

## Communications to the Editor

### Coordination of Dioxygen at a Dihydrogen-Binding Site: Crystal Structure of $[\text{RuH}(\eta^2\text{-O}_2)(\text{dippe})_2][\text{BPh}_4]$ (dippe = 1,2-Bis(diisopropylphosphino)ethane)

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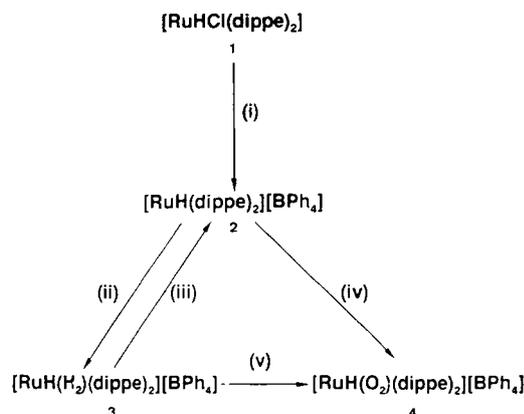
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The addition of dihydrogen to coordinatively unsaturated metal complexes has been successfully used for the preparation of dihydrogen<sup>1-3</sup> complexes. However, systems in which dioxygen is added to a dihydrogen-binding site are rare,<sup>4</sup> the only known example being  $[\text{OsHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2]$ , which reacts with both  $\text{H}_2$  and  $\text{O}_2$  to yield the corresponding adducts  $[\text{OsHCl}(\text{H}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2]$  and  $[\text{OsHCl}(\text{O}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2]$ .<sup>5</sup> No structural data are available for complexes containing both hydride and dioxygen ligands.

We are studying compounds of the bulky diphosphine ligand  $^i\text{Pr}_2\text{PCH}_2\text{CH}_2\text{P}^i\text{Pr}_2$  (dippe), which is known to form coordinatively-unsaturated metal complexes, such as the 14-electron  $[\text{FeR}_2(\text{dippe})]$  ( $\text{R} = \text{CH}_2\text{SiMe}_3, \text{CH}_2\text{Ph}, \text{CH}_2\text{CMe}_2\text{Ph}, \text{CH}_2\text{-CMe}_3$ ) dialkyls.<sup>6</sup> We have now shown that the complex *trans*- $[\text{RuHCl}(\text{dippe})_2]$  (**1**)<sup>7</sup> dissolves in nonpolar solvents like benzene to yield solutions that contain the discrete, neutral, six-coordinate ruthenium species. In methanol or ethanol, however, orange solutions of the five-coordinate, 16-electron cation  $[\text{RuH}(\text{dippe})_2]^+$ , which can be precipitated<sup>7</sup> as the tetraphenylborate salt (**2**), are produced. This complex does not bind  $\text{N}_2$ , but it reacts with dihydrogen in acetone or chloroform to furnish the labile dihydrogen complex  $[\text{RuH}(\text{H}_2)(\text{dippe})_2][\text{BPh}_4]$  (**3**),<sup>7</sup> which is stable only under an  $\text{H}_2$  atmosphere. The nature of the dihydrogen ligand has been established to  $T_1$  (longitudinal relaxation time) and  $^1J(\text{H},\text{D})$  measurements, which yielded  $T_1$  (min) = 10 ms (acetone- $d_6$ , 300 MHz, 228 K) and  $^1J(\text{H},\text{D})$  = 30 Hz. Both values are characteristic of a "nonclassical" hydride complex.<sup>4,8</sup> Several compounds of the type  $[\text{RuH}(\text{H}_2)(\text{diphos})_2]^+$

Scheme I<sup>a</sup>



<sup>a</sup> Reagents and conditions: (i) Na[BPh<sub>4</sub>] in MeOH or EtOH under dinitrogen; (ii) H<sub>2</sub>, acetone, or chloroform; (iii) dinitrogen, argon, or vacuum; (iv) air, acetone, or chloroform; (v) air, acetone, or chloroform.

are known.<sup>1,9</sup> Both the hydridodihydrogen **3** and the monohydride **2** react stoichiometrically with traces of oxygen with formation of the hydridodioxygen adduct  $[\text{RuH}(\text{O}_2)(\text{dippe})_2][\text{BPh}_4]$  (**4**) (yield  $\approx 70\%$ ), which exhibits fluxional behavior, as inferred from  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.<sup>7</sup> Complex **4** seems to be stable under an  $\text{N}_2$  or Ar atmosphere, and it does not lose dioxygen under vacuum in the solid state. In Scheme I are summarized the reactions and conditions in which compounds **1-4** are obtained.

The X-ray crystal structure of  $[\text{RuH}(\text{O}_2)(\text{dippe})_2][\text{BPh}_4]$  has been determined,<sup>10</sup> and a view of the cationic complex is displayed in Figure 1. It shows a distorted octahedral coordination around the ruthenium atom, with the dioxygen ligand bound in the side-on manner, having an O-O separation of 1.360(10) Å. This distance is longer than in the free  $\text{O}_2$  molecule (1.2074 Å),<sup>11</sup> as expected, but slightly shorter than in other  $\eta^2\text{-O}_2$  complexes such as  $[\text{Ir}(\text{O}_2)(\text{dppm})_2][\text{PF}_6]$  ( $d(\text{O}-\text{O}) = 1.453(2)$  Å)<sup>12</sup> and  $[\text{Rh}(\text{O}_2)(\text{dppe})_2][\text{PF}_6]$  ( $d(\text{O}-\text{O}) = 1.418(11)$  Å).<sup>13</sup> The hydride ligand appears *trans* to the dioxygen, with a Ru-H distance of 1.53 Å (the hydride H atom was located in a regular difference Fourier map and it was not refined). The phosphorus atoms are located in the distorted equatorial plane, with two mutually *trans* phosphorus atoms displaced away from the dioxygen and toward the hydride, possibly to minimize repulsions with the dioxygen ligand.

This work constitutes the first structural report of a hydridodioxygen complex and the second of dioxygen coordination at a dihydrogen-binding site.  $\text{H}_2$  and  $\text{O}_2$  active centers of this type may, nevertheless, be more common than previously thought.

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(10) Crystal data:  $\text{C}_{28}\text{H}_{45}\text{O}_2\text{P}_4\text{Ru}$ ,  $\text{C}_{24}\text{H}_{20}\text{B}$ ;  $M = 978.017$ , monoclinic, space group  $P2_1/n$  (No. 14),  $a = 16.698(2)$ ,  $b = 15.498(2)$ , and  $c = 20.635(4)$  Å,  $\beta = 103.40(1)^\circ$ ,  $V = 5194(3)$  Å<sup>3</sup>,  $d_{\text{calc}} = 1.25$  g cm<sup>-3</sup>,  $\mu(\text{Cu K}\alpha) = 39.50$  cm<sup>-1</sup>,  $F(000) = 2088$ ,  $T = 293$  K,  $R = 0.083$  for 3022 observed reflections ( $I > 3\sigma(I)$ ),  $R_w = 0.103$  (weighted  $w = \sigma_F^{-2}$ ). The sample (irregularly shaped,  $0.55 \times 0.40 \times 0.35$  mm) was studied on an AFC6S-Rigaku automatic diffractometer, with graphite-monochromated Cu K $\alpha$  radiation. Absorption (empirically determined by psi-scan method) and deterioration correction were applied. The structure was solved by the Patterson method and refined by full-matrix, least-squares methods using the TEXSAN software system.

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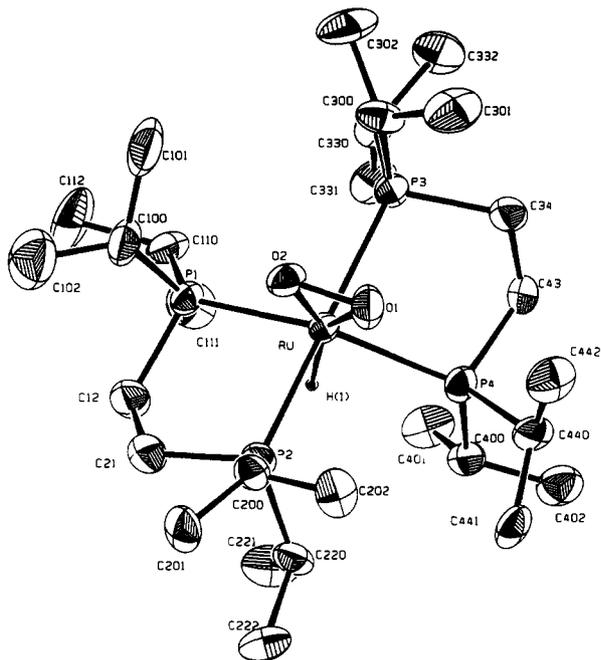
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(7) Satisfactory elemental analyses have been obtained for all the new compounds. The elemental analysis gave 0.0% for nitrogen in all the cases; this data is especially relevant for compound **4**.  $[\text{RuHCl}(\text{dippe})_2]$  was obtained by heating under reflux  $[\text{RuHCl}(\text{PPh}_3)_3]$  with 2 equiv of dippe in toluene. Selected spectral data for **1**: IR  $\nu(\text{RuH})$  1905 cm<sup>-1</sup>;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 298 K)  $\delta$  -21.61 (quintet,  $J(\text{H},\text{P}) = 19.3$  Hz, RuH);  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  71.82 (s). For **2**: IR  $\nu(\text{RuH})$  2188 cm<sup>-1</sup>;  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K)  $\delta$  -32.01 (quintet,  $J(\text{H},\text{P}) = 19.2$  Hz, RuH);  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  78.90 (s); no changes were observed at 228 K apart from broadening of the signal on the  $^{31}\text{P}\{^1\text{H}\}$  spectrum. For **3**:  $^1\text{H}$  NMR (acetone- $d_6$ , 228 K)  $\delta$  -11.06 (quintet,  $J(\text{H},\text{P}) = 18.3$  Hz,  $T_1 = 160$  ms, 300 MHz, RuH( $\text{H}_2$ )), -6.28 (s, br,  $T_1 = 10$  ms, 300 MHz, RuH( $\text{H}_2$ ));  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  82.8 (s). For **4**: no bands attributable to  $\nu(\text{RuH})$  or dioxygen were observed;  $^1\text{H}$  NMR (acetone- $d_6$ , 298 K)  $\delta$  -5.91 (quintet,  $J(\text{H},\text{P}) = 21.4$  Hz, RuH);  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  71.5 (s, br).  $^1\text{H}$  NMR (acetone- $d_6$ , 228 K)  $\delta$  -6.16 (triplet of triplets,  $J(\text{H},\text{P}) = 31$  Hz,  $J(\text{HP}') = 11$  Hz, RuH);  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta$  73.9 (triplet), 61.63 (triplet,  $^2J_{\text{PP}} = 14.6$  Hz). References:  $^1\text{H}$  NMR, SiMe<sub>4</sub>;  $^{31}\text{P}\{^1\text{H}\}$  NMR, H<sub>3</sub>PO<sub>4</sub>, 85%.

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**Figure 1.** Molecular structure of the cation  $[\text{RuH}(\text{O}_2)(\text{dippe})_2]^+$ . Hydrogen atoms, except hydride, are omitted. Selected bond distances (Å) and angles (deg): Ru–P1 2.381(4), Ru–P2 2.406(5), Ru–P3 2.445(5), Ru–P4 2.419(4), Ru–O1 2.040(10), Ru–O2 2.000(10), Ru–H(1), 1.53, O–O 1.360(10), P1–Ru–P4 141.9(2), P2–Ru–P3 172.6(2), O1–Ru–O2 39.4(4).

The bulky phosphine  $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2$  (dcpe; Cy = cyclohexyl) is known to exhibit a behavior similar to that of dippe, and it has analogous electron-donating capabilities. Accordingly, monohydride<sup>14</sup> and hydridodihydrogen<sup>1</sup> complexes like **2** and **3** are known. However, the reported chemical shift of  $-5.8$  ppm for the hydride signal of the monohydride  $[\text{RuH}(\text{dcpe})_2]^+$ <sup>14</sup> seems

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to be more consistent with a six-coordinate, 18-electron structure than with a coordinatively unsaturated, five-coordinate species, in which the hydride signal usually appears at much higher field. Furthermore, the splitting pattern of this hydride signal changes from a quintet at 310 K to a triplet of triplets at 213 K, as happens in our hydridodioxo complex **4**. Therefore, the reported NMR parameters for  $[\text{RuH}(\text{dcpe})_2]^+$  may rather correspond to  $[\text{RuH}(\text{O}_2)(\text{dcpe})_2]^+$ . We have recorded the  $^1\text{H}$  NMR spectra of  $[\text{RuHCl}(\text{dcpe})_2]$  in  $\text{CD}_3\text{OD}$  under dinitrogen, both with careful exclusion of  $\text{O}_2$  and upon exposure to air. In the absence of dioxygen, only a quintet at  $-32.2$  ppm,  $J(\text{H},\text{P}) = 19.3$  Hz attributable to the hydridic proton in  $[\text{RuH}(\text{dcpe})_2]^+$  can be observed in the hydride region. Interestingly enough, this resonance disappears upon exposure to air, and a new quintet at  $-5.85$ ,  $J(\text{H},\text{P}) = 21.3$  Hz, coincident with the reported data, is observed. The latter signal can be assigned to the hydride proton in  $[\text{RuH}(\text{O}_2)(\text{dcpe})_2]^+$ . Therefore, it seems that  $[\text{RuH}(\text{dcpe})_2]^+$  and  $[\text{RuH}(\text{dippe})_2]^+$  have similar affinity by  $\text{O}_2$ , and this would explain the presence of signals due to  $[\text{RuH}(\text{O}_2)(\text{dcpe})_2]^+$  in the NMR spectrum, unless extreme care had been taken in excluding  $\text{O}_2$ . The obvious difficulties in detecting an unexpected  $\eta^2\text{-O}_2$  ligand by the usual spectral means of characterization would explain the previous incorrect identification of this product. From our study, it can be concluded that the bulk of the auxiliary ligands plays an important role in the stabilization of dioxygen coordination at metal centers capable of dihydrogen-binding.

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**Supplementary Material Available:** Tables of X-ray crystallographic data, including atomic coordinates, interatomic distances and angles, and anisotropic thermal parameters (11 pages); listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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