

## Synthesis and Spectroscopic Properties of Elongated Ruthenium Dihydrogen Complexes: Temperature and Isotope Dependence of H–H Distances

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**Abstract:** Several dihydrogen complexes of ruthenium of the form  $[\text{Cp/Cp}^*\text{Ru}(\text{P}-\text{P})\text{H}_2]^+$  (P–P = chelating diphosphine ligand) have been prepared by reaction of the corresponding neutral chloride complexes with  $\text{H}_2$  in the presence of  $\text{NaB}(\text{ArF})_4$ . Treatment with  $\text{D}_2$  or  $\text{T}_2$  gas leads to incorporation of deuterium or tritium in the dihydrogen ligand. Measurement of the resulting H–D and H–T couplings as a function of the temperature and magnetic field gives results consistent with computational studies which predict that the H–H bond distance will increase with temperature and will be significantly shortened by isotopic substitution. The degree of the observed temperature dependence is found to be a critical function of the ancillary ligand set.

Shortly after the isolation and characterization of the first transition metal dihydrogen complexes by Kubas and co-workers,<sup>1</sup> a new class of cationic  $\text{H}_2$  adducts of the form  $[\text{CpRu}(\text{L})(\text{L}')\text{H}_2]^+$  was reported to result from protonation of the corresponding neutral hydride complexes. The first synthesis of this type was reported by Conroy-Lewis and Simpson in 1986. Protonation of  $\text{CpRu}(\text{PPh}_3)(\text{CN}-t\text{-Bu})\text{H}$  affords the stable, isolable complex  $[\text{CpRu}(\text{PPh}_3)(\text{CN}-t\text{-Bu})\text{H}_2]^+$ .<sup>2</sup> Subsequently, a large number of complexes of this type have been prepared with Cp or Cp\* ligands and a wide range of coligands, mostly chelating phosphines.<sup>3</sup> These cationic complexes generally exhibit tighter binding of  $\text{H}_2$  than do the original neutral complexes studied by Kubas, which makes their isolation and manipulation more straightforward.

On the basis of the well-established inverse correlation between H–D coupling and H–H distance  $r_{\text{HH}}$ ,<sup>4–6</sup> complexes of this family seem to present a very wide range of structures. At one extreme is the thermally labile species  $[\text{Cp}^*\text{Ru}(\text{CO})_2\text{H}_2]^+$  ( $J_{\text{HD}} = 32$  Hz,  $r_{\text{HH}} = 0.90$  Å), which loses  $\text{H}_2$  readily.<sup>7</sup> In contrast,  $[\text{Cp}^*\text{Ru}(\text{dppm})\text{H}_2]^+$  (**1**, dppm = bis-diphenylphos-

phinomethane) has  $J_{\text{HD}} = 21$  Hz, corresponding to  $r_{\text{HH}} = 1.10$  Å. In the case of complex **1**, this value for  $r_{\text{HH}}$  has been confirmed by a neutron diffraction study.<sup>8</sup> Consistent with the strong metal  $\text{H}_2$  interaction indicated by the long H–H distance, complex **1** binds  $\text{H}_2$  very tightly. 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 ( $\leq 1$  Å) and the distances usually associated with dihydride complexes ( $\geq 1.5$  Å). Such structures may represent an arrested intermediate state in the very important oxidative addition reaction.

The utility of determining  $r_{\text{HH}}$  from measurement of  $J_{\text{HD}}$  values was called into question when it was reported that the H–D isotopomer of complex **1** (**1-d<sub>1</sub>**) exhibits a small decrease in  $J_{\text{HD}}$  upon increasing the temperature from ca. 200 K to room temperature, which may signal a slight increase in the H–H (H–D) bond distance. Thermal population of vibrationally excited states was proposed to account for the decreased coupling at higher temperatures.<sup>8</sup> This hypothesis is supported by a computational study using density functional theory (DFT) calculations. This study also led to the intriguing suggestion that the bond distance in complex **1** will be sensitive to isotopic substitution, with the distance in the H–H complex predicted to be approximately 10% longer than that in the corresponding T–T complex.<sup>9</sup>

We now report a study of the temperature and isotope dependence of  $r_{\text{HH}}$  in complex **1** and several related species. In the course of this work, an improved synthetic procedure has been developed which allows for a more convenient preparation

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**Table 1.**  $^1\text{H}$  NMR Data for Hydride and Dihydrogen Resonances in 1–5

compound	$\delta$ RuH <sub>2</sub> , ppm <sup>a</sup> [ $J_{\text{HP}}$ , Hz]	$\delta$ Ru(H <sub>2</sub> ), ppm <sup>a</sup>	Ru(H <sub>2</sub> )/RuH <sub>2</sub> <sup>a</sup>	$J_{\text{HD}}$ Hz <sup>a</sup>	$\delta$ Ru–(HD) ppb <sup>a,b</sup>	Ru(HD) $J_{\text{H–P}}$ , Hz <sup>a,c</sup>
1 [Cp*Ru(dppm)H <sub>2</sub> ] <sup>+</sup>	–5.975 (28.8)	–6.774	67/33	20.6 ± 0.3	15 <sup>e</sup>	<i>d</i>
2 [CpRu(dppe)H <sub>2</sub> ] <sup>+</sup>	–8.589 (28.0)	–9.042	40/60	24.9 ± 0.1	38	2.1 ± 0.1
3 [CpRu(dmpe)H <sub>2</sub> ] <sup>+</sup>	–9.866 (30.7)	–10.156	85/15	22.3 ± 0.1	35	3.5 ± 0.05
4 [Cp*Ru(dppip)H <sub>2</sub> ] <sup>+</sup>	–6.276 (27.7)	–7.428	80/20	18.6 ± 0.3	16	<i>d</i>
5 [Cp*Ru(dmpm)H <sub>2</sub> ] <sup>+</sup>	–7.085 (33.2)	–7.881	94/6	15.9 ± 0.1	22	<i>d</i>

<sup>a</sup> CD<sub>2</sub>Cl<sub>2</sub>, 300 K, 750 MHz. <sup>b</sup> Upfield from Ru(H<sub>2</sub>)<sup>+</sup>. <sup>c</sup> Observed in Ru(HD)<sup>+</sup> isotopomer. <sup>d</sup> Not observed. <sup>e</sup>  $\delta$ Ru(HT)<sup>+</sup> is 22 ppb upfield from Ru(H<sub>2</sub>)<sup>+</sup> isotopomer.

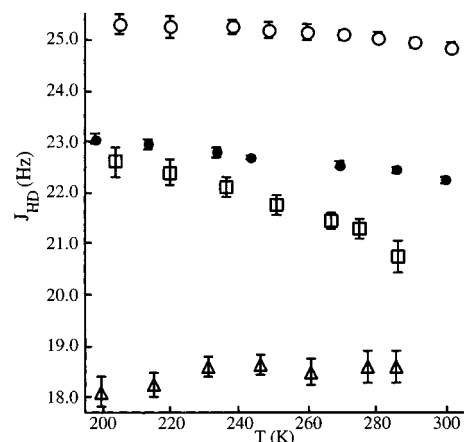
of complexes of this type. A portion of the results described here has been previously communicated.<sup>10</sup>

## Results

**Synthesis.** The previously reported chloride complexes Cp\*Ru(dppm)Cl,<sup>11</sup> Cp\*Ru(dmpm)Cl,<sup>11</sup> CpRu(dppe)Cl,<sup>12</sup> and CpRu(dmpe)Cl<sup>13</sup> were prepared using literature procedures (dppm = bis-diphenylphosphinomethane; dmpm = bis-dimethylphosphinomethane; dppe = bis-diphenylphosphinoethane; dmpe = bis-dimethylphosphinoethane). Reaction of the appropriate chelating phosphine ligand with Cp\*Ru(PPh<sub>3</sub>)<sub>2</sub>Cl<sup>14</sup> or CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl<sup>15</sup> affords these complexes in good yield. The new chloride complex Cp\*Ru(dppip)Cl was prepared by reaction of 2,2-bis(diphenylphosphino)propane (dppip) with Cp\*Ru(PPh<sub>3</sub>)<sub>2</sub>Cl.

Methylene chloride solutions of these chloride complexes in the presence of NaB(ArF)<sub>4</sub> under hydrogen gas (1 atm) react cleanly to afford the corresponding dihydrogen complexes [Cp\*Ru(dppm)(H<sub>2</sub>)]<sup>+</sup> (1), [CpRu(dppe)(H<sub>2</sub>)]<sup>+</sup> (2), [CpRu(dmpe)(H<sub>2</sub>)]<sup>+</sup> (3), [Cp\*Ru(dppip)(H<sub>2</sub>)]<sup>+</sup> (4), and [Cp\*Ru(dmpm)(H<sub>2</sub>)]<sup>+</sup> (5). Complexes 4 and 5 have not been previously reported. Complexes 1–3 have been previously prepared by protonation of the corresponding neutral hydride complexes.  $^1\text{H}$  NMR data for complexes 1–5 are summarized in Table 1.

**Dihydrogen/Dihydride Equilibria.** Complexes 1–5 exhibit two distinct sets of “hydride” resonances in their  $^1\text{H}$  NMR spectra, consistent with a slowly equilibrating mixture of a dihydrogen species and a dihydride (dihydrogen/dihydride ratios are given in Table 1). The dihydride resonance is a triplet, due to appreciable coupling to the two <sup>31</sup>P nuclei of the bidentate ligand. In some cases, a much smaller H–P coupling (2–3 Hz) can be resolved in the resonance associated with bound dihydrogen. In most cases studied here, the dihydrogen form is predominant, but the position of the equilibrium depends on the nature of the bidentate ligand, with single-carbon bridges or the replacement of aryl with alkyl groups very strongly favoring the dihydrogen form. Chemical shifts for the dihydrogen and dihydride resonances in 1–5 and coupling constant data are tabulated in Table 1. These chemical shifts are observed to have a small dependence upon the observation temperature. For example, the resonance due to the dihydride form of complex 2 shifts to higher field upon lowering the temperature by ca. 2 ppb/deg. The resonance due to the dihydrogen tautomer shows a similar but much smaller effect of ca. 0.2 ppb/deg.



**Figure 1.**  $J_{\text{HD}}$  versus temperature for complexes 1–4: [CpRu(dppe)HD]<sup>+</sup> (2, open circles); [CpRu(dmpe)HD]<sup>+</sup> (3, solid circles); [Cp\*Ru(dppm)HD]<sup>+</sup> (1, squares); [Cp\*Ru(dppip)HD]<sup>+</sup> (4, triangles). Error bars indicate estimated uncertainties.

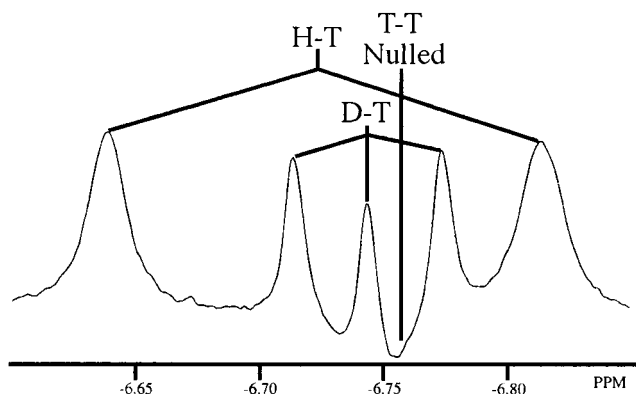
**Isotope Exchange and H–D Coupling.** Exposure of methylene chloride solutions of 1–5 to D<sub>2</sub> gas leads to incorporation of deuterium in the dihydrogen ligand over the course of several hours, as demonstrated by observation of large H–D couplings in the monodeuterated isotopomer. Partially tritiated samples of 1 were also prepared by brief exposure to T<sub>2</sub> gas. This exchange reaction is faster for complexes with a less basic ligand set.

At ambient temperature, the observed values for  $J_{\text{HD}}$  are 24.9 Hz (2), 22.3 Hz (3), 20.6 Hz (1), 18.6 Hz (4), and 15.9 Hz (5). Field independence of these values was confirmed by observations at a range of fields (5.8, 11.6, and 17.6 T). The  $J_{\text{HD}}$  values for complexes 2, 4, and 5 are independent of temperature within experimental error, while the couplings observed in complexes 1 and 3 show a small but appreciable increase upon lowering the temperature from 300 to ca. 200 K. Data for  $J_{\text{HD}}$  values as a function of temperature for complexes 1–4 are collected in Figure 1.

Partially tritiated samples of 1 were prepared by brief exposure of a partially deuterated sample to carrier free T<sub>2</sub> gas, affording a mixture of all possible isotopomers.  $^1\text{H}$  NMR spectra of this mixture allowed for the determination of  $J_{\text{HT}}$  and  $J_{\text{HD}}$  values, while  $J_{\text{DT}}$  was measured by direct observation in the  $^3\text{H}$  NMR spectrum (800 MHz). The sample employed had a preponderance of T<sub>2</sub> and relatively small amounts of TD, so an inversion recovery sequence was employed to null the more rapidly relaxing resonance (see below) due to bound TT, allowing for precise determination of  $J_{\text{TD}}$  (see Figure 2).

Careful examination of the  $^1\text{H}$  NMR spectra of partially deuterated and, in some cases, partially tritiated samples allows the measurement of the isotope effect on the chemical shifts. An example of these observations is the case of complex 1,

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**Figure 2.**  $^3\text{H}$  NMR spectrum (800 MHz) of **1**. The resonance due to bound  $\text{T}_2$  has been nulled by applying a  $180\text{-}\tau\text{-}90$  pulse sequence with  $\tau = 15$  ms.

where  $\delta_{\text{HD}} - \delta_{\text{HH}} = 15$  ppb and  $\delta_{\text{HT}} - \delta_{\text{HH}} = 22$  ppb. Complexes **2–5** exhibit somewhat larger isotope shifts  $\delta_{\text{HD}} - \delta_{\text{HH}}$ . These small shifts of the dihydrogen resonance to higher field upon substitution with a heavier isotope are independent of the observation temperature. Values for the isotope effects on the chemical shifts in **1–5** are tabulated in Table 1.

**Relaxation Time Measurements.** Using standard inversion recovery methods, the relaxation time ( $T_1$ ) for the bound hydrogen in **1** and for the bound tritium in **1- $t_2$**  was determined at a variety of temperatures ranging from 205 to 300 K. For the bound  $\text{T}_2$ , the maximum rate of relaxation ( $T_1$  min = 21 ms) was observed at 246 K (800 MHz). Analysis using a modification of the methodology of Halpern and co-workers<sup>16</sup> leads to a T–T distance in complex **1** of 1.05 Å.

## Discussion

**Synthesis.** Previous reports of the synthesis of complexes **1–3** have employed the protonation of the corresponding neutral hydride complexes. The hydride complexes are usually generated by reduction of the corresponding halide complexes with alkoxide or borohydride reagents. After the original report of complex **1**, Morris and co-workers reported that reaction of  $\text{Cp}^*\text{Ru}(\text{dppm})\text{Cl}$  with  $\text{AgBF}_4$  in the presence of hydrogen affords complex **1** in good yield.<sup>17</sup> We have found that the direct reaction of dihydrogen gas with the chloride complexes in the presence of  $\text{NaB}(\text{ArF})_4$  affords the cationic dihydrogen complexes **1–5** in quantitative (by NMR) yields. This one-pot procedure is much more convenient than the two-step method previously reported. Samples containing deuterium or tritium in the bound dihydrogen ligand were generated by exposure of methylene chloride solutions of complexes **1–5** to deuterium or tritium gas.

We note that the chloride complexes with the more basic phosphine ligands (such as  $\text{dmpm}$ ) react faster with hydrogen in the above reaction than do the complexes with less basic coligands such as  $\text{dppm}$ . This is consistent with labilization of chloride due to destabilizing interactions between chloride lone pairs and nonbonding d electrons at the metal center.

**Dihydrogen/Dihydride Equilibria.** It is well established that complexes of the general form  $\text{CpRu}(\text{PR}_3)_2\text{H}$  and  $\text{Cp}^*\text{Ru}$ -

$(\text{PR}_3)_2\text{H}$  can be protonated to give cationic dihydrides, which adopt a *transoid* capped four-legged piano stool structure. The *transoid* geometry for the dihydride form has been previously established by experiments with asymmetric bidentate phosphine ligands<sup>14</sup> and by crystallography in the case of  $[\text{Cp}^*\text{Ru}(\text{dippe})\text{-H}_2]^+$ <sup>18</sup> and  $[\text{Cp}^*\text{Ru}(\text{PMe}_3)_2\text{H}_2]^+$ .<sup>19</sup> When a bidentate phosphine ligand is employed, an equilibrium mixture of the dihydride and a dihydrogen complex is obtained. The ratio of these two tautomers obtained depends on the nature of the bidentate ligand employed, with one-carbon bridged ligands strongly favoring the dihydrogen form, while two-carbon bridges favor the dihydride form. This is understandable in that a single-carbon bridge between the phosphorus atoms will give a less stable arrangement when the P atoms are in a *transoid* geometry. Within the one-carbon bridged bidentate ligands, intuitive notions about the relative stability of the formally Ru(II) dihydrogen complex versus the Ru(IV) dihydride complex based on the donor properties of the ligand are not borne out by observation. For example, with  $\text{dppm}$  (complex **1**), 33% dihydride is observed, while for the better donor  $\text{dmpm}$  (complex **5**), the proportion of dihydride complex is only 6%. A possible steric explanation for this is suggested by an examination of the structural data for the dihydrogen form of complex **1**, which shows some steric congestion between the  $\text{Cp}^*$  methyl groups and the phenyl rings of the  $\text{dppm}$  ligand. In the case of  $\text{dmpm}$  (complex **5**), this steric interaction would be diminished, leading to a greater proportion of dihydrogen versus dihydride complex.

**H–D Coupling and the Determination of H–H Distances.** Samples containing deuterium in the bound dihydrogen ligand were generated by exposure of methylene chloride solutions of complexes **1–5** to HD or  $\text{D}_2$  gas. Ligand exchange rates were observed to be faster for complexes with less basic phosphine coligands. This observation is in contrast to the trend observed above in the lability of the chloride ligand to replacement by hydrogen.

In reported dihydrogen complexes which have been structurally characterized by neutron diffraction or solid-state NMR methods, an inverse correlation between the H–H distance and  $J_{\text{HD}}$  of the HD analogue has been observed.<sup>4,20</sup> The equation describing the inverse relationship between  $r_{\text{HH}}$  and  $J_{\text{HD}}$  from corrected neutron diffraction and solid-state NMR data is<sup>4</sup>

$$r_{\text{HH}} = 1.44 - 0.0168(J_{\text{HD}}) \quad (1)$$

Morris and co-workers have used a larger set of distances and  $J_{\text{HD}}$  values to develop a similar correlation for the H–H bond length.<sup>5</sup> They have also included uncorrected neutron data and distances determined from X-ray diffraction data along with the distances from solid-state NMR and corrected neutron data. However, results with this larger data set are similar to eq 1:

$$r_{\text{HH}} = 1.42 - 0.0167(J_{\text{HD}}) \quad (2)$$

Using eq 1 and the ambient temperature value for  $J_{\text{HD}}$  observed in complex **1** gives  $r_{\text{HH}} = 1.092$  Å. The use of eq 2 leads to  $r_{\text{HH}} = 1.071$  Å. Since the distances derived from neutron diffraction and solid-state NMR data are viewed as more

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**Table 2.** Couplings (Hz) and Derived Distances (Å) in Isotopomers of **1**

T (K)	$J_{\text{HD}}$ (Hz) <sup>a</sup>	$r_{\text{HD}}$ (Å)	$J_{\text{HT}}$ (Hz) <sup>b</sup>	$r_{\text{HT}}$ (Å)	$J_{\text{DT}}$ (Hz) <sup>c</sup>	$r_{\text{DT}}$ (Å)
286	20.8 ± 0.3	1.091 ± 0.005	149.2 ± 0.5	1.079 ± 0.001	23.4 ± 0.3	1.072 ± 0.005
275	21.3 ± 0.2	1.082 ± 0.004	150.4 ± 0.4	1.076 ± 0.001	24.0 ± 0.3	1.062 ± 0.005
267	21.5 ± 0.2	1.079 ± 0.004	151.8 ± 0.4	1.073 ± 0.001	24.1 ± 0.2	1.061 ± 0.004
251	21.8 ± 0.2	1.075 ± 0.004	153.6 ± 0.4	1.069 ± 0.001	24.4 ± 0.2	1.056 ± 0.004
236	22.1 ± 0.2	1.070 ± 0.004	155.8 ± 0.5	1.063 ± 0.001	25.1 ± 0.3	1.045 ± 0.005
220	22.4 ± 0.2	1.064 ± 0.004	158.7 ± 0.5	1.056 ± 0.001	25.6 ± 0.3	1.037 ± 0.005
204	22.6 ± 0.3	1.060 ± 0.005	160.8 ± 0.6	1.051 ± 0.0015	25.8 ± 0.4	1.034 ± 0.0055

<sup>a</sup> Recorded at 750 MHz. <sup>b</sup> Average of couplings obtained at 750 and 800 MHz. <sup>c</sup> Recorded at 800 MHz.

reliable, we favor the use of eq 1 in determining distances from coupling data. On the basis of a measurement uncertainty in  $J_{\text{HD}}$  of ±0.3 Hz, the uncertainty in these distances arising from measurement error is estimated to be ±0.005 Å. Since the line widths of the resonances being examined vary with temperature and the nature of the ligand set, it is actually an oversimplification to attribute a single uncertainty to these measurements. In general, line widths for the resonance due to bound H–D increase slightly at lower temperatures, due to relaxation and solvent viscosity effects. For complex **1**, an additional source of line broadening is the onset of dihydrogen/dihydride exchange, which becomes significant as the sample temperature approaches 300 K, as established by spin saturation transfer experiments by Morris and co-workers.<sup>5</sup> Thus the most precise data for H–D coupling in complex **1** is obtained for temperatures in the middle of the studied range. In contrast to complex **1**, the resonances due to bound HD in CpRu(dmpe)HD<sup>+</sup> (**3**) are quite sharp at higher temperatures, affording more precise values for the coupling (see below).

Complex **1** has been thoroughly studied by Morris and co-workers, who report  $r_{\text{HH}} = 1.10(3)$  Å on the basis of neutron diffraction data obtained at low temperature. This distance was confirmed by a study of the relaxation time ( $T_1$ ) for the dihydrogen ligand in **1**, which gave  $r_{\text{HH}} = 1.10$  Å, with the assumption that the dihydrogen ligand is in the slow rotation regime.<sup>8</sup> Uncertainties in H–H distances derived from  $T_1$  measurements are difficult to evaluate, with a reasonable uncertainty from measurement error alone being ca. ±3–5%.<sup>21</sup> Additional uncertainty arises from assumptions made about the rotational regime of the bound dihydrogen ligand and sources of relaxation other than H–H dipole–dipole relaxation.

Determination of  $r_{\text{HH}}$  from the  $J_{\text{HD}}$  value has the advantage that correction factors concerning the rotation regime of the dihydrogen ligand and other sources of relaxation do not have to be considered.<sup>16,22</sup> In the case of complex **1**, the H–H distances determined by neutron diffraction, relaxation, and H–D coupling are in excellent agreement.

Using eq 1 and the ambient temperature H–D coupling data for complexes **1–5** tabulated in Table 1, values for the H–H distance in the bound dihydrogen ligand ranging from 1.02 (**2**) to 1.17 Å (**5**) can be derived. By using  $J_{\text{HD}}$  values to derive H–H distances, we are explicitly assuming that the distance is independent of isotope substitution. In at least some cases, this is not correct (see below).

The observation of mixtures of bound HH and bound HD in complexes **1–5** also allows for the measurement of the small

upfield shift of the HD resonance from the H<sub>2</sub> signal ( $\delta_{\text{HD}} - \delta_{\text{HH}}$ ), which ranges from 15 to 35 ppb (see Table 1). These isotope shifts are typical of reported dihydrogen complexes<sup>23</sup> and are smaller than what is observed in H<sub>2</sub>/HD gas ( $\Delta\delta = +36$  ppb).<sup>24</sup> These small chemical shift differences are independent of temperature.

**Temperature and Isotope Dependence of Bond Distances in Bound Dihydrogen.** In complex **1**, the H–H distance derived from coupling data was found to vary significantly with observation temperature, increasing about 3% when the temperature was increased from 204 to 286 K (see Table 2). The observed couplings are independent of the magnetic field employed, which rules out the possibility that residual dipolar coupling could be responsible for the temperature dependence of the coupling.<sup>25</sup>

These observations are consistent with a detailed computational study of complex **1** using DFT methods by Lledós, Lluich, and co-workers.<sup>9</sup> These workers report a very unusual potential energy surface for the bound hydrogen in this molecule. The H–H distance can be significantly elongated with very little increase in energy. The calculations indicate that a vibrationally excited state (with a longer H–H distance of about 1.3 Å) can be significantly populated at moderate temperatures. Further analysis of this potential surface in terms of the reported Raman spectrum of **1** and the corresponding vibrational modes has also been reported.<sup>26</sup> Our observations of the temperature dependence of the H–D coupling in **1** are in excellent agreement with the computational predictions.

The DFT study also leads to the novel prediction that the observed bond distance will be quite sensitive to isotope substitution. For example, the bond distance for the T–T complex was predicted to be ca. 10% shorter than that in the corresponding H–H species. This remarkable difference in bond distances upon isotopic substitution is attributed to the highly anharmonic nature of the vibrational potential.<sup>9</sup>

To probe for the predicted isotope effects on bond distance, the use of tritium NMR spectroscopy is advantageous. The

(23) Reported isotope shifts in dihydrogen complexes are generally <50 ppb. Some reported exceptions are: (a)  $\Delta\delta = +90$  ppb for Ru(H<sub>2</sub>)(OEP)(THF) (OEP = octaethylporphyrin), +130 ppb for Os(H<sub>2</sub>)(OEP)(\*Im) (\*Im = 3-*tert*-butyl-4-phenylimidazole), and –200 ppb for Ru<sub>2</sub>(H<sub>2</sub>)(DPB)(\*Im)<sub>2</sub> (DPB = 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin)]-biphenylene). [Collman, J. P.; Wagenknecht, P. S.; Hutchison, J. E.; Lewis, N. S.; Lopez, M. A.; Guillard, R.; L'Her, M.; Bothner-By, A. A.; Mishra, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 5654–5664.] (b)  $\Delta\delta = +200$  ppb for [Cp<sub>2</sub>Ta(CO)(H<sub>2</sub>)]<sup>+</sup>. [Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalón, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1994**, *116*, 2635–2636.] (c)  $\Delta\delta = +80$  ppb for [Os(H<sub>2</sub>)(en)<sub>2</sub>OAc]<sup>2+</sup> (en = ethylenediamine; OAc = acetate). [Hasegawa, T.; Li, Z.-W.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352–5356.]

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magnetogyric ratio of  $^3\text{H}$  is 6.949 times larger than that of  $^2\text{H}$ , so couplings between H and T should be correspondingly larger than couplings between H and D, making the detection of small changes in the coupling much more reliable. The couplings  $J_{\text{HT}}$  and  $J_{\text{DT}}$  can be converted to the equivalent H–D couplings using  $\gamma_{\text{T}}/\gamma_{\text{D}} = 6.949$  and  $\gamma_{\text{T}}/\gamma_{\text{H}} = 1.067$ . The most precise data arise from the H–T coupling measurements, where the experimental uncertainty is estimated as  $\pm 0.4$  Hz, which corresponds to an uncertainty in the bond distance of  $\pm 0.001$  Å. The bond distances for bound H–D, H–T, and T–D as a function of temperature are tabulated in Table 2.

The derived bond distances at the higher temperatures are in reasonable agreement with the value of  $r_{\text{HH}} = 1.10(3)$  Å for complex **1** reported by neutron diffraction. It is clear from our data that substitution with heavier isotopes leads to a significant shortening of the bond distance in H–T and D–T complexes, as predicted by the DFT study of Lledos, Lluch, and co-workers.<sup>9</sup> For example, at 267 K,  $r_{\text{HD}} = 1.079 \pm 0.004$  Å, while  $r_{\text{TD}} = 1.061 \pm 0.004$  Å. It is particularly noteworthy that the value for  $r_{\text{HD}}$  is significantly shorter than the neutron diffraction value for  $r_{\text{HH}}$  and that replacing H with T leads to further shortening of the bond distance.

Interestingly, the temperature dependence of the bond distance is slightly different for the various isotopomers. For example, an increase in temperature from 204 to 286 K leads to a decrease in the H–D coupling in **1** and a corresponding increase in the derived bond distance of ca. 2.9%. Examination of the data for the D–T complex shows a similar trend, but with a change of ca. 3.7% over the same temperature range. This observation is also consistent with the DFT study, in that the heavier isotopomer is predicted to have more closely spaced vibrational energy levels, leading to greater population of excited vibrational states as the temperature is raised.<sup>9</sup>

An estimate of the bond distance in the T–T complex (**1-t<sub>2</sub>**) can be obtained by measurement of the maximum rate of relaxation ( $T_1$  min) in this complex. For the bound  $\text{T}_2$ , the maximum rate of relaxation ( $T_1$  min = 21 ms) was observed at 246 K (800 MHz). Analysis using the methodology of Halpern and co-workers<sup>16</sup> leads to a T–T distance of 1.06 Å in complex **1**. A more reliable bond distance of 1.05 Å was obtained by fitting the complete data set for all temperatures to the equation for dipole–dipole relaxation, using data for  $\tau_c$  versus temperature derived by determining the maximum rate of relaxation of  $^1\text{H}$  and  $^3\text{H}$  at various fields.<sup>14</sup>

As expected from the trend of shorter bond distances for the heavier isotopes, this bond distance for bound T–T is slightly shorter than that found from coupling data for the D–T analogue at a similar temperature (1.056 Å for the D–T complex at 251 K). In light of the experimental uncertainty associated with the measurement of bond distances by the relaxation method, which is inherently less precise than the coupling methodology, the agreement between the two methods is gratifying. A slightly shorter distance of ca. 1.01 Å was anticipated for the T–T complex, on the basis of the DFT study, suggesting that the computational study may underestimate the bond distance in this case.

**Temperature Dependence of H–D Coupling as a Function of Ligand Set.** Since the novel temperature dependence of the H–D coupling in complex **1** is attributed to an unusually soft vibrational potential for stretching of this elongated dihydrogen

ligand, it is of interest to explore this phenomenon as a function of the H–H distance, which is readily varied by changing the nature of the phosphine ligand. To this end, we have reexamined some related complexes from the literature. For example,  $[\text{CpRu}(\text{dppe})\text{H}_2]^+$  (**2**) exhibits an H–D coupling of 24.9 Hz in **2-d<sub>1</sub>**, consistent with an H–H distance of ca. 1.02 Å. Careful examination shows that the H–D coupling in this complex is invariant with temperature (see Figure 2). This result is intuitively reasonable, since a shorter H–H bond is reasonably expected to be stiffer and more resistant to elongation.

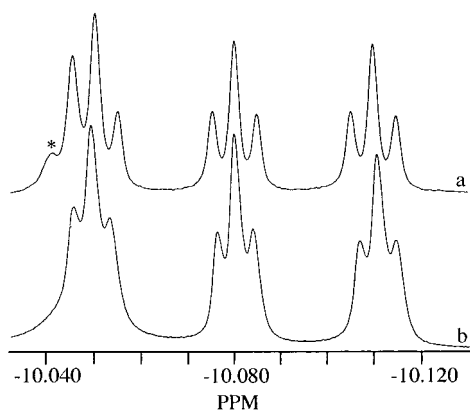
We reasoned that greater elongation of the H–H distance would result in a softer potential and perhaps an even greater effect of temperature upon the bond distances. To make a more elongated dihydrogen ligand, we envisaged that use of a more basic ligand set should lead to a more electron-rich Ru center and enhance back-donation to the H–H  $\sigma^*$  orbital. To test this idea, the new complexes  $[\text{Cp}^*\text{Ru}(\text{dppip})\text{H}_2]^+$  (**4**) and  $[\text{Cp}^*\text{Ru}(\text{dmpm})\text{H}_2]^+$  (**5**) were prepared. The H–D couplings at ambient temperature are 18.6 and 15.9 Hz, respectively. This shows that our strategy has been successful and that a highly elongated H–H distance of ca. 1.17 Å has been achieved in complex **5**.

Surprisingly, the H–D couplings in **4** and **5** are found to be invariant with temperature. This unexpected result suggests that the longer and weaker H–H bond in these complexes is not in fact accompanied by a suitably soft potential energy surface to allow for facile thermal excitation of low energy vibrational modes corresponding to further elongation of the H–H distance. Complexes such as **5** are difficult to describe in simple valence bond terms since the H–H distance seems to be intermediate between those expected for a dihydride and a dihydrogen complex. There may be justification for thinking of them as having significant dihydride character, with the hydrogen atoms quite strongly localized in their respective positions.

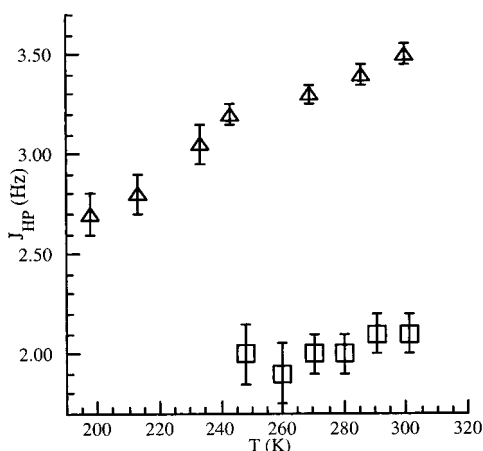
Since the temperature-dependent behavior of the coupling seemed to occur only in species such as **1**, with H–D couplings of ca. 21 Hz, we chose to reexamine the well-known complex  $[\text{CpRu}(\text{dmpe})\text{H}_2]^+$  (**3**), which we first reported in 1987 and identified as a dihydrogen complex on the basis of a measured H–D coupling of 22 Hz.<sup>27</sup> Examination of the H–D coupling in **3-d<sub>1</sub>** as a function of temperature reveals a small but significant variation with temperature. We find that the H–D coupling in **3** is 23.05 Hz at 200 K, decreasing to 22.30 Hz at 300 K (see Figure 1). While these changes are very small, the line widths of the proton resonances in **3-d<sub>1</sub>** are extremely narrow, leading to very precise data, with an estimated uncertainty in the measured couplings of  $\pm 0.05$  Hz. (see Figure 3).

The narrow lines observed for **3-d<sub>1</sub>** allowed us in our original observations of this complex to report the presence of a small H–P coupling ( $^2J_{\text{H-P}} = 3.6$  Hz) in the bound dihydrogen ligand.<sup>27</sup> Several reports of such couplings are now in the literature. It is generally observed in Ru complexes of the type under study here that small ( $\leq 5$  Hz) H–P couplings are indicative of the presence of a bound dihydrogen ligand, while larger H–P couplings are found for dihydride structures. In the course of our detailed examination of the NMR spectra of **3-d<sub>1</sub>** as a function of temperature, a pronounced temperature dependence of the H–P coupling was observed. At 200 K, a value of  $^2J_{\text{H-P}} = 2.7$  Hz was observed, increasing with temperature to 3.5 Hz at 300 K (see Figure 4). It is remarkable that this *two*

(27) Chinn, M. S.; Heinekey, D. *J. Am. Chem. Soc.* **1987**, *109*, 5865–5867.



**Figure 3.** Partial  $^1\text{H}$  NMR spectrum (750 MHz) of  $[\text{CpRu}(\text{dmpe})(\text{HD})]^+$  (**3-d<sub>1</sub>**) at (a) 298 K and (b) 215 K. \* indicates partially obscured resonance due to  $\text{H}_2$  isotopomer.



**Figure 4.**  $^2J_{\text{HP}}$  values between the bound HD and the phosphine ligand as a function of temperature:  $[\text{CpRu}(\text{dmpe})(\text{HD})]^+$  (**3**, triangles);  $[\text{CpRu}(\text{dppc})(\text{HD})]^+$  (**2**, squares).

*bond* coupling shows a much larger (ca. 30%) change upon increasing the observation temperature than does the one bond H–D coupling, which decreased by only 3.4% over a similar temperature range. In contrast, the values of  $^2J_{\text{H-P}}$  in complex **2** are independent of the observation temperature.

We surmise that this temperature-dependent H–P coupling is also due to thermal population of a vibrational excited state, which presumably has stronger Ru–H interactions, leading to more efficient transmission of coupling between  $^1\text{H}$  and  $^{31}\text{P}$ . An additional factor which is difficult to assess is the presumed angle dependence of the coupling. That this angle dependence can be significant is confirmed by the observation that complexes **2** and **3** (with a two-carbon bridge in the bidentate phosphine ligand) exhibit observable H–P couplings, while complexes with a one-carbon bridge (**1**, **4**, and **5**) show no such coupling. In contrast to the dihydrogen complexes, the transoid dihydride tautomers exhibit large and temperature independent values of  $^2J_{\text{H-P}}$ . We tentatively conclude that under circumstances where the structure of an elongated dihydrogen complex allows measurement of  $^2J_{\text{H-P}}$ , temperature dependence of this parameter can be a sensitive indicator of H–H bond stretching due to thermal excitation of low energy vibrational modes.

**Possible Dihydrogen/cis-Dihydride Equilibrium.** Although the DFT study found a single minimum in the PES, the observed temperature dependence of the coupling constants described above might also be explained by a rapid equilibrium between

the dihydrogen form (as seen in the low-temperature neutron structure of **1**) and a cis-dihydride complex, each representing distinct minima in the PES. If this hypothesis is correct, the observed couplings and chemical shifts would represent a population weighted average of these two isomers, which would be expected to shift with temperature. If such an equilibrium prevails, a temperature-dependent chemical shift for the resonance due to bound dihydrogen would be expected. Careful measurement shows that the chemical shift due to the bound dihydrogen in **1** is essentially independent of temperature, moving upfield by only 10 ppb upon changing the temperature from 220 to 300 K. This temperature dependence is actually smaller than that observed for the dihydride tautomer of complex **1**, which shifts by ca. 100 ppb over the same temperature range.

A dihydrogen/dihydride equilibrium should also lead to isotopic perturbation effects arising from nonstatistical distribution of deuterium (and tritium). These effects will be manifested by large and temperature-dependent values of the isotope shift. However, the isotope effects on the chemical shifts are small and temperature independent. For example, in complex **1**,  $\delta_{\text{HD}} - \delta_{\text{HH}} = 15$  ppb and  $\delta_{\text{HT}} - \delta_{\text{HH}} = 22$  ppb. The former of these values is actually in the low end of the range of isotope effects reported for bound dihydrogen in complexes of this type.<sup>28</sup> Similar observations were made for complex **3**. The lack of temperature dependence of the isotope shift is incompatible with the equilibrium hypothesis unless the chemical shifts of the dihydrogen and cis-dihydride tautomers are very similar or the occupation of these two different chemical environments by deuterium is essentially statistical. The former requirement is unlikely to be met, since the chemical shift difference between the dihydrogen and trans-dihydride forms of complexes **1–5** is substantial (see Table 1). Statistical occupancy of the two different chemical environments by a deuterium (or Triton) seems unlikely, since in a related Ru dihydrogen/hydride complex, there is a clear preference for deuterium to accumulate in the hydride site in preference to the dihydrogen ligand.<sup>29</sup>

The complexes studied in this work present a wide range of H–H distances (from ca. 1 Å in **2** to nearly 1.2 Å in **5**). If these outcomes are the result of a dihydride/dihydrogen equilibrium, then a considerable range of equilibrium constants must be represented (with complex **1** being in the middle of the range), all of which should exhibit some temperature dependence. Since only complex **1** (and to a lesser extent complex **3**) exhibits temperature-dependent couplings, these observations are not compatible with the equilibrium hypothesis. While the equilibrium hypothesis involving two different minima in the potential surface cannot be conclusively ruled out, we believe it to be unlikely.

## Summary and Conclusions

The results described here provide direct experimental verification of the conclusions of the DFT study of Lledós, Lluch, and co-workers.<sup>9</sup> The remarkable isotope dependence of the bond distance in the bound dihydrogen ligand of complexes **1** and **3** is attributed to the extremely flat and highly anharmonic potential energy surface which defines the H–H and M–H interactions in this complex. This allows the zero

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point energy differences among the various isotopomers to be directly reflected in the bond distances. The striking change of the bond distance upon small changes in temperature is due to thermal population of vibrational excited states which are only slightly higher in energy than the ground state. That these effects are exhibited by molecules which are readily isolable at ambient temperatures is very unusual.

Our studies of phosphine ligand variation show that this effect is acutely dependent upon the choice of coligands. In this particular family of cationic Ru complexes, measurable temperature dependence of H–H distances is only observed when the H–H distance is ca. 1.1 Å. Complexes with H–H distances slightly shorter or longer than this exhibit temperature independent H–H distances. It is important to note that the DFT study made use of the computationally expedient “ligand” H<sub>2</sub>-PCH<sub>2</sub>PH<sub>2</sub>. Thus subtle effects on the Ru–H<sub>2</sub> interaction caused by variations in the electronic properties of the bidentate phosphine ligand were not addressed. Our results suggest that such ligand variation has a significant effect on the vibrational potential experienced by the bound dihydrogen.

## Experimental Section

**General Procedures.** Unless stated otherwise, all manipulations were carried out under argon using Schlenk techniques. Complexes Cp\*Ru-(PPh<sub>3</sub>)<sub>2</sub>Cl, CpRu(dmpe)Cl, CpRu(dppe)H<sub>2</sub><sup>+</sup>, and [Cp\*Ru(dppm)H<sub>2</sub>]<sup>+</sup> were prepared according to literature procedures. Dihydrogen complexes **1** and **3** were prepared according to literature procedures by the protonation of neutral ruthenium hydrides with HBF<sub>4</sub>/diethyl ether. Corresponding monodeuterated isotopomers were prepared in situ by exchange with D<sub>2</sub> (g) or HD (g) in NMR tubes. The phosphine ligand dppip was prepared from 2,2-dichloropropane and Ph<sub>2</sub>PNa as described in the literature.<sup>30</sup> All other phosphines were obtained from Strem Chemicals and used as received. Hydrogen gas was purchased from Airgas and passed through a column of activated molecular sieves prior to use. HD (g) and D<sub>2</sub> (g) were used as received from Cambridge Isotopes. NaB(ArF)<sub>4</sub> was prepared by the published method.<sup>31</sup> Elemental analyses were performed by Galbraith. NMR spectra were recorded on Bruker AC-200, DPX-200, DRX-499, AM-500, and DMX-750 spectrometers. Proton NMR spectra were referenced to the solvent resonance with chemical shifts reported relative to TMS. <sup>31</sup>P chemical shifts were referenced to external 85% H<sub>3</sub>PO<sub>4</sub>. The NMR studies were carried out in high quality 5 mm NMR tubes, utilizing deuterated solvent distilled from standard drying agents. The conventional inversion–recovery method (180-τ-90) was used to determine the relaxation times T<sub>1</sub> of various isotopomers of **3** at 750 MHz. In each experiment, the waiting period was longer than 10 times the expected relaxation rate. Ten variable delays were employed, utilizing appropriate pulse widths determined for both <sup>1</sup>H and <sup>3</sup>H. The workup of spectra used for precise measuring of coupling constants used zero filling to 128 K data points prior to Fourier transform.

**Cp\*Ru(dppip)Cl.** A 500 mL Schlenk flask was charged with 550 mg (0.72 mmol) of Cp\*Ru(PPh<sub>3</sub>)<sub>2</sub>Cl, 302 mg (0.73 mmol) of dppip, and 200 mL of freshly distilled toluene. This slurry was purged for 10 min with argon and brought to reflux under argon producing an orange solution. After being refluxed for 3 h, the solution was allowed to cool and was stirred at ambient temperature overnight. The solution was chromatographed on a 12 cm column of silica packed in hexanes. Following elution of PPh<sub>3</sub> by benzene, Cp\*Ru(dppip)Cl was rapidly eluted with diethyl ether as an orange band. The ether solution was concentrated in vacuo and cooled to –35 °C overnight, affording red

crystals which were filtered in air, rinsed with ice cold pentane, and dried in vacuo (459 mg, 94%). The complex is indefinitely air stable in crystalline form and may be manipulated in solution in air for short periods (hours) at ambient temperature with no signs of decomposition. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.4–7.3 (br, 20H, C<sub>6</sub>H<sub>5</sub>), 1.82 (t, 3H, <sup>3</sup>J<sub>PH</sub> 15 Hz, CH<sub>3</sub>), 1.62 (s, 15H, Cp\*), 1.61 (t, 3H, <sup>3</sup>J<sub>PH</sub> 16 Hz, CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H}: δ 44 (s).

**Cp\*Ru(dppm)Cl and Cp\*Ru(dmpm)Cl.** These were prepared as above using dppm and dmpm, respectively. The yields were 76% for Cp\*Ru(dppm)Cl and 46% for Cp\*Ru(dmpm)Cl. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra matched those reported in the literature.

**[Cp\*Ru(dmpm)H<sub>2</sub>]B(ArF)<sub>4</sub> (**5**).** A 40 mL Schlenk tube was charged with 38 mg (0.093 mmol) of Cp\*Ru(dmpm)Cl, 88 mg (0.098 mmol) of NaB(ArF)<sub>4</sub>, and a Teflon stir bar. The tube was evacuated, and 15 mL of fluorobenzene was added by vacuum transfer. After back filling with 1.1 atm of H<sub>2</sub>, the tube was warmed slowly to ambient temperature with vigorous agitation to afford a colorless solution and a white precipitate of NaCl. After stirring for 1 h at room temperature, the solution was filtered under argon. The dihydrogen complex was crystallized by slow diffusion of cyclopentane into the solution. The solvents were removed via syringe under argon, and the crystals were rinsed with 2 × 5 mL of cyclopentane and dried in vacuo. Yield: 51 mg, 55%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>) Ru(H<sub>2</sub>): δ 3.47 (m, 1H, CH<sub>2</sub>), 2.98 (m, 1H, CH<sub>2</sub>), 1.97 (t, 15H, <sup>4</sup>J<sub>PH</sub> 1.5 Hz, Cp\*), 1.66 (m, 12H, CH<sub>3</sub>), –7.77 (s, 2H, br, H<sub>2</sub>). RuH<sub>2</sub>: δ 3.27 (t, 2H, <sup>2</sup>J<sub>PH</sub> 8.5 Hz, CH<sub>2</sub>), 2.03 (s, 15H, Cp\*), 1.72 (br m, 12H, CH<sub>3</sub>), –7.09 (t, 2H, <sup>2</sup>J<sub>PH</sub> 32.5 Hz, RuH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR: Ru(H<sub>2</sub>), δ –41.1 (s); RuH<sub>2</sub>, δ –31.1 (s). Anal. Calcd: C, 45.61; H, 3.51. Found: C, 45.65; H, 3.76.

**[Cp\*Ru(dppip)H<sub>2</sub>]B(ArF)<sub>4</sub> (**4**).** This was prepared as above in 58% yield. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): Ru(H<sub>2</sub>), δ 1.77 (s, 15H, Cp\*), 1.55 (t, 3H, <sup>3</sup>J<sub>PH</sub> 14.6 Hz, CH<sub>3</sub>), 0.83 (t, 3H, <sup>3</sup>J<sub>PH</sub> 17.6 Hz, CH<sub>3</sub>), –6.28 (s, br, 2H, H<sub>2</sub>); RuH<sub>2</sub>, δ 1.88 (s, 15H, Cp\*), 1.06 (t, 6H, <sup>3</sup>J<sub>PH</sub> 15.5 Hz, CH<sub>3</sub>), –7.43 (t, 2H, <sup>2</sup>J<sub>PH</sub> 27.7 Hz). Additionally, complex overlapping aryl resonances for both the dihydrogen and the dihydride isomers were observed at δ 7.10–7.60. <sup>31</sup>P{<sup>1</sup>H} NMR: Ru(H<sub>2</sub>), δ 53.7 (s); RuH<sub>2</sub>, δ 44.0 (s).

**In Situ Preparation of Isotopomers of Dihydrogen Complexes.** Dihydrogen complexes **1** and **3** were deuterated by dissolving the complexes in CD<sub>2</sub>Cl<sub>2</sub> and treating with D<sub>2</sub> gas (1 atm) until <sup>1</sup>H NMR indicated that 90% deuteration had been achieved. This allows for the observation of the monodeuterated isotopomer without interference from the H<sub>2</sub> isotopomer. A simpler method was developed for compounds **2**, **4**, and **5**. The dihydrogen complexes were prepared in situ as described above from the corresponding ruthenium chloride and NaB(ArF)<sub>4</sub> in CD<sub>2</sub>Cl<sub>2</sub>. The reaction was carried out under 1.1 atm of HD gas, affording samples that were nearly 100% HD isotopomer by <sup>1</sup>H NMR. Atom scrambling occurs slowly (hours) for these complexes at ambient temperatures. Storage of samples at temperatures lower than 273 K prevents isotopomer scrambling on a time scale of several days.

**Preparation of <sup>3</sup>H Labeled **1**.** In a typical procedure, a medium-walled NMR tube attached to a Kontes valve was charged with 1 mg of **1**. After dissolution in CD<sub>2</sub>Cl<sub>2</sub>, the solution was placed under 1.1 atm HD (g) overnight to afford a mixture of isotopomers with a deuterium content of ca. 50% as indicated by <sup>1</sup>H NMR spectroscopy. Following three freeze–pump–thaw cycles, the tube was attached to the stainless steel tritium manifold and placed under 200 Torr of T<sub>2</sub> gas for 2 h. This procedure affords a sample containing about 20% tritium in the bound dihydrogen. The T<sub>2</sub> (g) was removed via three freeze–pump–thaw cycles, and the tube was flame-sealed under vacuum.

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