

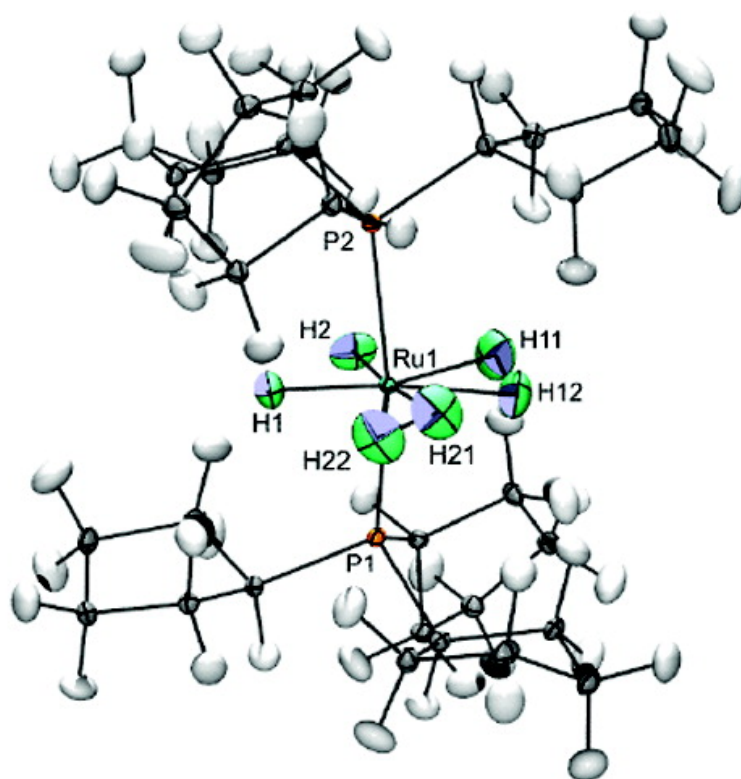
Communication

**Synthesis, Neutron Structure, and Reactivity of the Bis(dihydrogen) Complex  $\text{RuH}(\eta\text{-H})(\text{PCyp})$  Stabilized by Two Tricyclopentylphosphines**

Mary Grellier, Laure Vendier, Bruno Chaudret, Alberto Albinati, Silvia Rizzato, Sax Mason, and Sylviane Sabo-Etienne

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## Synthesis, Neutron Structure, and Reactivity of the Bis(dihydrogen) Complex $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCyp}_3)_2$ Stabilized by Two Tricyclopentylphosphines

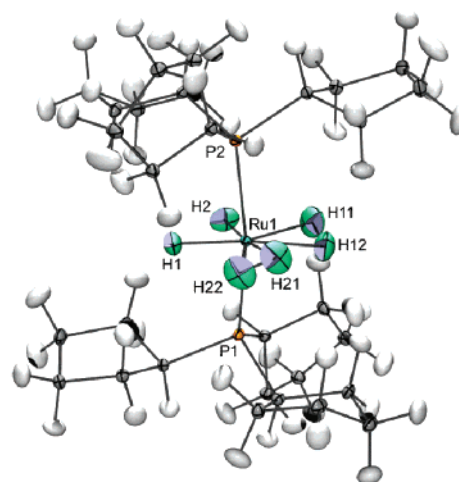
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Dihydrogen complexes were a curiosity 20 years ago when the first paper by Kubas demonstrated that dihydrogen could coordinate to a metal center without H–H bond breaking. The dihydrogen bonding in  $\text{W}(\eta^2\text{-H}_2)(\text{CO})_3(\text{P}^i\text{Pr}_3)_2$  was established unambiguously by single-crystal neutron diffraction, showing a H–H bond distance of 0.82 Å.<sup>1</sup> A number of polyhydride species were then reformulated, and the number of dihydrogen complexes grew rapidly.<sup>2</sup> Most complexes contain only one dihydrogen ligand in the octahedral coordination sphere of a  $d^6$  metal. However, very few complexes containing two dihydrogen ligands are known. Iridium,<sup>3</sup> osmium,<sup>4</sup> and very recently rhenium<sup>5</sup> bis(dihydrogen) complexes have only been characterized in solution by NMR spectroscopy, whereas chromium<sup>6</sup> bis(dihydrogen) complexes have been observed in noble-gas matrices. The bis(dihydrogen) ruthenium complexes are the only species that have been isolated as solids: the bis(phosphine)  $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2$  (**1**)<sup>7</sup> and  $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{P}^i\text{Pr}_3)_2$ ,<sup>8</sup> the mixed phosphine(carbene)  $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)(\text{IMes})$ ,<sup>9</sup> and the Tp compounds<sup>7b</sup>  $\text{TpRuH}(\eta^2\text{-H}_2)_2$  (Tp = hydridotris(3,5-dimethylpyrazolyl)borate or hydridotris(3-isopropyl-4-bromopyrazolyl)borate). The chemistry of **1**, incorporating two tricyclohexylphosphines, has been extensively studied by our group. Due to the presence of two labile dihydrogen ligands, a fascinating reactivity has been developed. For example, **1** is used as an entry for the design of other  $\sigma$  complexes, silane and borane compounds.<sup>10,11</sup> **1** is also an efficient catalyst precursor for a wide variety of reactions.<sup>12</sup> Remarkably, **1** may be used for hydrogen storage. Up to 10 hydrogen atoms can be abstracted from **1**, and the reaction is reversible.<sup>13</sup> This is the result of a partial dehydrogenation of the cyclohexyl ring of the phosphine ligands, leading ultimately to the formation of the hydride complex  $\text{RuH}[(\eta^3\text{-C}_6\text{H}_8)\text{PCy}_2][(\eta^2\text{-C}_6\text{H}_9)\text{PCy}_2]$ . In some catalytic reactions, the formation of intermediate species leading to such partially dehydrogenated phosphine can be detrimental for the selectivity, due to the competition of several catalytic cycles. Thus, we were interested in preparing an analogous complex in which such reaction could be limited. We assumed that the tricyclopentylphosphine, with a more constrained ring, would be a good candidate. In this Communication, we describe the synthesis of a new bis(dihydrogen) complex, which displays remarkable activity toward H/D exchange.

Treatment of  $\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})(\eta^6\text{-C}_8\text{H}_{10})$  with 3 bar  $\text{H}_2$  in the presence of 2 equiv of tricyclopentylphosphine ( $\text{PCyp}_3$ ) in pentane resulted in the isolation of a cream-colored solid, analyzed as  $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCyp}_3)_2$  (**2**).<sup>14</sup> The molecular structure of **2** was determined by single-crystal X-ray and neutron diffraction (see Supporting Information).<sup>15,16</sup> This is the first report of a neutron structure determination of a bis(dihydrogen) complex (see Figure 1 and Table



**Figure 1.** Neutron structure of  $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCyp}_3)_2$  (**2**). Ellipsoids drawn at 50% probability.

1). The coordination geometry around the metal center is a distorted octahedron defined by the two phosphines in a trans configuration (making an angle of  $168.9(1)^\circ$ ), two cis dihydrogen ligands and two hydrides trans to them, defining the equatorial plane. As already observed in similar complexes, the P atoms are slightly bent toward the two hydride ligands.<sup>17</sup>

**Table 1.** Selected Bond Distances (Å) and Angles (deg) for  $\text{RuH}_2(\eta^2\text{-H}_2)_2(\text{PCyp}_3)_2$  (**2**)

neutron <sup>a</sup> /X-ray <sup>b</sup>		neutron <sup>a</sup> /X-ray <sup>b</sup>	
Ru–P1	2.312(3)/2.3121(4)	Ru–H21	1.764(5)/1.75(4)
Ru–P2	2.307(3)/2.3110(4)	Ru–H22	1.745(5)/1.69(3)
Ru–H1	1.628(4)/1.58(4)	Ru–m11 <sup>c</sup>	1.692(5)
Ru–H2	1.625(4)/1.54(4)	Ru–m22 <sup>c</sup>	1.702(5)
Ru–H11	1.730(5)/1.66(3)	H11–H12	0.825(8)/0.70(4)
Ru–H12	1.753(5)/1.75(4)	H21–H22	0.835(8)/0.78(4)
P1–Ru–P2	168.9(1)/168.64(2)	H2–Ru–H21	173.5(3)/174(1)
H1–Ru–H2	81.9(3)/73(2)	H2–Ru–H22	157.7(3)/157(2)
H1–Ru–H11	157.8(3)/156(2)	m11–Ru–m22 <sup>c</sup>	99.8(3)
H1–Ru–H12	173.4(3)/176(1)		

<sup>a</sup> At 20 K. <sup>b</sup> At 100 K. <sup>c</sup> m11 and m22 are, respectively, the midpoints of the H11–H12 and H21–H22 separations.

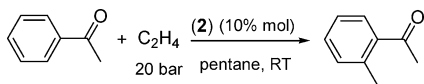
The two H–H separations are equal (at 0.825(8) and 0.835(8) Å) and comparable, for example, to that found in  $[\text{Ru}(\text{dppe})_2(\text{H})(\text{H}_2)]^+$ ,<sup>18</sup> a typical value for an “unstretched” dihydrogen ligand, involving only weak  $\pi$ -back-bonding from the Ru to the dihydrogen  $\sigma^*$  orbital. Excellent agreement is also found with the results from DFT calculations at the B3LYP level (H–H bond lengths of 0.853 Å).<sup>19</sup> There is a slight asymmetry in the bonding of the two H<sub>2</sub>

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**Scheme 1.** Murai's Reaction Catalyzed by **2** at Room Temperature



molecules, as can be judged from the Ru–(H<sub>2</sub>) distances (1.730(5), 1.753(5) Å and 1.745(5), 1.764(5) Å). Moreover, these two ligands are tilted with respect to the coordination plane by 24.6(5)° and 22.8(5)°. The ruthenium–hydride separations are equal and in the expected range for a classical M–H distance (1.628(4) and 1.625(4) Å). The distances between each hydride and the cis dihydrogen ligand are around 2.1 Å, ruling out the presence of any cis interaction.<sup>20</sup>

The NMR spectra show that **2** is fluxional down to 170 K. In the <sup>1</sup>H NMR spectrum measured at room temperature in C<sub>6</sub>D<sub>6</sub>, one triplet is observed at δ –7.98 (*J*<sub>H–P</sub> = 8.0 Hz) for the six hydrogens in rapid exchange. H/D exchange between the Ru–H and the C–D bonds of the deuterated benzene is observed within 1 h, leading to the formation of various isotopomers RuH<sub>x</sub>D<sub>6–x</sub>(PCyp<sub>3</sub>)<sub>2</sub> (with *x* = 0–6). After 5.5 h, integration of the hydride and the cyclopentyl proton signals shows 24% D incorporation. This is in remarkable contrast with the behavior of **1**, which displays no significant H/D exchange even after 24 h. This observation prompted us to test the activity of **2** toward the Murai reaction. Indeed, we have previously demonstrated that **1** was, at room temperature, the best active precursor for ethylene coupling to a functionalized arene.<sup>12d,e</sup> Now, by using **2** as catalyst precursor, we found a 90% conversion of acetophenone to 2-ethylacetophenone within 35 min (see Scheme 1), whereas 10 h was needed in the same conditions using **1** as the catalyst precursor.

In summary, the use of an alkylphosphine with a C<sub>5</sub> ring allows the stabilization of a new bis(dihydrogen) complex, RuH<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>)<sub>2</sub>-(PCyp<sub>3</sub>)<sub>2</sub> (**2**). The single-crystal neutron diffraction study of **2** is the first carried out for a bis(dihydrogen) complex, confirming the nature of the hydrogens in the ruthenium coordination sphere and showing the presence of two “unstretched”, asymmetrically bonded, dihydrogen ligands. We have also shown that **2** is not only stable at room temperature but also much more active for H/D exchange and C–C bond coupling than the well-known complex RuH<sub>2</sub>(η<sup>2</sup>-H<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> (**1**). We are currently exploring both the reactivity of **2** and its catalytic activity for a wide variety of reactions, with a special focus on C–H activation, hydrogenation, and dehydrogenation reactions.

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**Supporting Information Available:** X-ray and neutron crystallographic files for **2** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) Ru(η<sup>4</sup>-C<sub>8</sub>H<sub>12</sub>)(η<sup>6</sup>-C<sub>8</sub>H<sub>10</sub>) (0.200 g, 0.63 mmol) and PCyp<sub>3</sub> (316 μL, 0.63 mmol) were introduced into a Fischer–Porter bottle, and pentane (5 mL) was added. Pressurization to 3 bar dihydrogen and stirring for 45 min led to an orange solution. After the solution was cooled below –30 °C, a cream-colored solid was isolated after washing with cold pentane and rapid drying under vacuum (70% yield). For long periods, **2** should be kept at low temperature under argon. An easy access to large single crystals was found by solubilization of **2** in pentane at room temperature and further cooling at –35 °C for 2 h. Data for **2**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 293 K, 250.13 MHz) δ –7.98 (t, <sup>2</sup>*J*<sub>PH</sub> = 8.0 Hz, 6H, RuH<sub>6</sub>), 1.6–2.0 (54H, PCyp<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 293 K, 101.25 MHz) δ 81.1 (s); *T*<sub>1</sub> (C<sub>7</sub>D<sub>8</sub>, 170 K, 500 MHz) 95 ms for the hydride resonance (the minimum value could not be reached). Anal. Calcd for C<sub>30</sub>H<sub>60</sub>P<sub>2</sub>Ru: C, 61.70; H, 10.30. Found: C, 61.72; H, 10.64.
- (15) The X-ray data collection was carried out at 100 K on a STOE image plate diffractometer. Crystals are monoclinic, space group *P2<sub>1</sub>/n*, *a* = 14.928(2) Å, *b* = 9.4580(7) Å, *c* = 21.713(2) Å, β = 105.14(1)°, *V* = 2959.3(5) Å<sup>3</sup>, *Z* = 4. A total of 22 631 data were collected (5526 unique), *R* = 0.0275, *R<sub>w</sub>* = 0.070. Neutron diffraction data were collected at the ILL reactor, using the D19 diffractometer (equipped with three high-pressure square position-sensitive gas detectors), on a crystal of 2.0 × 2.0 × 1.1 mm<sup>3</sup>. The crystal was mounted, under argon, inside a thin-walled quartz tube on a Displex cryorefrigerator and cooled (~2 K/min) to 20 K. No significant changes in the crystal mosaic or splitting of peaks was observed during cooling. The space group *P2<sub>1</sub>/n* was confirmed at 20 K. Unit cell dimensions (from fittings of the centroids in 3D of 1979 strong reflections) are *a* = 14.8322(9) Å, *b* = 9.4259(6) Å, *c* = 21.679(1) Å, β = 105.377(2)°, *V* = 2922.4(3) Å<sup>3</sup>. A total of 12 878 reflections were collected, yielding 6498 unique reflections (4979 observed with *I*<sub>obs</sub> ≥ 2σ(*I*)). The starting structural model was based on the atomic coordinates of the heavy atoms from the X-ray structure, while all hydrogen atoms were located from Fourier difference maps. The structure was refined by full matrix least squares using ADPs for all atoms (*R* = 0.0521, *R<sub>w</sub>* = 0.1207, GOF = 1.070) and all the collected intensities. See also the Supporting Information.
- (16) There is good agreement between the X-ray and the neutron diffraction results (see Table 1). As expected, the distances obtained from X-ray data are systematically shorter than those from the neutron diffraction with much larger esd's. However, even in the absence of neutron measurements, we have shown that, in borane and silane chemistry, key information on hydride location may be obtained by combining X-ray, DFT, and NMR studies (see refs 10 and 11).
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