87(4)
Ir(1)–N(12)	2.13(3)	Ir(1)–Si(1)	2.405(11)
Ir(1)–N(22)	2.14(2)		
Bond Angles (deg)			
H(11)–Ir(1)–H(12)	69(6)	H(11)–Ir(1)–N(12)	113(6)
H(12)–Ir(1)–N(12)	177(7)	H(11)–Ir(1)–N(22)	77(5)
H(12)–Ir(1)–N(22)	93(5)	N(12)–Ir(1)–N(22)	84.2(6)
H(11)–Ir(1)–Si(1)	56(4)	H(12)–Ir(1)–Si(1)	54(7)
N(12)–Ir(1)–Si(1)	129.2(7)	N(22)–Ir(1)–Si(1)	128.4(4)

error and compare well with those found for other Ir–H complexes, e.g. 1.8 Å in  $\text{Tp}^{\text{Me}_2}\text{IrH}(\text{C}(\text{CH}_3)_2\text{CH}_2\text{O})(n\text{-Bu})$ <sup>15b,55</sup> and 1.59 Å (neutron data) in  $(\text{C}_5\text{Me}_5)\text{IrH}_2(\text{SiEt}_3)_2$ .<sup>53c</sup> The same is true for the Ir–Si bond, 2.40(1) vs 2.39 Å in the last mentioned  $\text{C}_5\text{Me}_5$  complex. Although the uncertainty in the Ir–H positions makes other structural interpretations possible, for example one with triple bridging Ir–H $\cdots$ Si interactions,<sup>53a</sup> we prefer to consider the  $\text{SiEt}_3$  group as capping the otherwise distorted octahedral structure (for example, the H(12)–Ir–N(12) angle is 177(7)°, and all the N–Ir–Si angles have almost identical values (ca. 129°). This last structural proposal is best in agreement with the lack of a measurable coupling constant between the hydrides and the  $^{29}\text{Si}$  nucleus (solution state).

Deuteration studies have also been carried out with **2\***. The monodeuterated species **2\*–d<sub>1</sub>** can be easily obtained from  $\text{Tp}^{\text{Me}_2}\text{--}\text{IrH}_2(\text{thiophene})$  and neat  $\text{DSiEt}_3$ , while **2\*–d<sub>2</sub>** was synthesized from  $\text{Tp}^{\text{Me}_2}\text{IrD}_2(\text{thiophene-}d_4)$ <sup>56</sup> and  $\text{HSiEt}_3$  in  $\text{C}_6\text{D}_6$ . In this particular case, the labels in the starting dideuteride are efficiently transferred into the ethyl residues of the neat silane before the desired H– $\text{SiEt}_3$  addition reaction occurs, but the presence of an excess of  $\text{C}_6\text{D}_6$  partially offsets this deleterious D–H exchange.<sup>56</sup> By using a  $\text{C}_6\text{D}_6\text{:HSiEt}_3$  ratio of ca. 5:1, a mixture of **2\*–d<sub>n</sub>** ( $n = 0\text{--}2$ ), with the all-protio compound predominating, can be obtained. As mentioned above, compounds **2\*–d<sub>n</sub>**, once formed, do not experience easily any further deuteration. As was the case for the parent dihydride,<sup>35</sup> the H–D coupling cannot be resolved in either of these deuterated species; therefore, its magnitude must be  $\leq 1$  Hz. Interestingly, the  $^1\text{H}$  NMR spectra of mixtures of **2\*–d<sub>n</sub>** show that  $\Delta\delta_n$  is, in both cases, small but positive ( $\Delta\delta_1 = +22$ ,  $\Delta\delta_2 = +22$  ppb, independently of the solvent,  $\text{C}_6\text{D}_6$  or acetone- $d_6$ , and the temperature, 25 or  $-70^\circ\text{C}$ ), i.e., resembling the effect observed for  $\text{Tp}^{\text{Me}_2}\text{IrH}_2\text{--}(\text{thiophene})$ . We believe it appropriate to extend these data to the tetrahydrides **1** and **1\*** and to propose on this basis that the  $J_{\text{HD}}$  coupling constant between the B sites of these complexes is almost insignificant ( $\leq 1$  Hz). Hence, the average  $J_{\text{HD}}$  values in these species are mainly due to an unusually strong coupling between the A and B sites of the  $C_{3v}$  structure. It is possible that the calculations of the IPR effect carried out above for **1\*–d<sub>n</sub>** are somewhat in error because the existence of *intrinsic cisoid* D effects has not been taken into account. However, this correction is expected to be rather small, in which case the consideration of these effects would mainly complicate more the IPR analysis.

## Conclusions

The complexes  $\text{Tp}^{\text{Me}_2}\text{IrH}_4$  are best formulated as tetrahydride species of Ir(V) with a  $C_{3v}$  structure in which a hydride ligand

(55) Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288.

(56) The dideuteride  $\text{Tp}^{\text{Me}_2}\text{IrD}_2(\text{thiophene-}d_4)$  was easily obtained by H–D exchange of the all-protio species with  $\text{C}_6\text{D}_6$ .<sup>13b</sup>

is capping the face of the remaining hydrides in an otherwise distorted octahedral structure. Due to the existence of Ir–H bonds of two different kinds, a nonstatistical fractionation of D in the two types of hydride sites available is observed upon deuteration, and this constitutes a very rare example of an IPR effect on a classical polyhydride.<sup>48c</sup> It is also the first one that shows, in addition, resolved  $J_{HD}$  couplings.  $\text{Tp}^{\text{Me}_2}\text{IrH}_4$  exchanges easily its hydrides with deuteriums not only in deuterated protolytic solvents but also, albeit under somewhat more forcing conditions, in  $\text{C}_6\text{D}_6$  and other substrates. This behavior has been exploited in a somewhat limited catalytic deuteration of THF by  $\text{D}_2\text{O}$ . The very stable species  $\text{Tp}^{\text{Me}_2}\text{IrH}_3(\text{SiEt}_3)$  is also best formulated, on the basis of spectroscopic and X-ray diffraction studies, as an Ir(V) species with a similar  $C_{3v}$  geometry. In this case, the  $\text{SiEt}_3$  group acts as the capping ligand.

## Experimental Section

**General Procedures.** Microanalyses were done by the Microanalytical Service of the University of Seville. Infrared spectra were obtained using Perkin-Elmer spectrometers, models 577 and 684. The NMR instruments were Bruker AMX-500, Bruker DRX-400, and Bruker AMX-300 spectrometers. Spectra are referenced to external  $\text{SiMe}_4$  ( $\delta = 0$  ppm) using the residual protio solvent peaks as internal standards ( $^1\text{H}$  NMR experiments) or the characteristic resonances of the solvent nuclei ( $^{13}\text{C}$  NMR experiments).  $^{29}\text{Si}$  NMR spectra were referenced with respect to  $\text{SiMe}_4$ .  $^2\text{H}$  NMR spectra were obtained in the unlocked mode with the resonance of the solvent as internal standard.  $T_1$  measurements were carried out by the inversion–recovery method, with the temperature of the NMR probes being accurate to  $\pm 1$  K. All manipulations were performed under dry, oxygen-free dinitrogen by following conventional Schlenk techniques. The complexes  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$ ,<sup>9</sup>  $\text{TpIr}(\text{C}_2\text{H}_4)_2$ ,<sup>17</sup> and  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{thiophene})$ <sup>13</sup> were obtained by published procedures.

**$\text{Tp}^{\text{Me}_2}\text{IrH}_4$  (1\*).** A suspension of  $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$  (0.65 g, 1.2 mmol) in cyclohexane (40 mL) was evacuated in a Fisher-Porter bottle and pressurized with  $\text{H}_2$  (3 atm). The resulting mixture was heated at 90 °C for 3 days. The volatiles were removed in vacuo, and the pale yellow residue was washed with cold ( $-10$  °C) methanol. The resulting white microcrystalline solid is  $>95\%$  pure by  $^1\text{H}$  NMR spectroscopy. Yield: 90%. IR (Nujol mull): 2163  $\text{cm}^{-1}$  (IrH).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  –14.71 (s, 4 H, 4 IrH), 2.15 (s, 9 H, 3 Me), 2.19 (s, 9 H, 3 Me), 5.57 (s, 3 H, 3  $\text{CH}_{\text{pz}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  12.0, 16.8 (Me), 105.1 ( $\text{CH}_{\text{pz}}$ ). Anal. Calcd for **1\***: C, 36.5; H, 5.3; N, 17.0. Found: C, 36.6; H, 5.1; N, 16.5.

**Reaction of 1\* with CO.** A 40-mg sample of complex **1\*** was suspended in  $\text{C}_6\text{H}_{12}$  (20 mL) in a Fisher-Porter bottle and the resulting mixture pressurized with CO (3 atm). After 24 h at 90 °C, the system was vented and the resulting solution evaporated to dryness.  $^1\text{H}$  NMR analysis of the crude residue revealed total conversion and a yield higher than 90% in the formation of  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{CO})$ .<sup>14</sup>

**Reaction of 1\* with  $\text{PMe}_3$ .** A mixture of 40 mg of complex **1\***, 5 mL of  $\text{C}_6\text{H}_{12}$ , and 0.2 mL of  $\text{PMe}_3$  was placed in a Teflon-sealed glass ampule and heated at 130 °C for 14 h. After cooling at room temperature, the resulting suspension was taken to dryness and the residue analyzed by NMR spectroscopy in  $\text{CDCl}_3$ . The compound, formulated as  $[\text{cis-IrH}_2(\text{PMe}_3)_4]\text{Tp}^{\text{Me}_2}$ , is  $>95\%$  pure by this analysis. IR (Nujol mull): 2067, 2056, and 2034  $\text{cm}^{-1}$  (IrH).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta$  –13.01 (apparent dt, 2 H, AA' part of an AA'M<sub>2</sub>XX' spin system,  $^2J_{\text{HM}} = 21.9$  Hz,  $J_{\text{HX}}(\text{app}) = 99.8$  Hz, IrH<sub>2</sub>), 0.02 (s, 9 H, 3 CMe), 1.65 (d, 18 H,  $^2J_{\text{HP}} = 7.6$  Hz, 2 cis- $\text{PMe}_3$ ), 1.71 (pseudo t, 18 H,  $J_{\text{HP}}(\text{app}) = 3.3$  Hz, 2 trans- $\text{PMe}_3$ ), 2.21 (s, 18 H, 6 CMe), 5.76 (s, 3 H, 3  $\text{CH}_{\text{pz}}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta$  –60.6 (t,  $^2J_{\text{MX}} = 20$  Hz, 2 P<sub>X</sub>), –54.5 (t, 2 P<sub>M</sub>). These assignments were secured by selective  $^{31}\text{P}\{\text{Me}\}$  and  $^1\text{H}\{^{31}\text{P}\}$  decoupling experiments. As stated in the text, when the reaction of **1\*** and  $\text{PMe}_3$  was carried out at low  $\text{PMe}_3$  concentrations (molar ratio **1\***: $\text{PMe}_3$  ca. 1:1) and at low conversions, the known dihydride  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{PMe}_3)$ <sup>14</sup> was observed by  $^1\text{H}$  NMR spectroscopy, mainly along with unreacted **1\***.

**Table 2.** Crystal Data and Structure Refinement for  $\text{Tp}^{\text{Me}_2}\text{IrH}_3(\text{SiEt}_3)$  (**2\***)

empirical formula	$\text{C}_{21}\text{H}_{39}\text{BN}_6\text{SiIr}$
formula wt	606.68
temp	298(2) K
wavelength	0.710 73 Å
cryst syst	orthorhombic
space group	$Pmc2_1$
unit cell dimens	$a = 13.6992(12)$ Å $b = 12.0084(10)$ Å $c = 15.9968(12)$ Å $\alpha = \beta = \gamma = 90^\circ$
vol., Z	2631.6(4) Å <sup>3</sup> , 4
density (calcd)	1.531 $\text{mg}/\text{m}^3$
abs coeff	5.138 $\text{mm}^{-1}$
$F(000)$	1212
crystal size	0.05 × 0.10 × 0.18 mm
$\theta$ range for data collection	2.26–23.31°
limiting indices	$-13 \leq h \leq 15$ , $-13 \leq k \leq 2$ , $-15 \leq l \leq 13$
no. of coll'd rflns	6842
no. of indep rflns	3358 ( $R_{\text{int}} = 0.0649$ )
absorption correction	empirical by SADABS (ref 59)
max and min transmission	0.1036 and 0.0526
refinement method	full-matrix least-squares on $F^2$
no. of data/restraints/parameters	3358/6/279
goodness-of-fit on $F^2$	1.202
final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0576$ , $wR2 = 0.1447$
R indices (all data)	$R1 = 0.0647$ , $wR2 = 0.1517$
absolute structure parameter	0.02(3)
largest diff peak and hole	0.704 and $-1.764 \text{ e} \text{ \AA}^{-3}$

**$\text{Tp}^{\text{Me}_2}\text{IrH}_3(\text{SiEt}_3)$  (**2\***).** A mixture of  $\text{Tp}^{\text{Me}_2}\text{IrH}_2(\text{thiophene})$  (0.20 g, 0.33 mmol) and  $\text{HSiEt}_3$  (5 mL) was heated, in a sealed ampule, at 80 °C for 24 h. The volatiles were removed in vacuo, and the residue was analyzed by  $^1\text{H}$  NMR. The conversion to **2\*** was quantitative. The solid was washed several times with MeOH ( $5 \times 5$  mL) to eliminate the excess  $\text{Et}_3\text{SiH}$  and dried under vacuum. Yield:  $>90\%$ . This complex can be crystallized from  $\text{CH}_2\text{Cl}_2$ –EtOH mixtures. IR (Nujol mull): 2168  $\text{cm}^{-1}$  (IrH).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  –18.30 (s, 3 H, 3 IrH), 1.21 (t, 9 H,  $^3J_{\text{HH}} = 7.8$  Hz,  $\text{Si}(\text{CH}_2\text{CH}_3)_3$ ), 1.36 (q, 6 H,  $\text{Si}(\text{CH}_2\text{CH}_3)_3$ ), 2.10 (s, 9 H, 3  $\text{Me}_{\text{pz}}$ ), 2.17 (s, 9 H, 3  $\text{Me}_{\text{pz}}$ ), 5.55 (s, 3 H, 3  $\text{CH}_{\text{pz}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  8.6 ( $\text{SiCH}_2\text{CH}_3$ ), 12.2 ( $\text{Me}_{\text{pz}}$ ), 15.2 ( $\text{SiCH}_2\text{CH}_3$ ), 16.0 ( $\text{Me}_{\text{pz}}$ ), 105.6 ( $\text{CH}_{\text{pz}}$ ), 143.1, 150.4 ( $\text{CMe}_{\text{pz}}$ ).  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ , 25 °C):  $\delta$  –75.2 (m,  $J_{\text{SiH}} = 6$  Hz). Anal. Calcd for **2\***: C, 41.5; H, 6.6; N, 13.8. Found: C, 41.7; H, 6.5; N, 13.5. **2\*-d<sub>1</sub>** was obtained following the same procedure but using  $\text{DSiEt}_3$ . For **2\*-d<sub>2</sub>**,  $\text{Tp}^{\text{Me}_2}\text{IrD}_2(\text{thiophene-}d_4)$ <sup>56</sup> and  $\text{HSiEt}_3$  were employed as starting materials, but in this particular case a mixture of  $\text{C}_6\text{D}_6$ – $\text{HSiEt}_3$  in ca. 5:1 ratio was used (see Results and Discussion). This gave a mixture of **2\*-d<sub>n</sub>** ( $n = 0$ –2) species, with the  $d_0$  isotopomer predominating.  $^2\text{H}$  NMR ( $\text{C}_6\text{H}_6$ , 25 °C):  $\delta$  –18.17 br for both **2\*-d<sub>1</sub>** and **2\*-d<sub>2</sub>**. This sample was impure, containing  $\text{Tp}^{\text{Me}_2}\text{IrD}(\text{C}_6\text{D}_5)(\text{N}_2)$ :  $\delta$  Ir–D –17.82.<sup>57</sup>

**X-ray Structure Determination of  $\text{Tp}^{\text{Me}_2}\text{IrH}_3(\text{SiEt}_3)$  (**2\***).** A summary of the fundamental crystal data is given in Table 2. A crystal of prismatic shape was coated with epoxy resin and mounted in a CCD detector diffractometer. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ir were taken from the *International Tables for X-ray Crystallography*.<sup>58</sup> The structure was solved by Patterson and Fourier methods. A final refinement<sup>59</sup> on  $F^2$  for all reflections was undertaken, including the hydrogen atoms as fixed contributions at their

(57) Unpublished results from this laboratory.

(58) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.

(59) Sheldrick, G. M. Programs SADABS, SHELXS-97, and SHELXL-97. Göttingen, 1997.



calculated positions, except those coordinated to the Ir atoms that were located in a Fourier difference map, and their coordinates were refined. As can be seen in Figure 6, the molecule has a symmetry plane that includes one of the pyrazolyl rings and the Ir, Si, and H(12) atoms and should contain one of the ethyl groups of the SiEt<sub>3</sub>. In fact, the asymmetric unit consists of two halves of different molecules, but a relatively important positional disorder involves the ethyl groups, especially the one that should be contained in the *m* plane. The atoms of these groups, C(1), C(2), C(1'), and C(2'), have been refined with a population factor of 0.5. In that way, the structure has been refined to *R* values that allow the localization of the H coordinated to the Ir atom.

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**Supporting Information Available:** Complete crystallographic data for 2\* (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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