

# Dioxygen Complexes from the Reactions of $[\text{Cp}^*\text{RuH}_2(\text{PP})]^+$ ( $\text{PP} = \text{dppm}, \text{dppe}$ ) with Air

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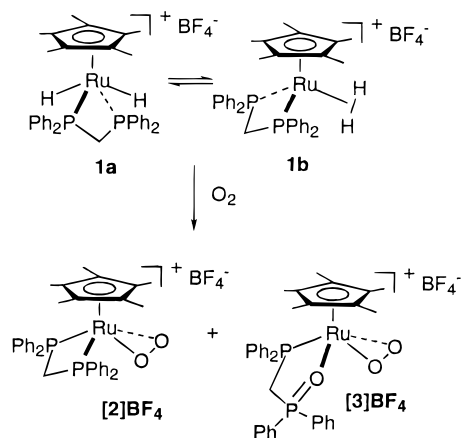
Received April 29, 1999

Exposure of  $[\text{Cp}^*\text{RuH}_2(\text{dppm})]\text{BF}_4$  in acetone or methanol to air produced a mixture of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BF}_4$  and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BF}_4$ . Reaction of  $\text{Cp}^*\text{RuCl}(\text{dppm})$  with  $\text{NaBPh}_4$  in methanol in air produced the dioxygen complex  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BPh}_4$ , which has been characterized by X-ray diffraction. Reaction of  $\text{Cp}^*\text{RuCl}(\text{dppm})$  with  $\text{H}_2\text{O}_2$  in the presence of  $\text{NaBPh}_4$  in air produced  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BPh}_4$  and  $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{PPh}_2$ . Reaction of  $[\text{Cp}^*\text{RuH}_2(\text{dppe})]\text{BF}_4$  in acetone or methanol with air also produced a mixture of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppe})]\text{BF}_4$  and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BF}_4$ .

## Introduction

Reactions of  $\text{L}_n\text{M}(\text{H}_2)$  (e.g.  $\text{OsHCl}(\text{H}_2)(\text{CO})(\text{P}(i\text{-Pr})_3)_2$ ,<sup>1</sup>  $[\text{OsH}(\text{H}_2)(\text{dppe})_2]^+$ ,<sup>2</sup>  $[\text{RuH}(\text{H}_2)(\text{dippe})_2]^+$  (dippe =  $(i\text{-Pr})_2\text{PCH}_2\text{CH}_2\text{P}(i\text{-Pr})_2$ )<sup>3</sup>) or  $\text{L}_n\text{MH}_2$  (e.g.  $\text{RuH}_2(\text{Ph}_2\text{PNMeNMePPh}_2)_2$ ,<sup>4a</sup>  $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ )<sup>4b</sup>) with oxygen usually lead to the displacement of the  $\text{H}_2$  molecule by  $\text{O}_2$  to give  $\text{L}_n\text{M}(\text{O}_2)$ . During the course of investigating the chemical properties of  $[\text{Cp}^*\text{RuH}_2(\text{dppm})]^+$ , we have found that reaction of  $[\text{Cp}^*\text{RuH}_2(\text{dppm})]^+$  with air produced a mixture of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]^+$  and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]^+$ . Similar results were also observed for the reaction of  $[\text{Cp}^*\text{RuH}_2(\text{dppe})]^+$  with air. While the formation of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{PP})]^+$  ( $\text{PP} = \text{dppm}, \text{dppe}$ ) from these reactions is probably not surprising, as several closely related dioxygen complexes  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{PR}_3)_2]^+$  have been reported,<sup>5–8</sup> production of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]^+$  and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]^+$  is rather unusual. In this paper, the characterization of the new dioxygen complexes and the possible mechanism for the interesting reactions will be presented.

## Scheme 1



## Results and Discussion

**Reaction of  $[\text{Cp}^*\text{RuH}_2(\text{dppm})]\text{BF}_4$  and  $\text{Cp}^*\text{RuCl}(\text{dppm})$  with Air.** The complex  $[\text{Cp}^*\text{RuH}_2(\text{dppm})]\text{BF}_4$  (1) is known to exist as a mixture of the dihydride form *trans*- $[\text{Cp}^*\text{RuH}_2(\text{dppm})]\text{BF}_4$  (1a) and the dihydrogen form  $[\text{Cp}^*\text{Ru}(\text{H}_2)(\text{dppm})]\text{BF}_4$  (1b) in a ratio of 1:2.<sup>9,10</sup> Exposure of acetone solutions of 1 to air produced a brown solution from which complexes  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BF}_4$  ([2]BF<sub>4</sub>) and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BF}_4$  ([3]BF<sub>4</sub>) can be isolated (Scheme 1). An in situ <sup>31</sup>P NMR spectrum of the reaction mixture showed that the major product of the reaction is [3]BF<sub>4</sub>. [3]BF<sub>4</sub> is not formed from further oxidation of [2]BF<sub>4</sub> by air, as the isolated complex [2]BF<sub>4</sub> did not react further with air to give [3]BF<sub>4</sub>. Similar results were obtained when pure oxygen gas instead of air was used.

[2]BF<sub>4</sub> and [3]BF<sub>4</sub> were also produced when methanol solutions of 1 were exposed to air. However, [2]BF<sub>4</sub>

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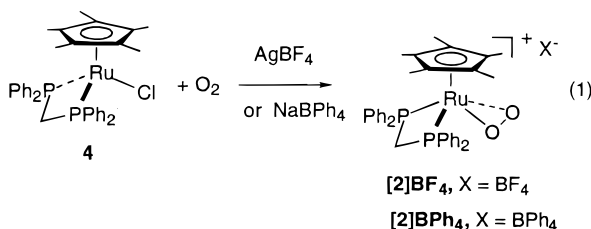
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was produced as the major product in this solvent (the relative ratio of **[2]BF<sub>4</sub>** to **[3]BF<sub>4</sub>** was 4.5:1, as indicated by an in situ <sup>31</sup>P NMR spectrum). Thus, the relative amounts of **[2]BF<sub>4</sub>** and **[3]BF<sub>4</sub>** from the oxidation reaction appear to be solvent-dependent.

**[2]BF<sub>4</sub>** could also be obtained cleanly by exposure of methanol solutions of **[Cp\*Ru(dppm)]BF<sub>4</sub>** (generated in situ from the reaction of AgBF<sub>4</sub> and Cp\*RuCl(dppm) (**4**)<sup>9</sup>) to air (eq 1). Similarly, stirring a methanol solution

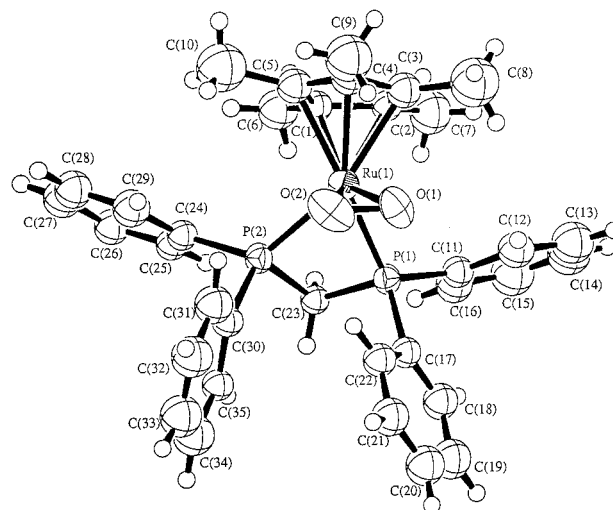


of Cp\*RuCl(dppm) in the presence of NaBPh<sub>4</sub> in air for 3 h produced **[Cp\*Ru(O<sub>2</sub>)(dppm)]BPh<sub>4</sub>** (**[2]BPh<sub>4</sub>**). Apparently O<sub>2</sub> from air was absorbed by **[Cp\*Ru(dppm)]<sup>+</sup>** to form **[2]BF<sub>4</sub>** or **[2]BPh<sub>4</sub>**. In principle, N<sub>2</sub> and H<sub>2</sub>O in air can also react with **[Cp\*Ru(dppm)]<sup>+</sup>** to form the known complexes **[Cp\*Ru(N<sub>2</sub>)(dppm)]<sup>+</sup>** and **[Cp\*Ru(H<sub>2</sub>O)(dppm)]<sup>+</sup>**.<sup>11</sup> However, such complexes were not detected in our experiments. The dioxygen ligand in **[2]BF<sub>4</sub>** or **[2]BPh<sub>4</sub>** is bound so tightly that it could not be displaced by N<sub>2</sub> or H<sub>2</sub>.

Complex **2** was characterized by elemental analysis, IR, MS, and <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy. In particular, the FAB-MS (NBA matrix) of **[2]BF<sub>4</sub>** displayed peaks at *m/z* 653 assignable to **[Cp\*Ru(O<sub>2</sub>)(dppm)]<sup>+</sup>** and at *m/z* 621 assignable to **[Cp\*Ru(dppm)]<sup>+</sup>**. In the IR spectrum of **[2]BF<sub>4</sub>**, a weak band assignable to ν<sub>O-O</sub> was observed at 924 cm<sup>-1</sup>, which is absent in the IR spectrum of Cp\*RuCl(dppm), Cp\*RuH(dppm), and **[Cp\*RuH<sub>2</sub>(dppm)]BF<sub>4</sub>**. Similarly, a weak band at 928 cm<sup>-1</sup> assignable to ν<sub>O-O</sub> was observed for **[2]BPh<sub>4</sub>**. The ν<sub>O-O</sub> values are within the range reported for L<sub>n</sub>M(O<sub>2</sub>) complexes.<sup>12</sup> The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR data are fully consistent with the structural assignment. The structure has been confirmed by an X-ray diffraction study on **[2]BPh<sub>4</sub>** (see below).

Formation of **[Cp\*Ru(O<sub>2</sub>)(dppm)]<sup>+</sup>** provides an additional example of metal fragments that can form both dihydrogen and dioxygen complexes. Reported examples of such metal fragments include OsHCl(CO)(P(*i*-Pr)<sub>3</sub>)<sub>2</sub>,<sup>1</sup> [OsH(dppe)<sub>2</sub>]<sup>+</sup>,<sup>2</sup> [RuH(dippe)<sub>2</sub>]<sup>+</sup>,<sup>3</sup> [RuH(dcpe)<sub>2</sub>]<sup>+</sup>,<sup>3</sup> and [OsCl(dcpe)<sub>2</sub>]<sup>+</sup>.<sup>13</sup>

Complex **[3]BF<sub>4</sub>** was characterized by elemental analysis, IR, MS, <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopy. In particular, the FAB-MS of **[3]BF<sub>4</sub>** displayed peaks at *m/z* 669 corresponding to **[Cp\*Ru(O<sub>2</sub>)(Ph<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub>)]<sup>+</sup>** and at *m/z* 637 corresponding to **[Cp\*Ru(Ph<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub>)]<sup>+</sup>**. The IR spectrum displayed bands at 928 cm<sup>-1</sup> assignable to ν<sub>O-O</sub> and at 1124 cm<sup>-1</sup> assignable to ν<sub>P=O</sub>. For comparison, the IR bands for coordinated P=O were observed at 1127 cm<sup>-1</sup> for **[Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(η<sup>2</sup>-Ph<sub>2</sub>PCH<sub>2</sub>-**



**Figure 1.** Molecular structure of the cation **[Cp\*Ru(O<sub>2</sub>)(dppm)]<sup>+</sup>**.

CH<sub>2</sub>P(O)Ph<sub>2</sub>)]SbF<sub>6</sub><sup>14a</sup> and at 1120 and 1130 cm<sup>-1</sup> for **[Pd(Ph<sub>2</sub>PCH<sub>2</sub>P(O)Ph<sub>2</sub>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>**.<sup>14b</sup> The presence of chelating Ph<sub>2</sub>PCH<sub>2</sub>P(O)PPh<sub>2</sub> in **[3]BF<sub>4</sub>** is further supported by its <sup>1</sup>H and <sup>31</sup>P NMR data. The <sup>1</sup>H NMR (in acetone-*d*<sub>6</sub>) showed two sets of methylene proton signals at 4.20 and 4.51 ppm, and a Cp\* signal at 1.66 ppm which couples to only one of the phosphorus atoms. The <sup>31</sup>P NMR (in acetone-*d*<sub>6</sub>) showed two doublets at 39.7 and 67.5 ppm assignable to P(O)Ph<sub>2</sub> and PPh<sub>2</sub>. The <sup>31</sup>P chemical shifts are significantly downfield compared to those observed for typical Cp\*Ru(η<sup>2</sup>-dppm) complexes such as Cp\*RuH(dppm) (17.5 ppm),<sup>9a</sup> **[Cp\*RuH<sub>2</sub>(dppm)]BF<sub>4</sub>** (23.4 ppm),<sup>9</sup> and **[Cp\*Ru(L)(dppm)]BF<sub>4</sub>** (L = H<sub>2</sub>, 4.9 ppm;<sup>9a</sup> CH<sub>3</sub>CN, 10.48 ppm;<sup>11</sup> H<sub>2</sub>O, 11.2 ppm;<sup>11</sup> N<sub>2</sub>, 3.45 ppm<sup>11</sup>) but are consistent with the presence of the five-membered chelating ring<sup>15</sup> in **[3]BF<sub>4</sub>**. Ligands of the type PPh<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>P(O)Ph<sub>2</sub> (*n* = 1–3) have been previously synthesized and used for transition-metal complexation.<sup>14,16</sup>

**Description of the Structure of [Cp\*Ru(O<sub>2</sub>)(dppm)]BPh<sub>4</sub>.** The structure of **[Cp\*Ru(O<sub>2</sub>)(dppm)]<sup>+</sup>** has been confirmed by an X-ray diffraction study on **[Cp\*Ru(O<sub>2</sub>)(dppm)]BPh<sub>4</sub>**. The view of the cationic complex **[Cp\*Ru(O<sub>2</sub>)(dppm)]<sup>+</sup>** is shown in Figure 1. The crystallographic details and selected bond distances and angles are given in Tables 1 and 2, respectively.

The structure can be described as a three-legged piano stool with the O<sub>2</sub> and the two PPh<sub>2</sub> groups as the legs. The overall geometry of the complex is very similar to that observed for the three-legged piano-stool dihydrogen complex **[Cp\*Ru(H<sub>2</sub>)(dppm)]BF<sub>4</sub>**.<sup>10</sup> For example, in both cases, the X<sub>2</sub> ligands are oriented in such a fashion to maximize the dπ(Ru)–σ\*(H<sub>2</sub>) and dπ(Ru)–π\*(O<sub>2</sub>) bonding;<sup>17</sup> the O(1)–Ru–O(2) angle (39.9(4)°) in **[3]BPh<sub>4</sub>** is close to the H–Ru–H angle (38(1)°) in **[Cp\*Ru(H<sub>2</sub>)(dppm)]BF<sub>4</sub>**.<sup>10</sup>

The two PPh<sub>2</sub> groups are bonded to ruthenium with slightly different Ru–P bond distances (Ru–P(1) =

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**Table 1. Crystallographic Details for  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BPh}_4$** 

formula	$\text{C}_{59}\text{H}_{57}\text{BO}_2\text{Ru}$
fw	971.93
color, habit	red, block
cryst dimens (mm)	$0.23 \times 0.24 \times 0.27$
cryst syst	orthorhombic
space group	<i>Pbca</i> (No. 61)
<i>a</i> , Å	16.628(1)
<i>b</i> , Å	19.607(2)
<i>c</i> , Å	30.763(3)
<i>V</i> , Å <sup>3</sup>	10029(1)
<i>Z</i>	8
<i>d</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.287
<i>T</i> (°C)	23.0
<i>F</i> <sub>000</sub>	4048.00
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	4.18
max $2\theta$ , deg	45.0
scan type	$\omega$ - $2\theta$
scan rate, deg min <sup>-1</sup>	16.0 (in $\omega$ ) (up to 4 scans)
scan width, deg	$0.60 + 0.35 \tan \theta$
no. of rflns measd	7205
no. of observns ( $I > 1.5\sigma(I)$ )	2544
no. of variables	286
<i>R</i> , <i>R</i> <sub>w</sub>	0.067, 0.055
GOF	1.75
final max, min $\Delta\rho$ , e Å <sup>-3</sup>	+1.11, -0.47

**Table 2. Selected Bond Distances (Å) and Angles (deg) for  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BPh}_4$** 

O(1)–O(2)	1.37(1)	Ru–O(1)	2.003(9)	Ru–O(2)	2.002(9)
Ru–P(1)	2.345(4)	Ru–P(2)	2.382(4)	Ru–C(1)	2.27(1)
Ru–C(2)	2.30(1)	Ru–C(3)	2.24(1)	Ru–C(4)	2.24(1)
Ru–C(5)	2.22t	C(1)–C(2)	1.43(2)	C(1)–C(5)	1.46(2)
C(2)–C(3)	1.39(2)	C(3)–C(4)	1.39(2)	C(4)–C(5)	1.37(2)
P(1)–Ru–P(2)	67.5(1)	P(1)–Ru–O(1)	86.7(3)		
P(1)–Ru–O(2)	103.6(3)	P(1)–Ru–C(1)	112.0(4)		
P(1)–Ru–C(2)	98.8(3)	P(1)–Ru–C(3)	117.1(4)		
P(1)–Ru–C(4)	153.1(4)	P(1)–Ru–C(5)	149.6(4)		
P(2)–Ru–O(1)	119.9(3)	P(2)–Ru–O(2)	93.3(3)		
P(2)–Ru–C(1)	92.4(4)	P(2)–Ru–C(2)	119.5(3)		
P(2)–Ru–C(3)	152.9(4)	P(2)–Ru–C(4)	135.9(4)		
P(2)–Ru–C(5)	102.1(4)	O(1)–Ru–O(2)	39.9(4)		

2.345(4) Å; Ru–P(2) = 2.382(4) Å. The Ru–P bond distances are longer than those observed for the related ruthenium complexes  $[\text{CpRu}(\eta^2\text{-dppm})(\eta^1\text{-dppm})]\text{PF}_6$  (2.295(3), 2.325(3), 2.323(2) Å)<sup>18</sup> and  $[\text{Cp}^*\text{Ru}(\text{H}_2)(\text{dppm})]\text{BF}_4$  (2.297(8), 2.314(9) Å).<sup>10</sup> The P(1)–Ru–P(2) angle (67.5(1)°) is slightly smaller than the corresponding angles reported for other chelating dppm in complexes such as  $[\text{CpRu}(\eta^2\text{-dppm})(\eta^1\text{-dppm})]\text{PF}_6$  (70.0(1)°),<sup>18</sup>  $[\text{Cp}^*\text{Ru}(\text{H}_2)(\eta^2\text{-dppm})]\text{BF}_4$  (71.4(3)°),<sup>10</sup> and  $\text{CpFePh}(\text{dppm})$  (73.8(0)°).<sup>19</sup> The Ru–C distances are in the range 2.22(1)–2.30(1) Å, which are very similar to those reported for related Cp\* ruthenium complexes, for example,  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dippe})]^+$ ,<sup>5</sup>  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dippe})]^+$ ,<sup>6</sup> and  $[\text{Cp}^*\text{Ru}(\text{H}_2)(\text{dppm})]^+$ .<sup>10</sup>

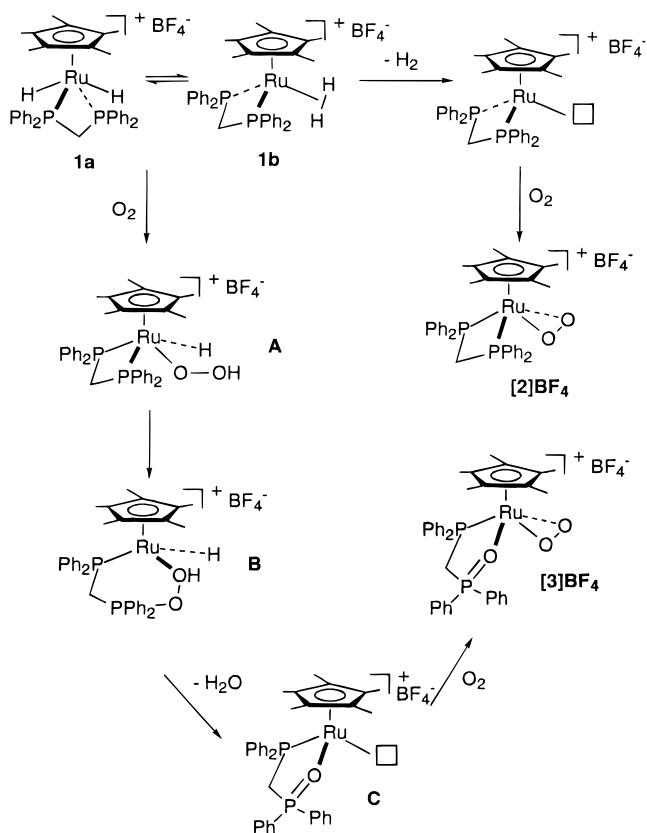
The dioxygen is symmetrically bound to ruthenium with O(1)–O(2) = 1.37(1) Å, Ru–O(1) = 2.003(9) Å, and Ru–O(2) = 2.002(9) Å. The O–O distance is longer than that in the superoxide KO<sub>2</sub> (1.28 Å)<sup>20</sup> and shorter than that in H<sub>2</sub>O<sub>2</sub> (1.46 Å).<sup>21</sup> The Ru–O bond distances and O(1)–Ru–O(2) angle are similar to those reported for other ruthenium dioxygen complexes such as  $[\text{RuH}(\text{O}_2)\text{-}$

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**Scheme 2**

(dippe)<sub>2</sub>BF<sub>4</sub><sup>3</sup> and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{PR}_3)_2]^+$  ((PR<sub>3</sub>)<sub>2</sub> = dppe,<sup>5</sup> dippe,<sup>6</sup> (P–O)<sub>2</sub> (P–O = (1,3-dioxan-2-ylmethyl)diphenylphosphine,<sup>7</sup> and dppf<sup>8</sup>)). The O–O distance in **[2]BF<sub>4</sub>** (1.37(1) Å) is comparable to those of  $[\text{RuH}(\text{O}_2)(\text{dippe})_2]\text{BPh}_4$  (1.360(10) Å),<sup>3</sup>  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dippe})]\text{BF}_4$  (1.398(5) Å),<sup>5</sup>  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppf})]\text{BF}_4$  (1.381(11) Å),<sup>8</sup> and  $[\text{Cp}^*\text{Ru}(\text{O}_2)\text{-}(\text{P}(\text{O})_2)\text{BPh}_4$  (1.394(9) Å)<sup>7</sup> but is shorter than those of  $[\text{OsCl}(\text{O}_2)(\text{dcpe})_2]\text{BPh}_4$  (1.45(1) Å)<sup>13</sup> and  $[\text{OsH}(\text{O}_2)\text{-}(\text{dppe})_2]^+$  (1.430(5) Å).<sup>2</sup>

**Mechanism for the Formation of [2]BF<sub>4</sub> and [3]BF<sub>4</sub> from the Reaction of 1 with Air.** The complex **[2]BF<sub>4</sub>** is presumably formed by displacement of the H<sub>2</sub> ligand in **1** with O<sub>2</sub>. Similar reactivity has been observed for complexes such as  $\text{OsHCl}(\text{H}_2)(\text{CO})(\text{P}(\text{i-Pr})_3)_2$ ,<sup>1</sup>  $[\text{RuH}(\text{H}_2)(\text{dppe})_2]^+$ ,<sup>2</sup>  $[\text{RuH}(\text{H}_2)(\text{dippe})_2]^+$ ,<sup>3</sup>  $\text{RuH}_2\text{-}(\text{Ph}_2\text{PNMeNMePPh}_2)_2$ ,<sup>4a</sup> and  $\text{RuH}_2(\text{CO})_2(\text{PPh}_3)_2$ .<sup>4b</sup> However, production of **[3]BF<sub>4</sub>**, a Ph<sub>2</sub>P(O)CH<sub>2</sub>PPh<sub>2</sub>-containing complex, from the reaction of **1** with air is not straightforward. It has been reported that reaction of  $[\text{CpRu}(\text{N}_2)(\text{dippe})]\text{BPh}_4$  with O<sub>2</sub> produced the bis(phosphine oxide) (*i-Pr*)<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>P(O)(*i-Pr*)<sub>2</sub> along with  $\text{CpRu}(\eta^6\text{-C}_6\text{H}_5\text{BPh}_3)$ .<sup>6b</sup> No intermediate could be observed in the reaction. It was suggested that (*i-Pr*)<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>P(O)(*i-Pr*)<sub>2</sub> is probably formed through the intermediate  $[\text{CpRu}(\text{O}_2)(\text{i-Pr})_2\text{PCH}_2\text{CH}_2\text{P}(\text{i-Pr})_2]^+$ . In the case of reaction of  $[\text{Cp}^*\text{RuH}_2(\text{dppm})]^+$  with air, the major products are  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]^+$  and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]^+$ . We have shown experimentally that  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]^+$  is unlikely to be the intermediate for the formation of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]^+$ .

A plausible mechanism for the formation of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]^+$  is shown in Scheme 2, which involves the peroxide intermediate (A) formed by reac-

tion of **1** with O<sub>2</sub>. Intramolecular oxygen transfer from the hydroperoxo ligand to one of the coordinated phosphorus atoms would give the peroxophosphine complex **B**. Subsequent elimination of H<sub>2</sub>O would give the coordinatively unsaturated complex [Cp\*Ru(Ph<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub>)]<sup>+</sup> (**C**), which picks up a O<sub>2</sub> molecule to give [Cp\*Ru(O<sub>2</sub>)(Ph<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub>)]<sup>+</sup>.

Oxidation of phosphines by hydroperoxides to give phosphine oxides is one of the typical reactions of phosphines.<sup>24</sup> Hydroperoxide ion has been shown to be involved in the oxidation of phosphines by oxygen catalyzed by Pt(PPh<sub>3</sub>)<sub>2</sub>(O<sub>2</sub>).<sup>25</sup> Intramolecular O-transfer from peroxy groups to coordinated phosphines to generate phosphine oxides has been reported for complexes such as RhCl(OOH)(acac)(PPh<sub>3</sub>)<sub>2</sub><sup>26</sup> and RhCl(O<sub>4</sub>C)(PEt<sub>2</sub>-Ph)<sub>3</sub>.<sup>27</sup> Formation of peroxide complexes from the reactions of metal alkyls<sup>28</sup> or hydrides<sup>29</sup> with O<sub>2</sub> and production of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> catalyzed by transition-metal complexes has been reported.<sup>30</sup> In support of the involvement of the hydroperoxo intermediate in the formation of **[3]BF<sub>4</sub>**, it was demonstrated that reaction of Cp\*RuCl(dppm) with H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> in the presence of NaBPh<sub>4</sub> produced a mixture of **[3]BPh<sub>4</sub>** and dppm oxide (major), whereas the same reaction in the absence of hydrogen peroxide only gave **[2]BPh<sub>4</sub>**. Reaction of **[2]BPh<sub>4</sub>** in acetone-*d*<sub>6</sub> with H<sub>2</sub>O<sub>2</sub> produced slowly an uncharacterized insoluble black precipitate. The solution only showed <sup>31</sup>P signals assignable to **[2]BPh<sub>4</sub>** and Ph<sub>2</sub>P(O)CH<sub>2</sub>P(O)Ph<sub>2</sub>. This observation again implies that the dioxygen complex **[2]BPh<sub>4</sub>** is not the intermediate for the formation of [Cp\*Ru(O<sub>2</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>P(O)Ph<sub>2</sub>)]<sup>+</sup>.

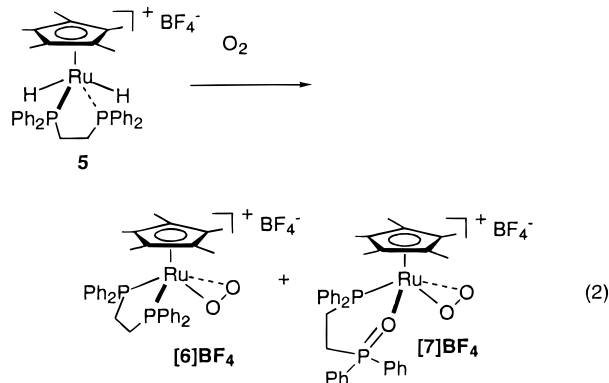
In the proposed mechanism for the formation of **[3]BF<sub>4</sub>**, water is suggested as the side product. To confirm the formation of water in the reaction, we have studied the reaction of air with [Cp\*RuD<sub>2</sub>(dppm)]<sup>+</sup>, which was prepared by reaction of [Cp\*Ru(dppm)]<sup>+</sup> with D<sub>2</sub> gas. Indeed, the <sup>2</sup>D NMR spectra of methanol or acetone solutions of [Cp\*RuD<sub>2</sub>(dppm)]<sup>+</sup> after exposure to air showed signals assignable to D<sub>2</sub>O.

It is not very clear to us why more **[3]BF<sub>4</sub>** relative to **[2]BF<sub>4</sub>** was produced in acetone but more **[2]BF<sub>4</sub>** relative to **[3]BF<sub>4</sub>** was produced in methanol. Possibly, methanol helped to dissociate the H<sub>2</sub> molecule to give the intermediate [Cp\*Ru(dppm)]<sup>+</sup> or [Cp\*Ru(dppm)(MeOH)]<sup>+</sup>, which facilitates the formation of **[2]BF<sub>4</sub>**.

**Reaction of [Cp\*RuH<sub>2</sub>(dppe)]BF<sub>4</sub> with Air.** Formation of [Cp\*Ru(O<sub>2</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>P(O)Ph<sub>2</sub>)]<sup>+</sup> (or the per-

oxide intermediate) from the reaction of [Cp\*RuH<sub>2</sub>(dppm)]<sup>+</sup> with oxygen must be related to the reactivity of O<sub>2</sub> toward the RuH<sub>2</sub> or/and Ru(H<sub>2</sub>) functionality. Unfortunately, the effect of RuH<sub>2</sub> and Ru(H<sub>2</sub>) functionalities in the reaction of [Cp\*RuH<sub>2</sub>(dppm)]<sup>+</sup> with air is not clear because the hydride complex exists as a mixture of the dihydrogen form [Cp\*Ru(H<sub>2</sub>(dppm)]BF<sub>4</sub> and the dihydride form *trans*-[Cp\*RuH<sub>2</sub>(dppm)]BF<sub>4</sub>. To see the effect of RuH<sub>2</sub> and Ru(H<sub>2</sub>) functionalities, we have investigated the reaction of air with [Cp\*RuH<sub>2</sub>(dppe)]BF<sub>4</sub> (**5**), which adopts the dihydride form only.<sup>5</sup>

Exposure of acetone or methanol solutions of **5** to air also produced [Cp\*Ru(O<sub>2</sub>)(dppe)]BF<sub>4</sub> (**[6]BF<sub>4</sub>**) and [Cp\*Ru(O<sub>2</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>P(O)Ph<sub>2</sub>)]BF<sub>4</sub> (**[7]BF<sub>4</sub>**) (eq 2).



The reaction is slower than that of the dppm analogue. Thus, [Cp\*RuH<sub>2</sub>(dppe)]BF<sub>4</sub> is still observable by NMR after an acetone solution of **5** was exposed to air for 4 h. Like the dppm analogue, the relative amounts of **[6]BF<sub>4</sub>** and **[7]BF<sub>4</sub>** are solvent-dependent. In acetone, about equal amounts of **[6]BF<sub>4</sub>** and **[7]BF<sub>4</sub>** were produced; in methanol, the dioxygen complex **[6]BF<sub>4</sub>** is the major product.

The dioxygen complex [Cp\*Ru(O<sub>2</sub>)(dppe)]<sup>+</sup> has been reported previously and can be prepared easily from the reaction of [Cp\*Ru(dppe)]<sup>+</sup> with oxygen.<sup>5</sup> The dioxygen complex [Cp\*Ru(O<sub>2</sub>)(dppe)]<sup>+</sup> formed in the oxidation experiments could be easily identified by comparing the NMR data to those of authentic samples prepared from the reaction of [Cp\*Ru(dppe)]BF<sub>4</sub> with oxygen.<sup>5</sup> Unfortunately, we have not been able to obtain pure samples of **[7]BF<sub>4</sub>** by either recrystallization or column chromatography. Samples of **[7]BF<sub>4</sub>** obtained were contaminated with the dioxygen complex **[6]BF<sub>4</sub>**. The identity of [Cp\*Ru(O<sub>2</sub>)(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub>)]<sup>+</sup>, however, is clearly indicated by the NMR, IR, and MS data. In particular, the FAB-MS of the isolated product displayed clusters of peaks at *m/z* 683 corresponding to [Cp\*Ru(O<sub>2</sub>)(Ph<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub>)]<sup>+</sup> and at *m/z* 651 corresponding to [Cp\*Ru(Ph<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub>)]<sup>+</sup>. The IR spectrum displayed bands at 852 cm<sup>-1</sup> assignable to ν<sub>O-O</sub> and at 1056 cm<sup>-1</sup> assignable to ν<sub>P=O</sub>. The presence of chelating Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(O)PPh<sub>2</sub> in **[7]BF<sub>4</sub>** is further supported by its <sup>13</sup>C and <sup>31</sup>P NMR data. The <sup>13</sup>C NMR (in CD<sub>2</sub>Cl<sub>2</sub>) showed methylene signals at 18.7 and 22.4 ppm and a Cp\* signal at 8.2 ppm. Consistent with the proposed structure, the <sup>31</sup>P NMR (in CD<sub>2</sub>Cl<sub>2</sub>) showed two doublets at 50.7 and 32.8 ppm assignable to PPh<sub>2</sub> and P(O)Ph<sub>2</sub>, respectively.

The fact that [Cp\*RuH<sub>2</sub>(dppe)]BF<sub>4</sub> (**5**), which adopts the dihydride form only, can also react with air to give

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$[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]^+$  may suggest that formation of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2(\text{CH}_2)_n\text{P}(\text{O})\text{Ph}_2)]^+$  is related to the  $\text{RuH}_2$  functionality. However, the involvement of the  $\text{Ru}(\text{H}_2)$  functionality cannot be excluded completely, because of the possibility of equilibrium between the  $\text{Ru}(\text{H}_2)$  and  $\text{RuH}_2$  tautomers.<sup>9</sup>

**Summary.** The reaction of  $[\text{Cp}^*\text{RuH}_2(\text{dppm})]^+ / [\text{Cp}^*\text{Ru}(\text{H}_2)(\text{dppm})]^+$  in acetone or methanol with air produced a mixture of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BF}_4$  and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BF}_4$ . Similarly, the reaction of  $[\text{Cp}^*\text{RuH}_2(\text{dppe})]^+$  in acetone or methanol with air also produced  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppe})]\text{BF}_4$  and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BF}_4$ . These reactions appear to be solvent-dependent. Acetone favors the formation of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{P}(\text{CH}_2)_x\text{P}(\text{O})\text{Ph}_2)]^+$  ( $x = 1, 2$ ); methanol favors the formation of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{P}(\text{CH}_2)_x\text{PPh}_2)]^+$  ( $x = 1, 2$ ).  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{P}(\text{CH}_2)_x\text{P}(\text{O})\text{Ph}_2)]^+$  species are likely produced from hydroperoxo intermediates formed by reaction of  $\text{O}_2$  with the hydride complexes.

## Experimental Section

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Solvents were distilled under nitrogen from sodium-benzophenone (hexane, ether, benzene) or calcium hydride ( $\text{CH}_2\text{Cl}_2$ ). Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ).  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were collected on a JEOL EX-400 spectrometer or a Bruker ARX-300 spectrometer.  $^1\text{H}$  NMR chemical shifts are reported relative to TMS and  $^{31}\text{P}$  NMR chemical shifts relative to 85%  $\text{H}_3\text{PO}_4$ . IR spectra were collected on a Perkin-Elmer 1600 spectrometer.  $\text{Cp}^*\text{RuCl}(\text{dppm})$ ,<sup>9</sup>  $\text{Cp}^*\text{RuH}(\text{dppm})$ ,<sup>9</sup>  $[\text{Cp}^*\text{RuH}_2(\text{dppm})]\text{BF}_4$ ,<sup>9</sup>  $\text{Cp}^*\text{RuCl}(\text{dppe})$ ,<sup>5</sup>  $[\text{Cp}^*\text{RuH}_2(\text{dppe})]\text{BF}_4$ ,<sup>5</sup> and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppe})]\text{BF}_4$ <sup>5</sup> were prepared according to literature methods. All other reagents were used as purchased from Aldrich.

**$[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BPh}_4$  (**[2]BF<sub>4</sub>**).** A mixture of  $\text{Cp}^*\text{RuCl}(\text{dppm})$  (0.10 g, 0.15 mmol) and  $\text{NaBPh}_4$  (0.080 g, 0.23 mmol) in 10 mL of methanol was stirred under air for 3 h to give a light brown solid. The solid was collected by filtration, washed with methanol (5 mL) and ether (10 mL), and then dried under vacuum. Yield: 0.089 g, 60%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{O}-\text{O}}$  928 (w).  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  1.63 (t,  $J(\text{PH}) = 1.4$  Hz, 15 H,  $\text{C}_5(\text{CH}_3)_5$ ), 4.91 (dt,  $J(\text{PH}) = 11.2$  Hz,  $J(\text{HH}) = 15.1$  Hz, 1 H,  $\text{CH}_2$ ), 5.20 (dt,  $J(\text{PH}) = 12.3$  Hz,  $J(\text{HH}) = 15.1$  Hz, 1 H,  $\text{CH}_2$ ), 6.9–7.9 (m, 40 H, Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR (acetone- $d_6$ ):  $\delta$  -11.0 (s). Anal. Calcd for  $\text{C}_{55}\text{H}_{57}\text{BO}_2\text{P}_2\text{Ru}$ : C, 72.91; H, 5.91. Found: C, 72.46; H, 5.86.

**$[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BF}_4$  (**[2]BF<sub>4</sub>**).** A mixture of  $\text{Cp}^*\text{RuCl}(\text{dppm})$  (0.10 g, 0.15 mmol) and  $\text{AgBF}_4$  (0.030 g, 0.15 mmol) in 10 mL of methanol was stirred under air for 3 h. The reaction mixture was filtered through a column of Celite. The filtrate was concentrated, and ether (10 mL) was added to give light brown crystals. The product was collected by filtration, washed with ether, and then dried under vacuum. Yield: 0.090 g, 81%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{O}-\text{O}}$  924 (w).  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  1.63 (t,  $J(\text{PH}) = 1.4$  Hz, 15 H,  $\text{C}_5(\text{CH}_3)_5$ ), 4.91 (dt,  $J(\text{PH}) = 11.2$  Hz,  $J(\text{HH}) = 15.1$  Hz, 1 H,  $\text{CH}_2$ ), 5.20 (dt,  $J(\text{PH}) = 12.3$  Hz,  $J(\text{HH}) = 15.1$  Hz, 1 H,  $\text{CH}_2$ ), 7.4–7.9 (m, 20 H, Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR (acetone- $d_6$ ): -11.0 (s).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.5 (s,  $\text{Cp}^*$ ), 37.2 (t,  $J(\text{PC}) = 28.1$  Hz,  $\text{CH}_2$ ), 108.0 (s,  $\text{Cp}^*$ ), 126.0–133.2 (m, Ph). Anal. Calcd for  $\text{C}_{35}\text{H}_{37}\text{BF}_4\text{O}_2\text{P}_2\text{Ru}$ : C, 56.85; H, 5.04. Found: C, 56.58; H, 5.02.

**Formation of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BF}_4$  (**[3]BF<sub>4</sub>**) and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BF}_4$  (**[2]BF<sub>4</sub>**) from the Reaction of  $[\text{Cp}^*\text{RuH}_2(\text{dppm})]\text{BF}_4$  with Air.** A 1.0 g (1.4 mmol) portion of  $[\text{Cp}^*\text{RuH}_2(\text{dppm})]\text{BF}_4$  dissolved in 100 mL of acetone was stirred under air for 20 min to give a brown solution. The solvent was removed under vacuum to give a

brown solid. The solid was collected by filtration and recrystallized using a minimum amount of acetone to give a reddish brown microcrystalline solid of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BF}_4$ . The product was collected by filtration, washed with ether, and dried under vacuum. Yield: 0.46 g, 43%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{P}=\text{O}}$  1124 (s),  $\nu_{\text{O}-\text{O}}$  928 (w).  $^1\text{H}$  NMR (acetone- $d_6$ ):  $\delta$  1.66 (d,  $J(\text{PH}) = 1.6$  Hz, 15 H,  $\text{C}_5(\text{CH}_3)_5$ ), 4.20 (ddd,  $J(\text{PH}) = 13.1$ , 11.0 Hz,  $J(\text{HH}) = 14.4$  Hz, 1 H,  $\text{CH}_2$ ), 4.51 (ddd,  $J(\text{PH}) = 13.2$ , 5.6 Hz,  $J(\text{HH}) = 14.4$  Hz, 1 H,  $\text{CH}_2$ ), 7.3–8.0 (m, 20 H, Ph).  $^{31}\text{P}\{^1\text{H}\}$  NMR (acetone- $d_6$ ):  $\delta$  39.7 (d,  $J(\text{PP}) = 25.7$  Hz), 67.5 (d,  $J(\text{PP}) = 25.7$  Hz).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.4 (s,  $\text{Cp}^*$ ), 30.6 (dd,  $J(\text{PC}) = 66.6$ , 16.4 Hz,  $\text{CH}_2$ ), 108.6 (s,  $\text{Cp}^*$ ), 128.0–134.4 (m, Ph). Anal. Calcd for  $\text{C}_{35}\text{H}_{37}\text{BF}_4\text{O}_3\text{P}_2\text{Ru}$ : C, 55.64; H, 4.94. Found: C, 55.86; H, 4.90. The filtrate from recrystallization of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BF}_4$  was passed through a silica gel column using  $\text{CH}_2\text{Cl}_2/\text{acetone}$  (3:1) as the eluent to give a brown solution. The eluted solution was concentrated, and ether was added to give brown crystals of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BF}_4$ . The product was collected by filtration, washed with ether, and dried under vacuum. Yield: 0.20 g, 19%. For comparative purposes, the  $^{31}\text{P}$  chemical shifts of  $\text{dppm}$ ,  $\text{dppmO}$ , and  $\text{dppmO}_2$  in acetone- $d_6$  were also collected:  $\text{dppm}$ ,  $\delta$  -23.5 (s);  $\text{dppmO}$ ,  $\delta$  -28.6 (d,  $J(\text{PP}) = 50.9$  Hz), 26.6 (d,  $J(\text{PP}) = 50.9$  Hz);  $\text{dppmO}_2$ ,  $\delta$  24.6 (s).

**Reaction of  $\text{Cp}^*\text{RuCl}(\text{dppm})$  with  $\text{H}_2\text{O}_2$ .** To an NMR tube (opened to air) containing  $\text{Cp}^*\text{RuCl}(\text{dppm})$  and  $\text{NaBPh}_4$  dissolved in acetone- $d_6$  (0.7 mL) was added ca. 0.10 mL of 30%  $\text{H}_2\text{O}_2$  in water. A  $^{31}\text{P}$  NMR spectrum was collected 5 min later. The  $^{31}\text{P}$  NMR showed signals assignable to  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BF}_4$  and  $\text{dppm}$  oxide.

**Confirmation of the Formation of  $\text{D}_2\text{O}$  from the Reaction of  $[\text{Cp}^*\text{RuD}_2(\text{dppm})]\text{BF}_4$  with Air.** A mixture of 20 mg (0.03 mmol) of  $\text{Cp}^*\text{RuCl}(\text{dppm})$  and 7 mg (0.03 mmol) of  $\text{AgBF}_4$  dissolved in 0.7 mL of acetone in an NMR tube was sonicated for 30 min. The reaction mixture was then subjected to 1 atm of  $\text{D}_2$  for 1 h to generate  $[\text{Cp}^*\text{RuD}_2(\text{dppm})]\text{BF}_4$  in situ, and then the mixture was exposed to air and left to stand overnight. A  $^2\text{D}$  NMR spectrum was collected.  $^2\text{D}$  NMR (acetone):  $\delta$  3.92 (s,  $\text{D}_2\text{O}$ ). Formation of  $\text{D}_2\text{O}$  in methanol can be confirmed similarly by the observation of the  $\text{D}_2\text{O}$  signal at 5.0 ppm.

**Formation of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppe})]\text{BF}_4$  (**[6]BF<sub>4</sub>**) and  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]\text{BF}_4$  (**[7]BF<sub>4</sub>**) from the Reaction of  $[\text{Cp}^*\text{RuH}_2(\text{dppe})]\text{BF}_4$  with Air.** A 0.52 g (0.70 mmol) portion of  $[\text{Cp}^*\text{RuH}_2(\text{dppe})]\text{BF}_4$  dissolved in 10 mL of acetone was exposed to air for 5 days to give a brown solution. The solvent was removed under vacuum to give a brown solid. The residue showed predominant signals due to **[6]BF<sub>4</sub>** and **[7]BF<sub>4</sub>**. Attempts to separate the two compounds by column chromatography and recrystallization were unsuccessful. **[6]BF<sub>4</sub>** could be obtained cleanly from the reaction of  $[\text{Cp}^*\text{Ru}(\text{dppe})]\text{BF}_4$  with air.<sup>5</sup> Selected characterization data for **[6]BF<sub>4</sub>**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  68.5 (s);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.57 (s, 15 H,  $\text{C}_5(\text{CH}_3)_5$ ), 2.67 (m, 4 H,  $\text{CH}_2$ ), 7.1–7.8 (m, 20 H, Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  9.0 (s,  $\text{Cp}^*$ ), 26.4 (t,  $J(\text{PC}) = 38.6$  Hz,  $\text{CH}_2$ ), 107.2 (s,  $\text{Cp}^*$ ), 128.7–133.2 (m, Ph). Selected characterization data for **[7]BF<sub>4</sub>**: IR (KBr,  $\text{cm}^{-1}$ )  $\nu_{\text{P}=\text{O}}$  1056 (s),  $\nu_{\text{O}-\text{O}}$  852 (w);  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  1.34 (d,  $J(\text{PH}) = 1.5$  Hz,  $\text{C}_5(\text{CH}_3)_5$ ), 1.80–3.36 (m,  $\text{CH}_2$ ), 6.95–7.73 (m, Ph);  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  32.8 (d,  $J(\text{PP}) = 15.3$  Hz), 50.7 (d,  $J(\text{PP}) = 15.3$  Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.2 (s,  $\text{Cp}^*$ ), 18.7, (dd,  $J(\text{PC}) = 26.8$ , 5.5 Hz,  $\text{CH}_2$ ), 22.4 (t,  $J(\text{PC}) = 34.0$  Hz), 107.3 (s,  $\text{Cp}^*$ ), 125.8–133.2 (m, Ph); FAB-MS  $m/e$  685 ( $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]^+$ ), 651 ( $[\text{Cp}^*\text{Ru}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)]^+$ ). For comparative purposes, the  $^{31}\text{P}$  chemical shift of  $\text{dppe}$ ,  $\text{dppeO}$ , and  $\text{dppeO}_2$  were collected in acetone- $d_6$ :  $\text{dppe}$ ,  $\delta$  -14.0 (s);  $\text{dppeO}$ ,  $\delta$  -13.6 (d,  $J(\text{PP}) = 47.9$  Hz), 29.6 (d,  $J(\text{PP}) = 47.9$  Hz);  $\text{dppeO}_2$ ,  $\delta$  30.1 (s).

**Crystallographic Analysis of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BPh}_4$ .** Suitable crystals for X-ray diffraction study were obtained by slow diffusion of  $\text{Et}_2\text{O}$  into an acetone solution of  $[\text{Cp}^*\text{Ru}(\text{O}_2)(\text{dppm})]\text{BPh}_4$  at room temperature. A weakly diffracting crystal

was mounted on a glass fiber by means of epoxy resin on an Enraf-Nonius diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for unit-cell determination and data collection. A summary of crystallographic data and structure, solution, and refinement details is given in Table 1. Lorentz-polarization and  $\psi$ -scan absorption correction<sup>31</sup> were applied to all intensity data. The structure was solved by direct methods (SIR88)<sup>32</sup> and subsequently difference Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis with Ru, P, and O atoms varied anisotropically. Hydrogen atoms

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were generated in their ideal positions ( $d(\text{C-H}) = 0.95 \text{ \AA}$ ). All calculations were performed on a Silicon Graphics computer using the program package TEXSAN.<sup>33</sup> Selected bond distances and angles are given in Table 2.

**Acknowledgment.** We acknowledge financial support from the Hong Kong Research Grants Council.

**Supporting Information Available:** Tables of all bond distances and angles, atomic coordinates and thermal parameters, and anisotropic displacement coefficients. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM990317B

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