Dioxygen Complexes from the Reactions of $[Cp*RuH_2(PP)]^+$ (PP = dppm, dppe) with Air

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Exposure of $[Cp*RuH_2(dppm)]BF_4$ in acetone or methanol to air produced a mixture of [Cp*Ru(O₂)(dppm)]BF₄ and [Cp*Ru(O₂)(Ph₂PCH₂P(O)Ph₂)]BF₄. Reaction of Cp*RuCl(dppm) with NaBPh₄ in methanol in air produced the dioxygen complex [Cp*Ru(O₂)(dppm)]BPh₄, which has been characterized by X-ray diffraction. Reaction of Cp*RuCl(dppm) with H₂O₂ in the presence of NaBPh₄ in air produced [Cp*Ru(O₂)(Ph₂PCH₂P(O)Ph₂)]BPh₄ and Ph₂P- $(O)CH_2P(O)PPh_2$. Reaction of $[Cp^*RuH_2(dppe)]BF_4$ in acetone or methanol with air also produced a mixture of $[Cp*Ru(O_2)(dppe)]BF_4$ and $[Cp*Ru(O_2)(Ph_2PCH_2CH_2P(O)Ph_2)]BF_4$.

Introduction

Reactions of $L_pM(H_2)$ (e.g. OsHCl(H₂)(CO)(P(*i*-Pr)₃)₂,¹ $[OsH(H_2)(dppe)_2]^+$,² $[RuH(H_2)(dippe)_2]^+$ (dippe = (*i*- $Pr)_2PCH_2CH_2P(i-Pr)_2)^3$) or L_nMH_2 (e.g. $RuH_2(Ph_2PN-$ MeNMePPh₂)₂,^{4a} RuH₂(CO)₂(PPh₃)₂^{4b}) with oxygen usually lead to the displacement of the H₂ molecule by O₂ to give $L_n M(O_2)$. During the course of investigating the chemical properties of $[Cp*RuH_2(dppm)]^+$, we have found that reaction of [Cp*RuH₂(dppm)]⁺ with air produced a mixture of [Cp*Ru(O₂)(dppm)]⁺ and [Cp*Ru- $(O_2)(Ph_2PCH_2P(O)Ph_2)]^+$. Similar results were also observed for the reaction of $[Cp*RuH_2(dppe)]^+$ with air. While the formation of $[Cp^*Ru(O_2)(PP)]^+$ (PP = dppm, dppe) from these reactions is probably not surprising, as several closely related dioxygen complexes [Cp*Ru- $(O_2)(PR_3)_2]^+$ have been reported, ⁵⁻⁸ production of $[Cp^*Ru-$ (O₂)(Ph₂PCH₂P(O)Ph₂)]⁺ and [Cp*Ru(O₂)(Ph₂PCH₂CH₂P- $(O)Ph_2$ ⁺ is rather unusual. In this paper, the characterization of the new dioxygen complexes and the possible mechanism for the interesting reactions will be presented.

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Results and Discussion

Reaction of [Cp*RuH₂(dppm)]BF₄ and Cp*RuCl-(**dppm**) with Air. The complex [Cp*RuH₂(dppm)]BF₄ (1) is known to exist as a mixture of the dihydride form trans- $[Cp*RuH_2(dppm)]BF_4$ (1a) and the dihydrogen form $[Cp*Ru(H_2)(dppm)]BF_4$ (1b) in a ratio of 1:2.^{9,10} Exposure of acetone solutions of 1 to air produced a brown solution from which complexes [Cp*Ru(O₂)-(dppm)]BF₄ ([2]BF₄) and [Cp*Ru(O₂)(Ph₂PCH₂P(O)-Ph₂)]BF₄ ([3]BF₄) can be isolated (Scheme 1). An in situ ³¹P NMR spectrum of the reaction mixture showed that the major product of the reaction is [3]BF₄. [3]BF₄ is not formed from further oxidation of [2]BF₄ by air, as the isolated complex [2]BF₄ did not react further with air to give [3]BF₄. Similar results were obtained when pure oxygen gas instead of air was used.

[2]BF₄ and [3]BF₄ were also produced when methanol solutions of 1 were exposed to air. However, [2]BF4

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was produced as the major product in this solvent (the relative ratio of $[2]BF_4$ to $[3]BF_4$ was 4.5:1, as indicated by an in situ ³¹P NMR spectrum). Thus, the relative amounts of $[2]BF_4$ and $[3]BF_4$ from the oxidation reaction appear to be solvent-dependent.

[2]BF₄ could also be obtained cleanly by exposure of methanol solutions of $[Cp*Ru(dppm)]BF_4$ (generated in situ from the reaction of AgBF₄ and Cp*RuCl(dppm) **(4)**⁹) to air (eq 1). Similarly, stirring a methanol solution



of Cp*RuCl(dppm) in the presence of NaBPh₄ in air for 3 h produced [Cp*Ru(O₂)(dppm)]BPh₄ (**[2]BPh₄**). Apparently O₂ from air was absorbed by [Cp*Ru(dppm)]⁺ to form **[2]BF₄** or **[2]BPh₄**. In principle, N₂ and H₂O in air can also react with [Cp*Ru(dppm)]⁺ to form the known complexes [Cp*Ru(N₂)(dppm)]⁺ and [Cp*Ru-(H₂O)(dppm)]⁺.¹¹ However, such complexes were not detected in our experiments. The dioxygen ligand in **[2]BF₄** or **[2]BPh₄** is bound so tightly that it could not be displaced by N₂ or H₂.

Complex **2** was characterized by elemental analysis, IR, MS, and ¹H, ¹³C, and ³¹P NMR spectroscopy. In particular, the FAB-MS (NBA matrix) of **[2]BF**₄ displayed peaks at m/z 653 assignable to $[Cp*Ru(O_2)-(dppm)]^+$ and at m/z 621 assignable to $[Cp*Ru(dppm)]^+$. In the IR spectrum of **[2]BF**₄, a weak band assignable to ν_{O-O} was observed at 924 cm⁻¹, which is absent in the IR spectrum of Cp*RuCl(dppm), Cp*RuH(dppm), and $[Cp*RuH_2(dppm)]BF_4$. Similarly, a weak band at 928 cm⁻¹ assignable to ν_{O-O} was observed for **[2]BPh**₄. The ν_{O-O} values are within the range reported for $L_nM(O_2)$ complexes.¹² The ¹H and ³¹P{¹H} NMR data are fully consistent with the structural assignment. The structure has been confirmed by an X-ray diffraction study on **[2]BPh**₄ (see below).

Formation of $[Cp^*Ru(O_2)(dppm)]^+$ 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)₃)₂,¹ [OsH(dppe)₂]⁺,² [RuH(dippe)₂]⁺,³ [RuH(dcpe)₂]⁺,³ and [OsCl(dcpe)₂]⁺.¹³

Complex **[3]BF**₄ was characterized by elemental analysis, IR, MS, ¹H, ¹³C, and ³¹P NMR spectroscopy. In particular, the FAB-MS of **[3]BF**₄ displayed peaks at m/z 669 corresponding to $[Cp*Ru(O_2)(Ph_2CH_2P(O)-Ph_2)]^+$ and at m/z 637 corresponding to $[Cp*Ru(Ph_2-CH_2P(O)Ph_2)]^+$. The IR spectrum displayed bands at 928 cm⁻¹ assignable to ν_{O-O} and at 1124 cm⁻¹ assignable to $\nu_{P=O}$. For comparison, the IR bands for coordinated P=O were observed at 1127 cm⁻¹ for $[Pd(\eta^3-C_3H_5)(\eta^2-Ph_2PCH_2-$



Figure 1. Molecular structure of the cation [Cp*Ru(O₂)-(dppm)]⁺.

CH₂P(O)Ph₂)]SbF₆^{14a} and at 1120 and 1130 cm⁻¹ for $[Pd(Ph_2PCH_2P(O)Ph_2)_2](PF_6)_2$.^{14b} The presence of chelating $Ph_2PCH_2P(O)PPh_2$ in **[3]BF**₄ is further supported by its ¹H and ³¹P NMR data. The ¹H NMR (in acetone d_6) 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 ³¹P NMR (in acetone- d_6) showed two doublets at 39.7 and 67.5 ppm assignable to $P(O)Ph_2$ and PPh_2 . The ³¹P chemical shifts are significantly downfield compared to those observed for typical Cp*Ru(η^2 -dppm) complexes such as Cp*RuH(dppm) (17.5 ppm),9a [Cp*RuH2(dppm)]- BF_4 (23.4 ppm),⁹ and [Cp*Ru(L)(dppm)]BF₄ (L = H₂, 4.9 ppm;^{9a} CH₃CN, 10.48 ppm;¹¹ H₂O, 11.2 ppm;¹¹ N₂, 3.45 ppm¹¹) but are consistent with the presence of the fivemembered chelating ring¹⁵ in [3]BF₄. Ligands of the type $PPh_2(CH_2)_n P(O)Ph_2$ (n = 1-3) have been previously synthesized and used for transition-metal complexation.14,16

Description of the Structure of $[Cp*Ru(O_2)-(dppm)]BPh_4$. The structure of $[Cp*Ru(O_2)(dppm)]^+$ has been confirmed by an X-ray diffraction study on $[Cp*Ru(O_2)(dppm)]BPh_4$. The view of the cationic complex $[Cp*Ru(O_2)(dppm)]^+$ 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 O₂ and the two PPh₂ 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(H₂)(dppm)]BF₄.¹⁰ For example, in both cases, the X₂ ligands are oriented in such a fashion to maximize the $d\pi$ (Ru) $-\sigma^*$ (H₂) and $d\pi$ (Ru) $-\pi^*$ (O₂) bonding;¹⁷ the O(1)–Ru–O(2) angle (39.9(4)°) in **[3]BPh₄** is close to the H–Ru–H angle (38(1)°) in [Cp*Ru(H₂)-(dppm)]BF₄.¹⁰

The two PPh₂ groups are bonded to ruthenium with slightly different Ru–P bond distances (Ru-P(1) =

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Table 1. Crystallographic Details for [Cp*Ru(O₂)(dppm)]BPh₄

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Cp*Ru(O₂)(dppm)]BPh₄

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 [CpRu(η^2 -dppm)(η^1 -dppm)]PF₆ (2.295(3), 2.325(3), 2.323(2) Å)¹⁸ and [Cp*Ru(H₂)(dppm)]-BF₄ (2.297(8), 2.314(9) Å).¹⁰ The P(1)-Ru-P(2) angle $(67.5(1)^{\circ})$ is slightly smaller than the corresponding angles reported for other chelating dppm in complexes such as $[CpRu(\eta^2-dppm)(\eta^1-dppm)]PF_6$ (70.0(1)°),¹⁸ $[Cp^*Ru(H_2)(\eta^2-dppm)]BF_4$ (71.4(3)°),¹⁰ and CpFePh-(dppm) $(73.8(0)^\circ)$.¹⁹ 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, $[Cp*Ru(O_2)(dppe)]^+$,⁵ $[Cp*Ru(O_2)(dippe)]^+$,⁶ and $[Cp*Ru(H_2)(dppm)]^+$.¹⁰

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 KO₂ (1.28 Å)²⁰ and shorter than that in H_2O_2 (1.46 Å).²¹ The Ru–O bond distances and O(1)-Ru-O(2) angle are similar to those reported for other ruthenium dioxygen complexes such as [RuH(O₂)-



 $(dippe)_2$ |BPh₄³ and [Cp*Ru(O₂)(PR₃)₂)]⁺ ((PR₃)₂ = dppe, ⁵ dippe,⁶ $(P-O)_2$ (P-O = (1,3-dioxan-2-ylmethyl)diphenylphosphine,⁷ and dppf⁸)). The O-O distance in [2]BPh₄ (1.37(1) Å) is comparable to those of $[\text{RuH}(O_2)(\text{dippe})_2]$ -BPh₄ (1.360(10) Å),³ [Cp*Ru(O₂)(dppe)]BF₄ (1.398(5) Å),⁵ [Cp*Ru(O₂)(dppf)]BF₄ (1.381(11) Å),⁸ and [Cp*Ru(O₂)- $(P-O)_2$]BPh₄ (1.394(9) Å)⁷ but is shorter than those of $[OsCl(O_2)(dcpe)_2]BPh_4$ (1.45(1) Å)¹³ and $[OsH(O_2) (dppe)_2]^+ (1.430(5) \text{ Å}).^2$

Mechanism for the Formation of [2]BF₄ and [3]BF4 from the Reaction of 1 with Air. The complex [2]BF₄ is presumably formed by displacement of the H_2 ligand in **1** with O_2 . Similar reactivity has been observed for complexes such as OsHCl(H₂)(CO)(P(i- $Pr_{3}_{2,1}$ [RuH(H₂)(dppe)₂]⁺,² [RuH(H₂)(dippe)₂]⁺,³ RuH₂-(Ph₂PNMeNMePPh₂)₂,^{4a} and RuH₂(CO)₂(PPh₃)₂.^{4b} However, production of [3]BF₄, a Ph₂P(O)CH₂PPh₂-containing complex, from the reaction of 1 with air is not straightforward. It has been reported that reaction of $[CpRu(N_2)(dippe)]BPh_4$ with O_2 produced the bis(phosphine oxide) $(i-Pr)_2 P(O)CH_2 CH_2 P(O)(i-Pr)_2$ along with $CpRu(\eta^6-C_6H_5BPh_3)$.^{6b} No intermediate could be observed in the reaction. It was suggested that (*i*-Pr)₂P- $(O)CH_2CH_2P(O)(i-Pr)_2$ is probably formed through the intermediate $[CpRu(O_2)(i-Pr)_2PCH_2CH_2P(i-Pr)_2)]^+$. In the case of reaction of $[Cp*RuH_2(dppm)]^+$ with air, the major products are $[Cp*Ru(O_2)(dppm)]^+$ and $[Cp*Ru(O_2)(Ph_2PCH_2P(O)Ph_2)]^+$. We have shown experimentally that $[Cp*Ru(O_2)(dppm)]^+$ is unlikely to be the intermediate for the formation of [Cp*Ru(O₂)(Ph₂PCH₂P- $(O)Ph_2)]^+$.

A plausible mechanism for the formation of [Cp*Ru- $(O_2)(Ph_2PCH_2P(O)Ph_2)]^+$ is shown in Scheme 2, which involves the peroxide intermediate (A) formed by reac-

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tion of **1** with O₂. Intramolecular oxygen transfer from the hydroperoxo ligand to one of the coordinated phosphorus atoms would give the peroxophosphine complex **B**. Subsequent elimination of H_2O would give the coordinatively unsaturated complex [Cp*Ru(Ph₂CH₂P- $(O)Ph_2)$]⁺ (**C**), which picks up a O₂ molecule to give $[Cp*Ru(O_2)(Ph_2CH_2P(O)Ph_2)]^+$.

Oxidation of phosphines by hydroperoxides to give phosphine oxides is one of the typical reactions of phosphines.²⁴ Hydroperoxide ion has been shown to be involved in the oxidation of phosphines by oxygen catalyzed by Pt(PPh₃)₂(O₂).²⁵ Intramolecular O-transfer from peroxo groups to coordinated phosphines to generate phosphine oxides has been reported for complexes such as RhCl(OOH) (acac) (PPh₃)₂²⁶ and $RhCl(O_4C)$ (PEt₂-Ph)₃.²⁷ Formation of peroxide complexes from the reactions of metal alkyls²⁸ or hydrides²⁹ with O₂ and production of H₂O₂ from H₂ and O₂ catalyzed by transition-metal complexes has been reported.³⁰ In support of the involvement of the hydroperoxo intermediate in the formation of [3]BF₄, it was demonstrated that reaction of $Cp^*RuCl(dppm)$ with H_2O_2 and O_2 in the presence of NaBPh₄ produced a mixture of [3]BPh₄ and dppm oxide (major), whereas the same reaction in the absence of hydrogen peroxide only gave [2]BPh4. Reaction of [2]BPh₄ in acetone- d_6 with H₂O₂ produced slowly an uncharacterized insoluble black precipitate. The solution only showed ³¹P signals assignable to [2]BPh₄ and Ph₂P(O)CH₂P(O)Ph₂. This observation again implies that the dioxygen complex [2]BPh₄ is not the intermediate for the formation of [Cp*Ru(O2)(Ph2PCH2P- $(O)Ph_2)]^+$.

In the proposed mechanism for the formation of [3]BF₄, water is suggested as the side product. To confirm the formation of water in the reaction, we have studied the reaction of air with $[Cp*RuD_2(dppm)]^+$, which was prepared by reaction of $[Cp^*Ru(dppm)]^+$ with D₂ gas. Indeed, the ²D NMR spectra of methanol or acetone solutions of [Cp*RuD₂(dppm)]⁺ after exposure to air showed signals assignable to D_2O .

It is not very clear to us why more [3]BF₄ relative to [2]BF₄ was produced in acetone but more [2]BF₄ relative to [3]BF₄ was produced in methanol. Possibly, methanol helped to dissociate the H₂ molecule to give the intermediate [Cp*Ru(dppm)]⁺ or [Cp*Ru(dppm)-(MeOH)]⁺, which facilitates the formation of [2]BF₄.

Reaction of [Cp*RuH₂(dppe)]BF₄ with Air. Formation of $[Cp^*Ru(O_2)(Ph_2PCH_2P(O)Ph_2)]^+$ (or the per-

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oxide intermediate) from the reaction of [Cp*RuH₂-(dppm)]⁺ with oxygen must be related to the reactivity of O₂ toward the RuH₂ or/and Ru(H₂) functionality. Unfortunately, the effect of RuH₂ and Ru(H₂) functionalities in the reaction of $[Cp*RuH_2(dppm)]^+$ with air is not clear because the hydride complex exists as a mixture of the dihydrogen form [Cp*Ru(H₂)(dppm)]BF₄ and the dihydride form trans-[Cp*RuH₂(dppm)]BF₄. To see the effect of RuH_2 and $Ru(H_2)$ functionalities, we have investigated the reaction of air with [Cp*RuH₂-(dppe)]BF₄ (5), which adopts the dihydride form only.⁵

Exposure of acetone or methanol solutions of 5 to air also produced [Cp*Ru(O₂)(dppe)]BF₄ ([6]BF₄) and [Cp*Ru(O₂)(Ph₂PCH₂CH₂P(O)Ph₂)]BF₄ ([7]BF₄) (eq 2).



The reaction is slower than that of the dppm analogue. Thus, [Cp*RuH₂(dppe)]BF₄ 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]BF₄ and [7]BF₄ are solvent-dependent. In acetone, about equal amounts of [6]BF4 and [7]BF4 were produced; in methanol, the dioxygen complex [6]BF4 is the major product.

The dioxygen complex $[Cp*Ru(O_2)(dppe)]^+$ has been reported previously and can be prepared easily from the reaction of [Cp*Ru(dppe)]⁺ with oxygen.⁵ The dioxygen complex $[Cp*Ru(O_2)(dppe)]^+$ 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)]BF₄ with oxygen.⁵ Unfortunately, we have not been able to obtain pure samples of [7]BF₄ by either recrystallization or column chromatography. Samples of [7]BF4 obtained were contaminated with the dioxygen complex [6]BF₄. The identity of [Cp*Ru(O₂)(Ph₂PCH₂CH₂P(O)Ph₂)]⁺, 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- $(O_2)(Ph_2CH_2CH_2P(O)Ph_2)]^+$ and at m/z 651 corresponding to [Cp*Ru(Ph₂CH₂CH₂P(O)Ph₂)]⁺. The IR spectrum displayed bands at 852 cm⁻¹ assignable to v_{0-0} and at 1056 cm⁻¹ assignable to $v_{P=0}$. The presence of chelating Ph₂PCH₂CH₂P(O)PPh₂ in [7]BF₄ is further supported by its ¹³C and ³¹P NMR data. The ¹³C NMR (in CD₂Cl₂) showed methylene signals at 18.7 and 22.4 ppm and a Cp* signal at 8.2 ppm. Consistent with the proposed structure, the ³¹P NMR (in CD₂Cl₂) showed two doublets at 50.7 and 32.8 ppm assignable to PPh₂ and P(O)Ph₂, respectively.

The fact that $[Cp*RuH_2(dppe)]BF_4$ (5), which adopts the dihydride form only, can also reacts with air to give

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 $[Cp^*Ru(O_2)(Ph_2CH_2CH_2P(O)Ph_2)]^+$ may suggest that formation of $[Cp^*Ru(O_2)(Ph_2(CH_2)_nP(O)Ph_2)]^+$ is related to the RuH_2 functionality. However, the involvement of the Ru(H_2) functionality cannot be excluded completely, because of the possibility of equilibrium between the Ru(H_2) and RuH_2 tautomers.⁹

Summary. The reaction of $[Cp*RuH_2(dppm)]^+/[Cp*Ru-(H_2)dppm)]^+$ in acetone or methanol with air produced a mixture of $[Cp*Ru(O_2)(dppm)]BF_4$ and $[Cp*Ru(O_2)(Ph_2-PCH_2P(O)Ph_2)]BF_4$. Similarly, the reaction of $[Cp*RuH_2-(dppe)]^+$ in acetone or methanol with air also produced $[Cp*Ru(O_2)(dppe)]BF_4$ and $[Cp*Ru(O_2)(Ph_2PCH_2CH_2P-(O)Ph_2)]BF_4$. These reactions appear to be solventdependent. Acetone favors the formation of $[Cp*Ru(O_2)-(Ph_2P(CH_2)_xP(O)Ph_2)]^+$ (x = 1, 2); methanol favors the formation of $[Cp*Ru(O_2)(Ph_2P(CH_2)_xPPh_2)]^+$ (x = 1, 2). $[Cp*Ru(O_2)(Ph_2P(CH_2)_xP(O)Ph_2)]^+$ species are likely produced from hydroperoxo intermediates formed by reaction of 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 (CH₂Cl₂). Microanalyses were performed by M-H-W Laboratories (Phoenix, AZ). ¹H and ³¹P NMR spectra were collected on a JEOL EX-400 spectrometer or a Bruker ARX-300 spectrometer. ¹H NMR chemical shifts are reported relative to TMS and ³¹P NMR chemical shifts relative to 85% H₃PO₄. IR spectra were collected on a Perkin-Elmer 1600 spectrometer. Cp*RuCl-(dppm),⁹ Cp*RuH(dppm),⁹ [Cp*RuH₂(dppm)]BF₄,⁹ Cp*RuCl-(dppe),⁵ [Cp*RuH₂(dppe)]BF₄,⁵ and [Cp*Ru(O₂)(dppe)]BF₄⁵ were prepared according to literature methods. All other reagents were used as purchased from Aldrich.

[Cp*Ru(O₂)(dppm)]BPh₄ ([2]BPh₄). A mixture of Cp*RuCl-(dppm) (0.10 g, 0.15 mmol) and NaBPh₄ (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, cm⁻¹): ν_{O-O} 928 (w). ¹H NMR (acetone-*d*₆): δ 1.63 (t, *J*(PH) = 1.4 Hz, 15 H, C₅-(CH₃)₅), 4.91 (dt, *J*(PH) = 11.2 Hz, *J*(HH) = 15.1 Hz, 1 H, CH₂), 5.20 (dt, *J*(PH) = 12.3 Hz, *J*(HH) = 15.1 Hz, 1 H, CH₂), 6.9– 7.9 (m, 40 H, Ph). ³¹P{¹H} NMR (acetone-*d*₆): δ -11.0 (s). Anal. Calcd for C₅₉H₅₇BO₂P₂Ru: C, 72.91; H, 5.91. Found: C, 72.46; H, 5.86.

[Cp*Ru(O₂)(dppm)]BF₄ ([2]BF₄). A mixture of Cp*RuCl-(dppm) (0.10 g, 0.15 mmol) and AgBF₄ (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, cm⁻¹): ν_{0-0} 924 (w). ¹H NMR (acetone-*d*₆): δ 1.63 (t, *J*(PH) = 1.4 Hz, 15 H, C₅(CH₃)₅), 4.91 (dt, *J*(PH) = 11.2 Hz, *J*(HH) = 15.1 Hz, 1 H, CH₂), 5.20 (dt, *J*(PH) = 12.3 Hz, *J*(HH) = 15.1 Hz, 1 H, CH₂), 7.4–7.9 (m, 20 H, Ph). ³¹P{¹H} NMR (acetone-*d*₆): -11.0 (s). ¹³C{¹H} NMR (CDCl₃): δ 8.5 (s, Cp*), 37.2 (t, *J*(PC) = 28.1 Hz, CH₂), 108.0 (s, Cp*), 126.0–133.2 (m, Ph). Anal. Calcd for C₃₅H₃₇BF₄O₂P₂Ru: C, 56.85; H, 5.04. Found: C, 56.58; H, 5.02.

Formation of $[Cp^*Ru(O_2)(Ph_2PCH_2P(O)Ph_2)]BF_4$ -([3]BF₄) and $[Cp^*Ru(O_2)(dppm)]BF_4$ ([2]BF₄) from the Reaction of $[Cp^*RuH_2(dppm)]BF_4$ with Air. A 1.0 g (1.4 mmol) portion of $[Cp^*RuH_2(dppm)]BF_4$ 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 [Cp*Ru(O₂)(Ph₂PCH₂P(O)Ph₂)]-BF₄. The product was collected by filtration, washed with ether, and dried under vacuum. Yield: 0.46 g, 43%. IR (KBr, cm⁻¹): $\nu_{P=0}$ 1124 (s), ν_{O-0} 928 (w). ¹H NMR (acetone- d_6): δ 1.66 (d, J(PH) = 1.6 Hz, 15 H, $C_5(CH_3)_5$), 4.20 (ddd, J(PH) =13.1, 11.0 Hz, J(HH) = 14.4 Hz, 1 H, CH₂), 4.51 (ddd, J(PH) = 13.2, 5.6 Hz, J(HH) = 14.4 Hz, 1 H, CH₂), 7.3-8.0 (m, 20 H, Ph). ³¹P{¹H} NMR (acetone- d_6): δ 39.7 (d, J(PP) = 25.7 Hz), 67.5 (d, J(PP) = 25.7 Hz). ¹³C{¹H} NMR (CDCl₃): δ 8.4 (s, Cp*), 30.6 (dd, J(PC) = 66.6, 16.4 Hz, CH_2), 108.6 (s, Cp^*). 128.0-134.4 (m, Ph). Anal. Calcd for C₃₅H₃₇BF₄O₃P₂Ru: C, 55.64; H, 4.94. Found: C, 55.86; H, 4.90. The filtrate from recrystallization of [Cp*Ru(O₂)(Ph₂PCH₂P(O)Ph₂)]BF₄ was passed through a silica gel column using CH₂Cl₂/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 [Cp*Ru(O2)-(dppm)]BF₄. The product was collected by filtration, washed with ether, and dried under vacuum. Yield: 0.20 g, 19%. For comparative purposes, the ³¹P chemical shifts of dppm, dppmO, and dppmO₂ in acetone- d_6 were also collected: dppm, δ –23.5 (s); dppmO, δ -28.6 (d, J(PP) = 50.9 Hz), 26.6 (d, J(PP) = 50.9 Hz); dppmO₂, δ 24.6 (s).

Reaction of Cp*RuCl(dppm) with H₂O₂. To an NMR tube (opened to air) containing Cp*RuCl(dppm) and NaBPh₄ dissolved in acetone- d_6 (0.7 mL) was added ca. 0.10 mL of 30% H₂O₂ in water. A ³¹P NMR spectrum was collected 5 min later. The ³¹P NMR showed signals assignable to [Cp*Ru(O₂)(Ph₂-PCH₂P(O)Ph₂)]BF₄ and dppm oxide.

Confirmation of the Formation of D₂**O from the Reaction of [Cp*RuD**₂(**dppm)]BF**₄ with Air. A mixture of 20 mg (0.03 mmol) of Cp*RuCl(dppm) and 7 mg (0.03 mmol) of AgBF₄ 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 D₂ for 1 h to generate [Cp*RuD₂(dppm)]BF₄ in situ, and then the mixture was exposed to air and left to stand overnight. A ²D NMR spectrum was collected. ²D NMR (acetone): δ 3.92 (s, D₂O). Formation of D₂O in methanol can be confirmed similarly by the observation of the D₂O signal at 5.0 ppm.

Formation of [Cp*Ru(O₂)(dppe)]BF₄ ([6]BF₄) and [Cp*Ru(O₂)(Ph₂PCH₂CH₂P(O)Ph₂)]BF₄ ([7]BF₄) from the Reaction of [Cp*RuH₂(dppe)]BF₄ with Air. A 0.52 g (0.70 mmol) portion of [Cp*RuH₂(dppe)]BF₄ 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]BF4 and [7]BF₄. Attempts to separate the two compounds by column chromatography and recrystallization were unsuccessful. [6]BF4 could be obtained cleanly from the reaction of [Cp*Ru(dppe)]-BF₄ with air.⁵ Selected characterization data for [6]BF₄: ³¹P{¹H} NMR (CD₂Cl₂) δ 68.5 (s); ¹H NMR (CD₂Cl₂) δ 1.57 (s, 15 H, C₅(CH₃)₅), 2.67 (m, 4 H, CH₂), 7.1-7.8 (m, 20 H, Ph); ¹³C{¹H} NMR (CD₂Cl₂) δ 9.0 (s, Cp*), 26.4 (t, J(PC) = 38.6 Hz, CH₂), 107.2 (s, Cp*), 128.7-133.2 (m, Ph). Selected characterization data for [7]BF₄: IR (KBr, cm⁻¹) $\nu_{P=0}$ 1056 (s), $\nu_{\rm O-O}$ 852 (w); ¹H NMR (CD₂Cl₂) δ 1.34 (d, J(PH) = 1.5 Hz, $C_5(CH_3)_5),\ 1.80{-}3.36$ (m, $CH_2),\ 6.95{-}7.73$ (m, $Ph);\ {}^{31}P\{{}^{1}H\}$ NMR (CD₂Cl₂) δ 32.8 (d, J(PP) = 15.3 Hz), 50.7 (d, J(PP) = 15.3 Hz); ¹³C{¹H} NMR (CD₂Cl₂) δ 8.2 (s, Cp*), 18.7, (dd, *J*(PC) = 26.8, 5.5 Hz, CH₂), 22.4 (t, J(PC) = 34.0 Hz), 107.3 (s, Cp*), 125.8-133.2 (m, Ph); FAB-MS m/e 685 ([Cp*Ru(O₂)(Ph₂PCH₂- $CH_2P(O)Ph_2)]^+)$, 651 ([Cp*Ru(Ph_2PCH_2CH_2P(O)Ph_2)]^+). For comparative purposes, the ³¹P chemical shift of dppe, dppeO, and dppeO₂ were collected in acetone- d_6 : dppe, δ –14.0 (s); dppeO, δ -13.6 (d, J(PP) = 47.9 Hz), 29.6 (d, J(PP) = 47.9 Hz); dppeO₂, δ 30.1 (s).

Crystallographic Analysis of [Cp*Ru(O₂)(dppm)]BPh₄. Suitable crystals for X-ray diffraction study were obtained by slow diffusion of Et_2O into an acetone solution of [Cp*Ru(O₂)-(dppm)]BPh₄ 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 α radiation ($\lambda = 0.710$ 73 Å) 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 ψ -scan absorption correction³¹ were applied to all intensity data. The structure was solved by direct methods (SIR88)³² 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(C–H) = 0.95 Å). All calculations were performed on a Silicon Graphics computer using the program package TEXSAN.³³ Selected bond distances and angles are given in Table 2.

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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.

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