

## An Elongated Dihydrogen Complex of Iridium

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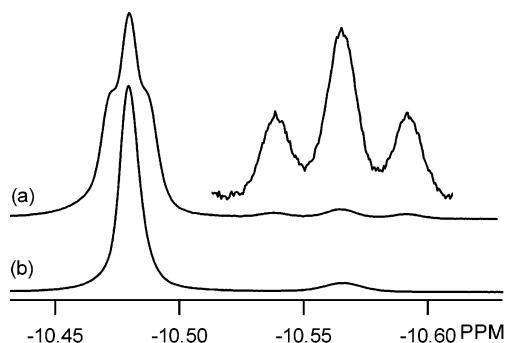
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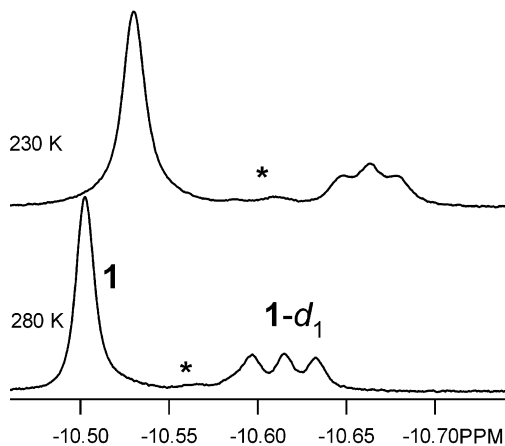
After the isolation and characterization of the first transition metal dihydrogen complexes by Kubas and co-workers,<sup>1</sup> an extensive set of cationic H<sub>2</sub> adducts of the form [Cp/Cp\*Ru(L)(L')H<sub>2</sub>]<sup>+</sup> were reported, with a wide range of co-ligands L, mostly chelating phosphines.<sup>2</sup> On the basis of the well-established inverse correlation between H–D coupling and H–H distance  $r_{\text{HH}}$ ,<sup>3,4</sup> these Ru complexes apparently represent a wide range of  $r_{\text{HH}}$  values, although only in the case of [Cp\*Ru(dppm)(H<sub>2</sub>)]<sup>+</sup> (dppm = bis-diphenylphosphinomethane) has the H–H distance been confirmed by neutron diffraction ( $r_{\text{HH}} = 1.10 \text{ \AA}$ ).<sup>5</sup> This complex exhibits temperature and isotope dependence of  $r_{\text{HH}}$ , as shown by NMR studies.<sup>6</sup> A computational study using density functional theory (DFT) indicates a single minimum in a very flat potential energy surface and attributes the increase in  $r_{\text{HH}}$  at higher temperatures to thermal population of vibrationally excited states.<sup>7</sup> Complexes of this type have been termed “elongated” dihydrogen complexes in that they seem to have H–H distances intermediate between those of dihydrogen complexes ( $\leq 1 \text{ \AA}$ ) and the distances usually associated with dihydride complexes ( $\geq 1.5 \text{ \AA}$ ). Such structures are of great interest in understanding the detailed mechanism of oxidative addition of hydrogen.

We now report the synthesis of [Cp\*Ir(dmpm)H<sub>2</sub>]<sup>2+</sup> (**1**) and its characterization by NMR spectroscopy. In contrast to the analogous complexes of ruthenium where halide loss from a neutral precursor allowed facile synthesis of monocationic dihydrogen complexes, preparation of dicationic complexes of Ir such as **1** requires halide abstraction from a positively charged precursor. The starting material [Cp\*Ir(dmpm)Cl]<sup>+</sup> was prepared<sup>8</sup> by reaction of [Cp\*IrCl<sub>2</sub>]<sub>2</sub> with dmpm in refluxing methanol.<sup>9</sup> Reaction of [Cp\*Ir(dmpm)Cl]<sup>+</sup> with halide abstracting reagents such as AgBF<sub>4</sub> and AgPF<sub>6</sub> under hydrogen led to complex product mixtures.<sup>10</sup>

Complex **1** was ultimately prepared by reaction of [Cp\*Ir(dmpm)Cl]<sup>+</sup> with (Et<sub>3</sub>Si)(BArF<sub>4</sub>)<sup>11</sup> (ArF = C<sub>6</sub>F<sub>5</sub>). In addition to the expected resonances due to Cp\* and phosphine ligands, the <sup>1</sup>H NMR spectrum of **1** exhibits two triplet resonances in the hydride region at  $-10.48$  ( $^2J_{\text{H-P}} = 6 \text{ Hz}$ ) and  $-10.56$  ppm ( $^2J_{\text{H-P}} = 20 \text{ Hz}$ ) in a ratio of 97:3 (see Figure 1). The presence of two hydride ligands was confirmed by the selectively decoupled <sup>31</sup>P NMR spectrum, which exhibits a triplet at  $-76.2$  ppm ( $^2J_{\text{H-P}} = 6 \text{ Hz}$ ) and a triplet at  $-46.5$  ppm ( $^2J_{\text{H-P}} = 20 \text{ Hz}$ ), for the major and minor species, respectively. Structural assignment for the isomers of **1** can be made by comparison to data reported by Jia and co-workers for the related [CpOs(dppm)H<sub>2</sub>]<sup>+</sup>, where cis and trans dihydrogen isomers were observed.<sup>12</sup> In a capped square pyramidal environment, larger H–P couplings result when hydrides are cis to adjacent P ligands. Thus the minor isomer is attributed to a species with a trans arrangement of the hydride ligands. The major isomer of **1** is apparently a *cis*-dihydride or a dihydrogen complex. Complex **1** is moderately thermally stable in solution at room temperature but is highly acidic, being readily deprotonated by very weak bases including triflate to afford the cationic monohydride



**Figure 1.** (a) Partial 750 MHz <sup>1</sup>H NMR spectrum (hydride region) of complex **1** in CD<sub>2</sub>Cl<sub>2</sub> at 298 K. The inset shows the resonance due to **1-trans** at 100× intensity. (b) <sup>1</sup>H{<sup>31</sup>P} spectrum.

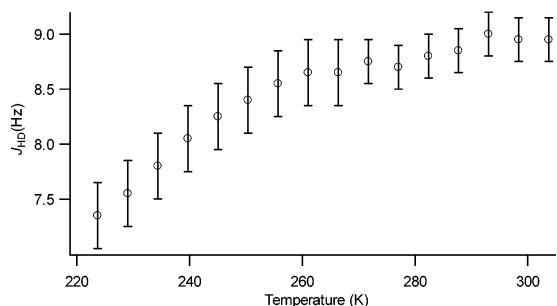


**Figure 2.** Partial (hydride region) 500 MHz <sup>1</sup>H{<sup>31</sup>P} NMR spectrum of a mixture of **1** and **1-d**<sub>1</sub>, showing the effect of temperature. The asterisk designates the resonance for the *trans* isomer of **1**.

complex [Cp\*Ir(dmpm)H]<sup>+</sup>.<sup>13</sup> The high acidity of **1** has hampered our efforts to isolate this complex in a pure state.

Treatment of solutions of **1** with D<sub>2</sub> gas (1 atm, room temperature) did not lead to incorporation of deuterium in the hydride ligands. Partially deuterated samples of **1** were prepared by carrying out the preparative reaction with HD gas, which led to mixtures of **1** and **1-d**<sub>1</sub>. As expected, the resonance due to **1-trans-d**<sub>1</sub> shows no resolvable HD coupling and a small isotope shift. In contrast, the resonance due to **1-cis-d**<sub>1</sub> exhibits  $^1J_{\text{H-D}} = 9.0 \text{ Hz}$  and a very substantial isotope shift to higher field of 91 ppb (303 K) (see Figure 2). Interestingly, both  $^1J_{\text{H-D}}$  and the isotope shift are temperature dependent. At lower temperatures, the value of  $^1J_{\text{H-D}}$  decreases to 7.3 Hz, while the isotope shift increases to 134 ppb at 223 K (see Figure 3).

Using standard inversion recovery methods, the relaxation time ( $T_1$ ) for the hydride resonance of **1-cis** was determined at a variety of temperatures ranging from 214 to 298 K. The  $T_{1(\text{min})}$  value is 145 ms at 240 K (500 MHz). Analysis using the methodology of



**Figure 3.** Plot of  $J_{H-D}$  versus temperature for **1-cis-d1**. Estimated uncertainties are  $\pm 0.3$  Hz at low temperatures and  $\pm 0.2$  Hz at higher temperatures.

Halpern and co-workers<sup>14</sup> gives  $r_{HH} = 1.49$  Å (assuming slow rotation of the bound hydrogen ligand). A careful analysis by Caulton and co-workers of the interpretation of  $T_1$  data in terms of rotation rates of bound dihydrogen suggests that  $H_2$  complexes of the  $[Cp/Cp^*Ru(L)(L')H_2]^+$  type are in the slow rotation regime.<sup>15</sup> By extension, we believe that the bound  $H_2$  in complex **1** is also rotating relatively slowly with respect to molecular tumbling. This value for  $r_{HH}$  is inconsistent with the value derived from the H–D coupling at this temperature, where  $J_{H-D} = 8.1$  Hz gives  $r_{HH} = 1.34$  Å, using the correlation reported by Chaudret and co-workers.<sup>4</sup> Note that this analysis assumes that the interatomic distance in the bound dihydrogen ligand is not affected by isotopic substitution, which may not be valid in the case of **1**. A dramatic reduction of the bond distance upon substitution of H by D would be required to account for a discrepancy of this magnitude.

The temperature dependence of  $J_{H-D}$  has been modeled in terms of a rapidly established equilibrium between an Ir(III) dihydrogen species and an Ir(V) *cis*-dihydride complex.



Qualitatively, the diminishing of  $J_{H-D}$  as temperature is lowered suggests that the dihydride form of **1** predominates. The apparent leveling off of the observed  $J_{H-D}$  values at higher temperature may be consistent with a small value of  $K_{eq}$ . A quantitative model requires some assumptions regarding the limiting structures of the two components and must also assume that each of the limiting forms has a temperature-independent structure. On the basis of the reported neutron structure and known H–T coupling of an Ir(V) trihydride, an H–H distance of approximately 1.7 Å with a corresponding  $J_{H-D}$  of ca. 3.5 Hz is reasonable for the *cis*-dihydride isomer of **1**.<sup>16</sup> A direct ruthenium analogue to complex **1** is reported to be a simple dihydrogen complex with (*T*-independent)  $J_{H-D} = 16$  Hz.<sup>6</sup> Using these limiting values for  $J_{H-D}$ , attempts were made to fit the data of Figure 3 for various values of  $K_{eq}$ . Although the general trend of the data could be reproduced, an exact fit was not possible with the assumption of a two-component system.

The Os complex  $[Os(dppe)_2Cl(H_2)]^+$  is the only other example reported to date of a dihydrogen complex where  $J_{H-D}$  increases with increasing temperature (13.6 Hz at 253 K; 14.2 Hz at 308 K). In this complex, neutron diffraction gives  $r_{HH} = 1.22$  Å.<sup>3b</sup> This temperature dependence was initially interpreted in terms of a dihydrogen/dihydride equilibrium, but subsequent computational

work suggests a very flat single minimum PES with the H–H distance influenced by librational motion.<sup>17</sup> This explanation may also prevail in the case of **1**, but the effect of temperature is considerably greater. Librational motion of bound  $H_2$  through a large angle has been previously shown to lead to anomalies in  $T_1$  data.<sup>18</sup>

If complex **1** does indeed represent a dihydrogen/*cis*-dihydride equilibrium system, this “structure” is without precedent. We are continuing to study complex **1** and related Ir derivatives with a view to confirming this hypothesis.

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**Supporting Information Available:** Relaxation time data for complex **1** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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