clusters and the expected angular dependence of the radial P–P coupling. For the toroidal $(S^\sigma)^2(P^\sigma)^4$ cluster $[Pt(Ag)(AuPPh_3)_8]^{3+}$, we observed that the coupling constants are dependent not only on the Au–Pt–Au angle but also on the Pt–Au–P angle, which for this type of clusters more strongly deviates from linearity when the Au–P group lies above or below the torus plane.

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Ruthenium in an O Donor Environment: Properties and Reactions of η^3-$(RPO(C_6H_4O)_2)^{2-}$, η^3-$(CpCo(PO(OEt)_2)_3)^-$ and η^3-$HC(POPh_2)_3$ Complexes of Ruthenium

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The tridentate oxygen donor ligands η^3-$(RPO(C_6H_4O)_2)^{2-}$ (bipo), η^3-$(CpCo(PO(OEt)_2)_3)^-$ (L′), and η^3-$HC(POPh_2)_3$ (Htriso) are shown to form a number of organometallic Ru(II) complexes. A single crystal X-ray study of **2b**, $[(\eta^6\text{-}ArH)Ru\{\eta^3\text{-}RPO(C_6H_4O)_2\}]$ (R = Ph, ArH = *p*-cymene) shows that the phosphorus-containing ligand is bound to the metal via the two phenolate groups and the phosphine oxide oxygen. The complex **2b** crystallizes in the space group $P\bar{1}$ with lattice constants $a = 10.407$ (6) Å, $b = 14.334$ (6) Å, $c = 13.25$ (1) Å, $\alpha = 75.85$ (5)°, $\beta = 129.85$ (4)°, $\gamma = 81.28$ (4)°, $V = 1340$ (1) Å^3, $Z = 2$, $R = 6.6\%$, and $R_w = 11.4\%$. The arene and carbonyl complexes $[HtrisoRu(\eta^6\text{-}ArH)](SbF_6)_2$, $[L'Ru(\eta^6\text{-}ArH)](SbF_6)$, $[HtrisoRu(CO)_3](SbF_6)_2$, and $[L'Ru(CO)_3](SbF_6)$ were prepared. $[L'Ru(CO)_3](SbF_6)$ reacts with Me_3NO to give $[L'Ru(CO)(solvent)_2](SbF_6)$ (solvent = THF, dioxane) or $L'Ru(CO)_2(OR)$ (R = Me, Ac, $CH(Me)_2$; solvent = MeOH, AcOH, Me_2CHOH). These solvento and alkoxide complexes are exceptionally stable to dissociation and β-elimination, respectively.

Introduction

We still know very little about how an O donor ligand environment affects organometallic chemistry and homogeneous catalysis.[3] The demonstration[4] of heterogeneous catalysis by site-isolated organometallic fragments supported on oxide surfaces suggests that interesting results will be found. Kläui and coworkers[5] have shown that the ν(CO) values for $\{CpCo(R_2PO)_3\}M(CO)_n$ are similar to those for alumina-supported metal carbonyl fragments.[6] The studies of Feher et al.[7] with trisilicates and work with $P_3O_9^{3-}$ by Klemperer et al.[8] have demonstrated that tridentate O ligands can form stable organometallic complexes that show unusual chemical reactivity.

Table I. Crystal Data for $RuPO_3C_{28}H_2$ (**2b**)

formula: $RuPO_3C_{28}H_{27}$	μ(Mo Kα) = 6.555 cm^{-1}
MW = 543.56	λ(Mo Kα) = 0.71069 Å
a = 10.407 (6) Å	D_{calc} = 1.347 g cm^{-3}
b = 14.334 (6) Å	Z = 2
c = 13.25 (1) Å	space group: $P1$ (No. 2)
α = 75.85 (5)°	no. of measd reflcns: 4758
β = 129.85 (4)°	no. of obs reflcns: 3492
γ = 81.28 (4)°	octants measd: $\pm h,+k,\pm l$
V = 1340 (1) Å^3	R = 6.6%
F(000) = 556	R_w = 11.4%

We are interested in O donor ligands not only to expand the study of heterogeneous catalysis but also to extend the field of organometallic chemistry beyond the P and C ligand set that currently dominates the field. We have shown[9] that Grim's[10] triso ligand stabilizes Ir(I), Ir(III), and Ir(V) complexes that are active homogeneous catalysts for a variety of hydrosilylation reactions. In this paper, we discuss our results for Ru with the tridentate oxygen donor ligands, η^3-$(RPO(C_6H_4O_2)^{2-}$ (bipo), η^3-$(CpCo(PO(OEt)_2)_3^-$ (L′) and η^3-$HC(POPh_2)_3$ (Htriso).

Results

The protonated ligands, $RP(O)(o\text{-}C_6H_4OH)_2$ (R = *o*-hydroxyphenyl (**1a**), phenyl (**1b**), *n*-propyl (**1c**)) react with 2 equiv

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Table II. Final Positional Parameters and U_{eq} for Non-Hydrogen Atoms of **2a**

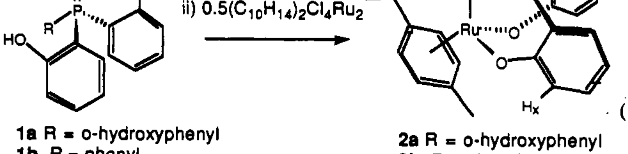
atom	x ($\sigma(x)$)	y ($\sigma(y)$)	z ($\sigma(z)$)	$10^{-3}U_{eq}$,[a] Å^2
Ru2	0.1747 (1)	0.0882 (1)	0.2031 (1)	21 (0)
P2	−0.1944 (4)	0.1622 (2)	0.1115 (3)	18 (1)
O2	−0.1128 (9)	0.1494 (6)	0.0507 (7)	21 (3)
O50	0.1712 (11)	−0.0401 (6)	0.3119 (10)	27 (4)
O60	0.1684 (10)	0.1571 (6)	0.3245 (8)	17 (4)
C51	0.0651 (14)	−0.0425 (9)	0.3342 (12)	20 (6)
C52	0.1239 (15)	−0.1361 (9)	0.4424 (13)	24 (6)
C53	0.0289 (16)	−0.1475 (9)	0.4805 (12)	25 (6)
C54	−0.1292 (16)	−0.0662 (10)	0.4120 (13)	26 (6)
C55	−0.1942 (15)	0.0272 (9)	0.3010 (12)	22 (6)
C56	−0.0141 (14)	0.0409 (8)	0.2556 (11)	19 (5)
C61	0.0374 (14)	0.2416 (8)	0.2763 (11)	20 (5)
C62	−0.1470 (14)	0.2582 (8)	0.1772 (11)	19 (5)
C63	−0.0283 (15)	0.3839 (9)	0.1409 (12)	21 (6)
C64	−0.2266 (19)	0.4132 (10)	0.1995 (14)	29 (7)
C65	−0.0449 (19)	0.3977 (10)	0.0246 (15)	30 (7)
C66	0.0852 (17)	0.3151 (11)	0.3323 (14)	30 (7)
C70	−0.4398 (14)	0.2096 (8)	−0.0385 (11)	19 (5)
C71	−0.5324 (16)	0.3078 (10)	−0.1150 (13)	29 (6)
C72	−0.7226 (18)	0.3464 (10)	−0.2801 (14)	33 (7)
C73	−0.8113 (17)	0.2856 (12)	−0.2893 (16)	39 (8)
C74	−0.7229 (18)	0.1891 (12)	−0.1792 (15)	33 (8)
C75	−0.5374 (16)	0.1498 (10)	−0.0534 (13)	27 (6)
C80	0.2469 (17)	0.1982 (10)	0.1245 (15)	29 (7)
C81	0.3998 (18)	0.1290 (12)	0.2738 (14)	35 (8)
C82	0.4657 (16)	0.0146 (12)	0.3304 (14)	37 (8)
C83	0.3684 (17)	−0.0384 (11)	0.2299 (14)	32 (7)
C84	0.2119 (17)	0.0428 (11)	0.0759 (14)	32 (7)
C85	0.1562 (16)	0.1538 (11)	0.0303 (13)	32 (7)
C86	0.1855 (25)	0.3141 (13)	0.0771 (20)	43 (12)
C87	0.3111 (31)	0.3497 (15)	0.0682 (26)	59 (17)
C88	−0.0215 (28)	0.3781 (14)	−0.0603 (25)	62 (14)
C89	0.4324 (21)	−0.1471 (10)	0.2888 (17)	36 (8)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$.

Table III. Selected Bond Lengths (Å) and Angles (deg) for **2b**

Ru2–O2	2.096 (7)	Ru2–C85	2.12 (2)
Ru2–O50	2.06 (1)	P2–C56	1.77 (1)
Ru2–O60	2.11 (1)	O2–P2	1.52 (1)
Ru2–C80	2.17 (2)	P2–C62	1.77 (1)
Ru2–C81	2.14 (2)	P2–C70	1.80 (1)
Ru2–C82	2.18 (1)	O50–C51	1.32 (2)
Ru2–C83	2.18 (2)	O60–C61	1.32 (2)
Ru2–C84	2.17 (2)		
O2–Ru2–O50	85.4 (3)	O2–P2–C70	107.4 (6)
O2–Ru2–O60	87.2 (3)	Ru2–O2–P2	116.2 (4)
O50–Ru2–O60	86.8 (5)	Ru2–O50–C51	129.3 (7)
O2–P2–C56	111.2 (6)	Ru2–O60–C61	128.8 (7)
O2–P2–C62	109.6 (7)		

of sodium hydride in CH_2Cl_2 to give the disodium salts. Subsequent reaction with the (η^6-cymene)dichlororuthenium(II) dimer[11] gives [(η^6-ArH)Ru{η^3-RPO(C_6H_4O)$_2$}] (**2a–c**), as shown in eq 1.



(1)

1a R = o-hydroxyphenyl
1b R = phenyl
1c R = n-propyl

2a R = o-hydroxyphenyl
2b R = phenyl
2c R = n-propyl

Complexes **2a–c** are air-stable, chromatographable orange microcrystalline solids and were fully characterized by ^1H, ^{31}P, and ^{13}C NMR and IR spectroscopy and microanalysis. The ^1H NMR spectra show coordination shifts in the aromatic region upon chelation of **1**. In particular, one set of ligand protons, probably ortho to the phenolate oxygen (H_x in eq 1), is shifted upfield by approximately 0.5 ppm to δ 6.35–6.45 on binding. While the ligands **1b** and **1c** show a ^{31}P NMR coordination shift of −6.4 ppm, **1a** shows no such shift on binding. This is probably a result of the additional hydrogen-bonding interaction between the hydroxyphenyl group and the phosphine oxide oxygen, possible only in **2a**. This H bond may also be responsible for the greatly decreased solubility of **2a** compared to **2b,c** in a variety of solvents.

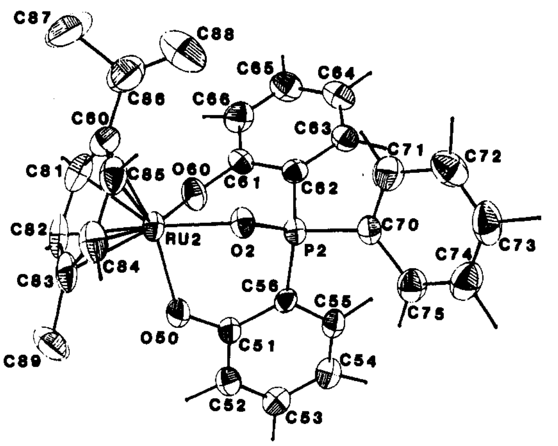


Figure 1. ORTEP drawing of **2b** showing 50% thermal ellipsoids.

The O donor ligand can be readily cleaved from the metal despite being η^3-bound; for example, **2a–c** decompose on reaction with CO or H_2O_2. In addition, the phenoxide group in bipo is susceptible to attack by electrophiles. For example, bromine reacts with **2a** to give [(η^6-ArH)$RuBr_2$]$_2$[10] and the bromination product from the ligand, tris(3,5-dibromo-2-hydroxyphenyl)phosphine.

Crystal Structure of 2b. The crystal structure of **2b** (Figure 1 and Tables I–III) shows that the bipo ligand is coordinated to Ru via two phenoxide and one P═O group so that the ligand acts as a tridentate chelate via all thee oxygen atoms. Although the bond lengths and angles involving the ligand seem reasonable, the average C–O–Ru angle of 129.1° is large. For most phenoxide and alkoxide complexes, this angle lies between 120.5 and 124.4°.[12] Interestingly, almost all previous complexes contain an additional alcohol H-bonded to the alkoxide group. The exception, *trans*-PdMe(OPh)(PMe_3)$_2$,[12a] has a Pd–O–C angle of 127.1° and does not contain a H-bonding group in the structure. The arene is η^6-bound, and the Ru–C(arene) distances of 2.14–2.18 Å are similar to those observed in (p-$MeC_6H_4CHMe_2$)$RuCl_2$($PMePh_2$)[13] and [(η^3-(pz)$_4$B)Ru(C_6H_6)](PF_6) (pz = pyrazolyl).[14]

Catalytic Reactions. Complexes **2a–c** are catalytically active and cyclotrimerize methyl propiolate both photochemically (254 nm, CH_2Cl_2) and thermally (100 °C, toluene). The initial rates for **2b** are 1.2 and 0.6 turnover/h, respectively. No catalyst degradation was apparent in either case over 17 h. This is important because catalyst degradation is a significant limitation of homogeneous catalysts.[15] ((ArH)$RuCl_2$)$_2$ is also a thermal (but not a photochemical) catalyst for acetylene cyclotrimerization. Although ((ArH)$RuCl_2$)$_2$ has a higher turnover number than **2b**, unidentified byproducts are formed with ((ArH)$RuCl_2$)$_2$ that are not seen for **2b**.

Other Arene Complexes. We prepared $PhPS(C_6H_4OH)_2$ (H_2bips, **4**) in the hope that the presence of sulfur would provide

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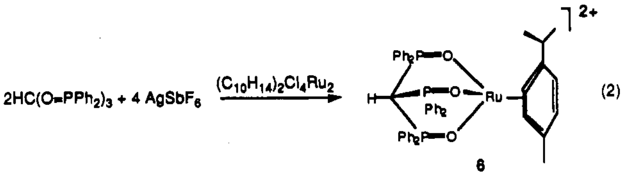
Table IV. Carbonyl Stretching Frequencies

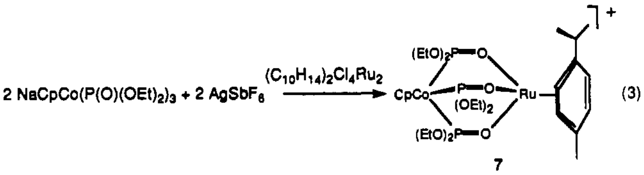
complex	ν(CO), cm^{-1}
free CO	2155
H(triso)Ru(CO)$_3$(SbF$_6$)$_2$ (**11a**)	2165, 2084
(triso)Ru(CO)$_3$(SbF$_6$) (**11b**)	2145, 2048
(L')Ru(CO)$_3$(SbF$_6$) (**8**)	2140, 2062
CpRu(CO)$_3$(BPh$_4$)[15]	2119, 2064
(L')Ru(thf)$_2$(CO)(SbF$_6$) (**9a**)	1939
(L')Ru(dioxane)$_2$(CO)(SbF$_6$) (**9b**)	1954
CpRu(PPh$_3$)$_2$(CO)(BPh$_4$)[15]	1981
(L')Ru(CO)$_2$(OMe) (**10a**)	2047, 1966
(L')Ru(CO)$_2$(OAc) (**10b**)	2049, 1972
(L')Ru(CO)$_2$(OCH(Me)$_2$) (**10c**)	2054, 1975

a more stable complex. However, PhP(S)(C$_6$H$_4$O)$_2$Ru(η^6-ArH) (**5**) also decomposed in the presence of CO.

In contrast, [(Htriso)Ru(η^6-ArH)](SbF$_6$)$_2$ (**6**) and [L'Ru(η^6-ArH)](SbF$_6$) (**7**) prepared as shown in eqs 2 and 3, failed to react with CO (1 atm) and H$_2$O$_2$, indicating that Htriso and L' are more strongly bound than bipo or bips. Arene complexes **6** and **7** are identified by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy and elemental analysis. Complex **7** is related to (C$_6$Me$_6$)Ru(P(O)(OEt)$_2$)$_2$ClRu(C$_6$Me$_6$) prepared by Kläui and Buchholz.[16]

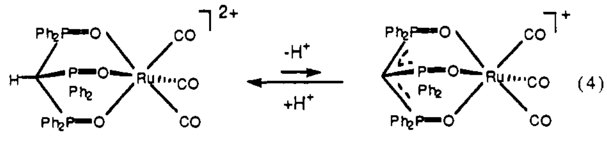


6



7

Carbonyl Complexes. Even though the arene complexes were quite unreactive, we decided to prepare carbonyl complexes. What appears to be [(Htriso)Ru(CO)$_3$](SbF$_6$)$_2$ (**8a**) is formed by reaction of Htriso and (RuCl$_2$(CO)$_3$)$_2$ and AgSbF$_6$. Isolation of **8a** is difficult perhaps due to the equilibrium shown in eq 4.



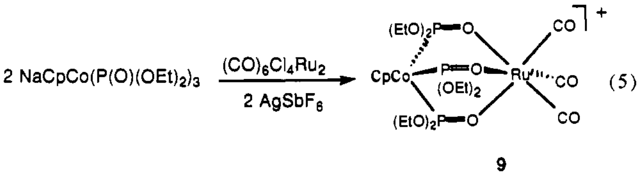
8a **8b**

In the presence of excess acid, a species identified as **8a** is formed but could not be isolated pure, nor could [(triso)Ru(CO)$_3$](SbF$_6$) (**8b**) be isolated in the presence of excess base. The IR spectra of the material isolated from either acid or base indeed showed that **8b** or **8a** were absent, respectively, but subsequent recrystallization of either product mixture from CH$_2$Cl$_2$ and ether yielded the same **8a**–**8b** mixture by IR. This suggests that **8a** may be an acid and perhaps water establishes the **8a**–**8b** equilibrium. The ν(CO) stretching frequencies for **8a** (2161, 2105 cm^{-1}) and **8b** (2147, 2048 cm^{-1}) (Table IV) are extremely high. These are the highest ν(CO) stretching frequencies known for Ru although Pd complexes, such as [CO(C$_6$H$_5$)PdL$_2$]ClO$_4$,[17] have equally high values. The high values are probably a result of the overall +2 charge, rare for a Ru carbonyl, and the high trans effect of the P=O ligand.[18]

Table V. ^{31}P NMR Data for L' Complexes

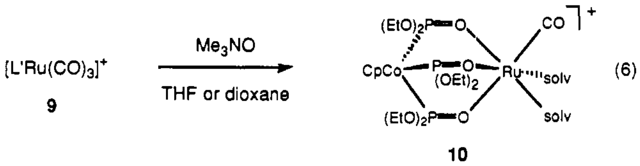
complex	δ, ppm	*J*, Hz
L'Ru(Ar)(SbF$_6$) (**7**)	81.1 (s)	
(L')Ru(CO)$_3$(SbF$_6$) (**8**)	119.2 (s)	
(L')Ru(thf)$_2$(CO)(SbF$_6$) (**9**)	128.0 (d), 114.2 (t)	140
(L')Ru(dioxane)$_2$(CO)(SbF$_6$) (**9b**)	129.6 (d), 114.1 (t)	139
(L')Ru(CO)$_2$(OMe) (**10a**)	122.9 (t), 113.8 (d)	140
(L')Ru(CO)$_2$(OAc) (**10b**)	121.3 (t), 114.0 (d)	140
(L')Ru(CO)$_2$(OCH(Me)$_2$) (**10c**)	124.1 (t), 114.5 (d)	143

Two equivalents of NaL' react with (RuCl$_2$(CO)$_3$)$_2$ and 2 equiv of AgSbF$_6$ to yield air-stable, pale yellow **9** (eq 5). Complex **9** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy and elemental analysis. The L' ligand is a weaker donor than Cp by comparison of the ν(CO) data for **9** and the known [CpRu(CO)$_3$](BPh)$_4$[19] (Table IV).



9

When Me$_3$NO reacts with **9** in an aprotic coordinating solvent, bis(solvento) complexes, such as [L'Ru(CO)(THF)$_2$](SbF$_6$) (**10a**) and [L'Ru(CO)(dioxane)$_2$](SbF$_6$) (**10b**) (eq 6), are formed. These

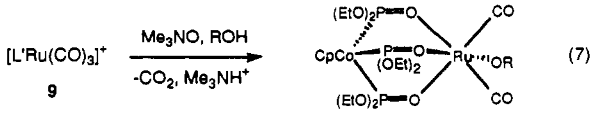


10

(solv = THF, **a**; solv = dioxane, **b**)

complexes are air-stable in the solid state at 25 °C for months, but decompose in days in solution. The ^{1}H NMR spectra of **10a** shows only a slight coordination shift in the THF on binding, but does show two types of OC*H*$_2$ resonances at 3.7 (m) and 3.6 (m) ppm. This indicates, in contrast to most solvento complexes, that neither dissociation nor rotation of THF are rapid on the NMR time scale. Furthermore, the ^{1}H NMR spectrum of **10a** in DMSO-d_6 (DMSO = dimethyl sulfoxide) remains unchanged to 50 °C when decomposition (as noted by the appearance of multiple Cp resonances in ^{1}H NMR spectrum) begins to occur. There is no evidence that this decomposition occurs by *initial* dissociation of THF although free THF is one of the decomposition products. The ^{1}H NMR spectrum of free dioxane is a sharp singlet at 3.63 in CDCl$_3$; however, in complex **10b** the dioxane resonances are moved downfield to 3.7 (m) and 3.9 (m) ppm. The ν(CO) bands at 1939 and 1954 cm^{-1} for **10a** and **10b**, respectively, are at much lower energy than that for [CpRu(PPh$_3$)$_2$(CO)](BPh$_4$)[19] (1981 cm^{-1}) indicating the solvent ligand is a stronger σ donor than PPh$_3$.

In protic solvents, such as methanol, acetic acid, or 2-propanol, tricarbonyl **9** reacts with Me$_3$NO to yield L'Ru(CO)$_2$(OR) (R = Me (**11a**), Ac (**11b**), CH(Me)$_2$ (**11c**)) (eq 7). Comparison of the ^{31}P NMR spectra of **10a**,**b** and **11a**–**c** indicates that the *P*=O group trans to CO resonates upfield relative to the *P*=O group trans to the solvent ligands.



11

Discussion

The O donor ligand L' stabilizes carbonyl derivatives of Ru much better than does bipo, bips, or Htriso. Nevertheless, the

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carbonyls in the L′ complex **9** are susceptible to nucleophilic attack. In protic solvents, e.g., ROH, reaction of **9** with Me_3NO forms a solvent species which after loss of a proton yields **11**. Complexes **11a**,**c** are examples of stable ruthenium alkoxides.[20] Such complexes often decompose rapidly via β-elimination;[21] however, $Cp^*Ru(CO)_2(OMe)$[20b] and $Cp^*Ru(bpy)(OMe)$[20c] are also known and stable. Complex **11c** does not β-eliminate even at 100 °C, indicating that the L′ probably does not even partially dissociate at 100 °C.

Insertion reactions[22] are common for alkoxide complexes, but **11a** failed to react with CO (25 °C, 1 atm) or phenyl acetylene (350 nm $h\nu$). We had hoped the η^1-acetate complex **11b** would readily undergo CO loss to form $L'Ru(\eta^2\text{-}O_2CCH_3)CO$ since the acetate ligand is known to labilize cis carbonyls.[23] Complex **11b**, however, remains unchanged after refluxing for several hours in toluene or on photolysis with 350-nm light in benzene.

In ether solvents, the reaction of **9** with $ONMe_3$ causes the loss of two CO ligands and the bis(solvento) complexes **10** are formed. Solvento complexes **10a**,**b** are highly unusual.[24,25] Instead of being labile, the solvent molecules in **10a**,**b** do not readily dissociate. **10a**,**b** fail to react with bis(diphenylphosphino)ethane, 2,2′-bipyridyl, methanol, olefins (cyclooctene, cyclopentene), silanes, or acetylenes at 25 °C, in refluxing CH_2Cl_2, in refluxing THF, or on irradiation with 254-nm light. In refluxing toluene, the complex decomposes, but no substitution products are isolated. This behavior is remarkably different from that of other octahedral d^6 cations, $[Ir(H)_2(PPh_3)_2(solv)_2](SbF_6)$[25a,b], a complex shown to activate the C-H bonds of alkanes and alkenes[25c–g] and an exceptionally active catalyst for silane alcoholysis,[25j] and $[CpRu(CO)_2(solv)][SbF_6]$[19] (solv = acetone), a complex known to undergo readily substitution.

Conclusion

The tridentate oxygen donor ligands $\eta^3\text{-}(RPO(C_6H_4O)_2)^{2-}$ (bipo), $\eta^3\text{-}(CpCo(PO(OEt)_2)_3)^-$ (L′) and $\eta^3\text{-}HC(POPh_2)_3$ (Htriso) form a number of Ru(II) complexes. $[L'Ru(CO)_3](SbF_6)$ (**9**) reacts with $ONMe_3$ to form the unusual solvento complexes **10a**,**b** and the stable alkoxide complexes **11a** and **11c**. The unusual properties observed may result from the O-donor environment.

Experimental Section

General Data. All manipulations were carried out in an argon atmosphere by using standard Schlenk techniques. NMR spectra were recorded on a Bruker WM-250 or a Bruker WM-500 spectrometer. $^{31}P\{^1H\}$ NMR were recorded with 85% H_2PO_4 as the reference. Chemical shifts are given in ppm and coupling constants in Hz. IR spectra were recorded on a Nicolet 5-SX FT spectrometer. Combustion analyses were performed by Galbraith Laboratories. Photolysis were carried out in a Rayonet photochemical reactor RMR-500 with four RPR 2540-Å lamps. Melting points were recorded on a Mel-Temp instrument.

Toluene was distilled from lithium aluminum hydride. Tetrahydrofuran (THF), ether, and hexanes were distilled from sodium benzophenone ketyl and dichloromethane from calcium hydride. (η^6-*p*-Cymene)dichlororuthenium (II) dimer,[11] tris(*o*-hydroxyphenyl)phosphine oxide (**1a**),[26] $((CO)_3RuCl)_2$,[27] $NaCpCo(P(O)(OEt)_2)\cdot H_2O$,[28] and Htriso[10] were prepared as previously described.

Bis(*o*-methoxyphenyl)phenylphosphine Oxide.[29] A dry three-neck, 250-mL round-bottom flask under argon was charged with a stir bar, Mg turnings (0.8 g), and ether (15 mL). One neck was equipped with a condenser, and the other two were equipped with pressure-equalizing addition funnels; one contained *o*-bromoanisole (0.034 mol, 4.2 mL) and the other phenylphosphonic dichloride (0.012 mol, 2.4 mL) in ether (20 mL). A few drops of *o*-bromoanisole and a crystal of I_2 were added to the Mg suspension with gentle heating. Once the reaction started the bromide was added dropwise and the heat removed. When the reaction was completed, the mixture was cooled in an ice bath and the phosphonic dichloride solution was added dropwise over 1 h. The mixture was quenched with acidified water (50 mL) and a white precipitate formed. The precipitate was filtered, dissolved in CH_2Cl_2 (20 mL), dried over $MgSO_4$, and filtered and solvent removed in vacuo. The white solid (59% yield) was used directly below. ^1H NMR (250 MHz, $CDCl_3$) (m = multiplet, s = singlet, b = broad, d = doublet, t = triplet, sp = septet): 7.79–7.69 (m, 2 H, Ph); 7.59–7.4 (m, 7 H, Ph); 6.99 (t, 2 H, $J_{H\text{-}H}$ = 8 Hz, Ph); 6.90 (m, 2 H, Ph); 3.52 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$/DMSO-d_6, 62.98 MHz) 160.2; 133.2 ($J_{P\text{–}C}$ = 9 Hz); 133.0; 130.6 ($J_{P\text{–}C}$ = 11 Hz); 130.2 ($J_{P\text{–}C}$ = 4 Hz); 126.9 ($J_{P\text{–}C}$ = 13 Hz); 120.2 ($J_{P\text{–}C}$ = 107 Hz); 54.5 (Me); P–C_{Ph} was not found. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.45 MHz) 25.7 ppm. IR (Nujol) 1182 cm^{-1} (P=O). Mp: 190–192 °C.

Bis(*o*-hydroxyphenyl)phenylphosphine Oxide (1b). Bis(*o*-methoxyphenyl)phenylphosphine oxide (1.3 g, 3.84 mmol) and anhydrous aluminum trichloride (1.5 g, 11 mmol) were suspended in toluene (20 mL), and the mixture was refluxed for 4 h. The mixture was cooled to 20 °C, and 2 N HCl (20 mL) was added. The toluene layer was separated. The aqueous layer was extracted twice with CH_2Cl_2. The organic fractions were combined, dried with brine and $MgSO_4$, and filtered, and solvent was reduced on a rotovap until a white solid precipitated out. The solid (0.8 g, 67%) was filtered, washed with ether and hexanes, and dried in vacuo. ^1H NMR (500 MHz, $CDCl_3$) 10.35 (s, 2 H, OH); 7.63–7.58 (m, 3 H, Ar); 7.50–7.42 (m, 4 H, Ar); 7.03–6.98 (m, 4 H, Ar); 6.88–6.84 (m, 2 H, Ar). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.98 MHz) 159.8 ($J_{P\text{–}C}$ = 3 Hz); 132.58; 131.6 ($J_{P\text{–}C}$ = 4 Hz); 130.2; 129.5 ($J_{P\text{–}C}$ = 10 Hz) 126.7 ($J_{P\text{–}C}$ = 12 Hz); 117.2 ($J_{P\text{–}C}$ = 7 Hz); 115.4 ($J_{P\text{–}C}$ = 7 Hz); P–C_{Ph} shifts were not found. $^{31}P\{^1H\}$ NMR 49.02. IR (Nujol) 1126 cm^{-1} (P=O). Mp: 229–230 °C. Anal. Calcd for $C_{18}H_{15}PO_3$: C, 69.66; H, 4.80; P, 9.99. Found: C, 69.23; H, 4.81; P, 9.76.

Bis(*o*-methoxyphenyl)-*n*-propylphosphine Oxide. The reaction was carried out as the phenyl analogue except *n*-propylphosphonic dichloride was used. The compound was obtained as an impure oil, which was dried in vacuo and used directly below. ^1H NMR (250 MHz, $CDCl_3$) 7.56 (dd, 2 H, $J_{H\text{-}H}$ = 2 Hz, $J_{P\text{-}H}$ = 13 Hz, Ar); 7.45 (t, 2 H, $J_{H\text{-}H}$ = 8 Hz, Ar); 6.99 (t, 2 H, $J_{H\text{-}H}$ = 7 Hz, Ar); 6.88 (m, 2 H, Ar); 3.71 (s, 6 H, Me); 2.5 (m, 2 H, PCH_2); 1.5 (m, 2 H, CH_2CH_3); 0.95 (t, 3 H, $J_{H\text{-}H}$ = 6 Hz, CH_3).

Bis(*o*-hydroxyphenyl)-*n*-propylphosphine Oxide (1c). Compound **1c** was prepared as **1b** in 37% yield from *n*-propylphosphonic dichloride. ^1H NMR (250 MHz, $CDCl_3$): 10.36 (s, 2 H, OH); 7.41–7.35 (m, 2 H, Ar); 7.25–7.17 (m, 2 H, Ar); 6.94–6.89 (m, 4 H, Ar); 2.31 (m, 2 H, PCH_2); 1.7 (m, 2 H, CH_2CH_3); 1.04 (t, 3 H, $J_{H\text{-}H}$ = 7 Hz, CH_3). $^{13}C\{^1H\}$ NMR (62.98 MHz, $CDCl_3$): 159.9 ($J_{P\text{–}C}$ = 3 Hz); 132.9; 131.0 ($J_{P\text{–}C}$ = 9 Hz); 118.3 ($J_{P\text{–}C}$ = 11 Hz); 116.0 ($J_{P\text{–}C}$ = 7 Hz); 114.2 ($J_{P\text{–}C}$ = 98 Hz); 31.0 ($J_{P\text{–}C}$ = 72 Hz, P–CH_2); 14.3 ($J_{P\text{–}C}$ = 16 Hz); 13.9 ($J_{P\text{–}C}$ = 4 Hz). $^{31}P\{^1H\}$ ($CDCl_3$, 202.45 MHz): 55.08 ppm. IR (Nujol): 1135 cm^{-1} (P=O). Mp: 156–157 °C. Anal. Calcd for $C_{15}H_{17}PO_3$: C, 65.20; H, 6.20; P, 11.20. Found: C, 65.01; H, 6.27; P, 11.50.

(η^6-Cymene)(η^3-tris(*o*-hydroxyphenyl)phosphine oxido-*O*,*O*′,*O*″)ruthenium(II) (2a). In a dry Schlenk tube, sodium hydride (24 mg, 60% oil dispersion, 0.6 mmol) was washed with hexanes (3×) and suspended in CH_2Cl_2 (50 mL). **1a** (100 mg, 0.3 mmol) was added followed after

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30 min by (η^6-cymene)dichlororuthenium(II) dimer (95 mg, 0.15 mmol). The mixture was stirred at 20 °C for 15 h. The mixture was filtered over Celite and volume reduced. Hexanes were added to afford a bright yellow precipitate (108 mg, 65% yield), which was filtered and dried in vacuo. ^1H NMR (500 MHz, $CDCl_3$): 10.6 (s, 1 H, OH); 7.67 (t, 1 H, Ar); 7.44 (t, 1 H, Ar); 7.2–6.95 (m, 8 H, Ar); 6.45 (m, 2 H, Ar); 5.38 (d, 2 H, J_{H-H} = 6 Hz, cymene); 5.17 (d, 2 H, cymene); 2.8 (sp, 1 H, J_{H-H} = 7 Hz, $CH(CH_3)_2$); 2.25 (s, 3 H, C–CH_3); 1.17 (d, 6 H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (62.98 MHz, CD_2Cl_2): 134.9; 133.9; 129.8 (J_{P-C} = 11 Hz); 122.3; 119.4; 114.5 (J_{P-C} = 13 Hz); 81.7; 77.4; 22.4. (Due to the poor solubility of **2a** in a variety of solvents only a few peaks were found.) $^{31}P\{^1H\}$ (202.45 MHz, $CDCl_3$): 49.67 ppm. IR (Nujol): 3084 cm^{-1} (OH); 1113 cm^{-1} (P=O). Anal. Calcd for $C_{28}H_{27}PO_4Ru$: C, 60.10; H, 4.86. Found: C, 60.23; H, 4.98.

(η^6-Cymene)(η^3-bis(*o*-hydroxyphenyl)phenylphosphine oxido-*O*,*O*′,*O*″)ruthenium(II) (2b). **2b** was prepared in a manner analogous to **2a** from sodium hydride (115 mg, 2.9 mmol, 60% oil dispersion), **1b** (1.3 mmol, 400 mg), and the ruthenium dichloride dimer (400 mg, 0.65 mmol) to yield **2b** (570 mg, 81% yield). A second crop (85 mg, 93% overall) of less pure material was obtained by cooling the mother liquor to −10 °C for 20 h. ^1H NMR (500 MHz, $CDCl_3$): 7.97 (m, 2 H, Ar); 7.60 (m, 1 H, Ar); 7.53 (m, 2 H, Ar); 7.10 (m, 2 H); 6.98 (dd, 2 H, J_{P-H} = 5 Hz, J_{H-H} = 8 Hz); 6.87 (ddd, 2 H, J_{H-H} = 2 Hz, J_{H-H} = 8 Hz, J_{P-H} = 14 Hz); 6.38 (m, 2 H); 5.40 (d, 2 H, J_{H-H} = 6 Hz); 5.15 (d, 2 H); 2.82 (sp, J_{H-H} = 7 Hz); 2.28 (s, 3 H, C–CH_3); 1.19 (d, 6 H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.98 MHz): 162.4 (C_{Ph}–O); 123.1 (J_{P-C} = 9 Hz); 122.8 (J_{P-C} = 20 Hz); 120.0 (J_{P-C} = 11 Hz); 118.8 (J_{P-C} = 13 Hz); 116.3 (J_{P-C} = 105 Hz); 112.2 (J_{P-C} = 8 Hz); 103.6; 103.8; 103.0 (J_{P-C} = 105 Hz); 87.5; 85.9; 72.0; 67.1; 21.8; 21.5; 12.2. $^{31}P\{^1H\}$ (202.45 MHz, $CDCl_3$): 42.6 ppm. IR (Nujol): 1118 cm^{-1} (P=O). Anal. Calcd for $C_{28}H_{31}O_3PRu \cdot H_2O$: C, 59.88; H, 5.21. Found: C, 59.98; H, 5.15.

Crystal Structure of 2b. A red crystal of **2b** suitable for X-ray diffraction was grown by slow diffusion of ether into CH_2Cl_2 solutions of **2b** at 0 °C and an 0.12-mm cube cut out from a large needle. The structure (Figure 1) was solved by direct methods with SHELXS86.[30] The compound crystallizes in the space group $P\bar{1}$ with lattice constants a = 10.407 (6) Å, b = 14.334 (6) Å, c = 13.25 (1) Å, α = 75.85 (5)°, β = 129.85 (4)°, γ = 81.28 (4)°, V = 1340 (12) Å^3, Z = 2, R = 6.6%, R_w = 11.4%. A total of 4758 independent reflections were collected on a Syntex P3 diffractometer with graphite-monochromated Mo Kα radiation. A total of 3492 reflections were considered observed ($I > 3\sigma(I)$). Refinement of scale factor and positional and isotropic thermal parameters for the non-hydrogen atoms were carried out to convergence. The positions of the nonmethyl hydrogen atoms were located from a difference Fourier synthesis. The final cycles of refinement allowed refinement of the nonhydrogen positions with anisotropic thermal parameters. Anomalous dispersion corrections were introduced for Ru and P. An ORTEP[31] diagram was drawn.

(η^6-Cymene)(η^3-bis(*o*-hydroxyphenyl)propylphosphine oxido-*O*,*O*′,*O*″)ruthenium(II) (2c). Compound **2c** was prepared in an analogous manner in 80% yield from **1c** (0.18 mmol, 50 mg), sodium hydride (0.3 mmol, 16 mg), and ruthenium dimer (0.09 mmol, 55 mg). ^1H NMR (250 MHz, $CDCl_3$): 7.06 (t, 2 H); 6.93 (m, 2 H); 6.81 (ddd, J_{H-H} = 2 Hz, J_{H-H} = 6 Hz, J_{P-H} = 13 Hz); 6.40 (m, 2 H); 5.34 (d, 2 H, J_{H-H} = 6 Hz); 5.07 (d, 2 H); 2.8 (sp, 1 H, J_{H-H} = 7 Hz, $CH(CH_3)_2$); 2.24 (s, 3 H, C–CH_3); 2.20 (m, 2 H); 1.70 (dt, 2 H, J_{P-H} = 14 Hz, J_{H-H} = 7 Hz); 1.17 (d, 6 H, $CH(CH_3)_2$); 1.08 (t, 3 H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 62.98 MHz): 171.4 (C_{Ph}–O); 133.1; 128.3 (J_{P-C} = 12 Hz); 122.2 (J_{P-C} = 7 Hz); 113.9 (J_{P-C} = 13 Hz); 97.5; 96.4; 82.5; 77.2; 31.4; 25.1 (J_{P-C} = 74 Hz); 22.6; 17.6; 15.9 (J_{P-C} = 15 Hz); 15.3 (J_{P-C} = 3 Hz); P–C_{Ph} was not found. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.45 MHz): 47.69 ppm. IR (Nujol): 1130 cm^{-1}. Anal. Calcd for $C_{25}H_{29}O_3PRu \cdot 0.5H_2O$: C, 57.90; H, 5.83. Found: C, 58.08; H, 5.85.

Reaction of 2a with Br_2. To a solution of **2a** (50 mg, 0.0893 mmol) in CH_2Cl_2 (30 mL) was added Br_2 (2 mL) and the mixture stirred for 18 h at 20 °C. Hexanes (25 mL) were added to afford a precipitate, which was filtered and dried in vacuo, to give (η^6-Cymene)ruthenium(II) dibromide dimer (30 mg, 85% yield) and tris(3,5-dibromo-2-hydroxyphenyl)phosphine oxide (**1d**) (16 mg, 22% yield). ^1H NMR ($CDCl_3$, 250 MHz): 8.9 (br, 3 H); 7.88 (d, 3 H, J_{H-H} = 2 Hz); 7.35 (dd, 3 H, J_{P-H} = 12 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): 39.5 ppm. IR ($CDCl_3$, NaCl plates): 1123 cm^{-1} (P=O). Tris(3,5-dibromo-2-hydroxyphenyl)phosphine oxide (**1d**) is not formed by direct reaction of Br_2 with **1a** but with catalytic (η^6-cymene)dichlororuthenium(II) dimer present.

Photochemical Reaction of 2b with Methyl Propiolate. A quartz tube was charged with **2b** (65 mg, 0.119 mmol), methyl propiolate (1 mL, 11.2 mmol), a stir bar, and CH_2Cl_2 (50 mL). The tube was placed in a photoreactor for 4 h. The solution was then transferred to a round-bottom flask and solvent removed on a rotovap. The residue was put though a column (100–200 mesh silica (5 × 5 mm), CH_2Cl_2 eluent) to yield trimethyl 1,3,5- (and trimethyl-1,2,4-) benzenetricarboxylate (4.99 mmol, 250 mg, 1.2 mol/(mol **2a** h)) in a 1:2.3 ratio. The reaction was run again for 17 h to give cyclotrimer (0.52 g, 21.8 mmol, 1.3 mol/(mol **2b** h)).

Thermal Reaction of 2b with Methyl Propiolate. A Schlenk tube equipped with a reflux condenser was charged with **2b** (47 mg, 0.086 mmol), methyl propiolate (1 mL, 11.2 mmol), and toluene (25 mL). The mixture was refluxed for 7 h, cooled and toluene removed in vacuo. The residue was put though a column (100–200 mesh silica (5 × 5 mm), CH_2Cl_2 eluent) to yield trimethyl 1,3,5- (and trimethyl-1,2,4-) benzenetricarboxylate (84 mg, 0.33 mmol, 0.55 mol/(mol **2b** h)) in a 1:1.8 ratio. Variable-temperature ^1H NMR spectroscopy shows that **2b** begins to react with methyl propiolate at 95 °C.

Bis(*o*-methoxyphenyl)phenylphosphine Sulfide (3). The Grignard of *o*-bromoanisole (4.2 mL, 0.034 mmol) was treated with phenylphosphonothioic dichloride (2.6 mL, 0.017 mmol) at 0 °C as previously described for the oxide analogue to give **3** (1.13 g, 21% yield). ^1H NMR ($CDCl_3$, 250 MHz): 7.88 (ddd, 2 H, J_{P-H} = 14 Hz, J_{H-H} = 9 Hz, J_{H-H} = 2 Hz); 7.76 (ddd, 2 H, J_{P-H} = 16 Hz, J_{H-H} = 8 Hz, J_{H-H} = 2 Hz); 7.49–7.33 (m, 5 H); 7.04 (dt, 2 H, J_{H-H} = 10 Hz); 6.87 (dd, 2 H, J_{H-H} = 2 Hz). $^{13}C\{^1H\}$ NMR (62.98 MHz, CD_2Cl_2): 160.2 (J_{P-C} = 3 Hz); 134.1 (J_{P-C} = 11 Hz); 133.2 (J_{P-C} = 10 Hz); 133.1, 132 (J_{P-C} = 11 Hz); 130.4; 121.0 (J_{P-C} = 88 Hz); 120.7 (J_{P-C} = 13 Hz); 111.4 (J_{P-C} = 6 Hz); 55.2; P–C_{Ph} was not found. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): 38.09 ppm. Mp: 182–183 °C. Anal. Calcd for $C_{20}H_{19}O_2PS \cdot 0.25H_2O$: C, 66.93; H, 5.48. Found: C, 66.94; H, 5.35.

Bis(*o*-hydroxyphenyl)phenylphosphine Sulfide (4). **3** (1 g, 0.0028 mol) was demethylated as described for **1b** above to give **4** (0.9 g, 44% yield). ^1H NMR ($CDCl_3$, 250 MHz): 9.06 (s, 2 H); 7.69–7.43 (m, 7 H); 7.03 (t, 2 H); 6.85 (m, 2 H); 6.67 (dd, 2 H, J_{P-H} = 15 Hz, J_{H-H} = 8 Hz). $^{13}C\{^1H\}$ NMR (62.98 MHz, $CDCl_3$/DMSO-d_6): 159.4 (J_{P-C} = 4 Hz); 133.2; 132.7; 132.4 (J_{P-C} = 107 Hz); 131.0; 130.6 (J_{P-C} = 3 Hz); 127.4 (J_{P-C} = 13 Hz); 118.6 (J_{P-C} = 13 Hz); 116.8 (J_{P-C} = 6 Hz); 114.2 (J_{P-C} = 89 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): 32.3 ppm. Mp: 196–197 °C. Anal. Calcd for $C_{18}H_{15}O_2PS$: C, 66.24; H, 4.6; P, 9.49. Found: C, 66.36; H, 4.65; P, 9.51.

(η^6-Cymene)(η^3-bis(*o*-hydroxyphenyl)phenylphosphine sulfido-*O*,*O*′,*S*)ruthenium(II) (5). Complex **5** was prepared as the oxide analogue (68 mg, 79% yield) from sodium hydride (13 mg, 0.4 mmol, 60% oil dispersion), **4** (50 mg, 0.0153 mmol), and the ruthenium dimer (47 mg, 0.0765 mmol). ^1H NMR ($CDCl_3$, 250 MHz): 8.11 (m, 2 H); 7.63–7.48 (m, 3 H); 7.12–6.91 (m, 6 H); 6.37 (m, 2 H); 5.38 (d, 2 H, J_{H-H} = 7 Hz); 5.28 (d, 2 H); 2.71 (sp, 1 H, J_{H-H} = 7 Hz); 2.26 (s, 3 H); 1.07 (d, 6 H). $^{13}C\{^1H\}$ NMR (62.98 MHz, CD_2Cl_2): 171.7 (J_{P-C} = 4 Hz); 134.0 (J_{P-C} = 9 Hz); 133.3 (J_{P-C} = 3 Hz); 129.8 (J_{P-C} = 9 Hz); 129.2 (J_{P-C} = 11 Hz); 123.5 (J_{P-C} = 9 Hz); 133.3 (J_{P-C} = 14 Hz); 112.6 (J_{P-C} = 91 Hz); 99.8; 99.6; 83.9; 80.8; 31.4; 22.0; 17.9; P–C_{Ph} was not found. $^{31}P\{^1H\}$ NMR (202.45 MHz, $CDCl_3$): 20.7 ppm. Anal. Calcd for $C_{28}H_{27}O_2PRuS \cdot 0.25CH_2Cl_2$: C, 58.31; H, 4.76. Found: C, 58.35; H, 4.89.

(η^3-Tris(diphenyloxophosphoranyl)methane)(η^6-cymene)ruthenium(II) Bis(hexafluoroantimonate) (6). Silver hexafluoroantimonate (112 mg, 0.32 mmol) was added to a CH_2Cl_2 (20 mL) solution of Htriso (100 mg, 0.16 mmol) and (η^6-cymene)ruthenium dichloride dimer (50 mg, 0.08 mmol) in the dark. The mixture was stirred at 25 °C for 3.5 h and filtered over Celite. The volume was reduced to ca. 5 mL and ether was added to afford an orange precipitate that was filtered and dried in vacuo. Recrystallization from CH_2Cl_2/ether yielded **6** (140 mg, 65% yield). ^1H NMR (250 MHz, CD_2Cl_2): 7.7–7.5 (m, 12 H, Ph); 7.3–7.1 (m, 18 H, Ph); 6.36 (d, 2 H, J = 6 Hz, cymene); 6.24 (d, 2 H, cymene); 5.46 (q, 1 H, J_{P-H} = 7 Hz, HCP_3); 3.34 (sp, 1 H, J = 7 Hz, $CHMe_2$); 1.83 (s, 3 H, CH_3); 1.29 (d, 6 H, $CH(CH_3)_2$). ^{13}C NMR (62.98 MHz, CD_2Cl_2): 134.3 *p*-Ph; 130.8 (J_{P-C} = 4 Hz); 129.9 (J_{P-C} = 8 Hz, Ph); 126.5 (J_{P-C} = 110 Hz, C_{Ph}–P); 101.5 (cymene); 96.7 (cymene); 78.4 (cymene); 78.1 (cymene); 38.3 (J_{P-C} = 34 Hz, HC–P); 32.4 (alkyl); 22.5 (alkyl); 19.02 (alkyl). ^{31}P NMR (202.45 MHz, CD_2Cl_2): 48.1 ppm. IR (Nujol): 1149, 1132, 1115 cm^{-1} (P=O). Anal. Calcd for $C_{47}H_{45}F_{12}P_3O_3RuSb_2$: C, 41.83; H, 3.42. Found: C, 41.71; H, 3.32.

[(Cyclopentadienyl)tris(diethyl phosphonato-*P*)cobaltato-*O*,*O*′,*O*″](η^6-cymene)ruthenium(II) Hexafluoroantimonate (7). A Schlenk tube was charged with (η^6-cymene)ruthenium dichloride dimer (300 mg, 0.49 mmol); sodium hexafluoroantimonate (254 mg, 0.97 mmol), $NaL' \cdot H_2O$ (516 mg, 0.97 mmol), and CH_2Cl_2 (50 mL) and stirred at 25 °C for 3 h. The solution was filtered over Celite and volume reduced to ca. 10

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mL. Hexanes were added to afford an orange precipitate that was filtered and dried in vacuo. Recrystallization from $\mathrm{CH_2Cl_2}$/ether yielded **7** (935 mg, 96% yield). ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): 5.38 (d, 2 H, J = 5.8 Hz, arene); 5.18 (d, 2 H, arene); 4.83 (s, 5 H, Cp); 4.0 (m, 12 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 2.77 (sp, 1 H, J = 7 Hz, $\mathrm{C}H\mathrm{(CH_3)_2}$); 2.11 (s, 3 H, $\mathrm{CH_3}$); 1.31 (d, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$); 1.28 (t, 18 H, $\mathrm{OCH_2C}H_3$). ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 63.98 MHz): 98.04 (cymene); 95.1 (cymene); 89.9 (Cp); 79.5 (cymene); 78.4 (cymene); 61.6 ($\mathrm{PO}C\mathrm{H_2CH_3}$); 31.1 (alkyl); 22.1 (alkyl); 17.1 (alkyl); 16.7 (alkyl). ^{31}P NMR (202.45 MHz, $\mathrm{CDCl_3}$): 81.1 ppm. IR (Nujol) 1157 (w), 1113 (s) cm^{-1} ($\mathrm{P{=}O}$). Anal. Calcd for $\mathrm{C_{27}H_{49}F_6CoO_9P_3RuSb}$: C, 32.22; H, 4.91; P, 9.23. Found: C, 32.30; H, 4.97; P, 9.25.

(η^3-Tris(diphenyloxophosphoranyl)methane)tricarbonylruthenium(II) Bis(hexafluoroantimonate) (8a) and (η^3-Tris(diphenyloxophosphoranyl)methanido)tricarbonylruthenium(II) Bis(hexafluoroantimonate) (8b). Silver hexafluoroantimonate (138 mg, 0.4 mmol) was added to a $\mathrm{CH_2Cl_2}$ (20 mL) solution of $\mathrm{HTrisO_3}$ (120 mg, 0.2 mmol) and ruthenium tricarbonyl dichloride dimer (50 mg, 0.09 mmol) in the dark. The mixture was stirred at 25 °C for 1 h and filtered over Celite. The volume was reduced to ca. 5 mL, and ether was added to afford a white precipitate that was filtered and dried in vacuo. Recrystallization from $\mathrm{CH_2Cl_2}$/ether yielded the mixture of products. ^{1}H NMR (250 MHz, acetone-d_6): 7.7–7.5 (m, Ph); 7.3–7.1 (m, Ph); 6.49 (q, 1 H, $J_{\mathrm{P-H}}$ = 7.5 Hz, $H\mathrm{CP_3}$). IR (Nujol): 2161 (s), 2105 (s); 2147 (m), 2048 (m) cm^{-1} (CO).

[(Cyclopentadienyl)tris(diethyl phosphonato-*P*)cobaltato-*O*,*O′*,*O″*]tricarbonylruthenium(II) Hexafluoroantimonate (9). A Schlenk tube was charged with tricarbonyl ruthenium dichloride dimer (400 mg, 0.78 mmol), $\mathrm{NaL'{\cdot}H_2O}$ (824 mg, 1.56 mmol), and $\mathrm{CH_2Cl_2}$ (50 mL), silver hexafluoroantimonate (580 mg, 1.68 mmol) was added in the dark, and the mixture was stirred at 25 °C for 1 h. The solution was filtered over Celite and volume reduced to ca. 10 mL. Hexanes were added to afford a pale yellow precipitate that was filtered and dried in vacuo. Recrystallization from $\mathrm{CH_2Cl_2}$/ether yielded **9** (970 mg, 67% yield). ^{1}H NMR (250 MHz, acetone-d_6): 5.34 (s, 5 H, Cp); 4.25 (m, 12 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 1.39 (t, 18 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$). ^{13}C NMR (62.98 MHz, $\mathrm{CD_2Cl_2}$): 186.1 (CO); 90.8 (Cp); 62.7 ($\mathrm{O}C\mathrm{H_2CH_3}$); 16.7 ($\mathrm{OCH_2}C\mathrm{H_3}$). ^{31}P NMR (202.45 MHz, $\mathrm{CD_2Cl_2}$): 119.2 ppm. IR (Nujol): 2140, 2061 cm^{-1} (CO); 1161 cm^{-1} ($\mathrm{P{=}O}$). Anal. Calcd for $\mathrm{C_{21}H_{35}O_{12}P_3RuSb}$: C, 26.05; H, 3.64. Found: C, 25.98; H, 4.02.

[(Cyclopentadienyl)tris(diethyl phosphonato-*P*)cobaltato-*O*,*O′*,*O″*]carbonylbis(tetrahydrofuran)ruthenium(II) Hexafluoroantimonate (10a). A dry Schlenk tube was charged with **9** (219 mg, 0.24 mmol), THF (20 mL), and trimethylamine oxide dihydrate (53 mg, 0.48 mmol) and stirred at 25 °C for 1 h. Solvent was removed in vacuo and $\mathrm{CH_2Cl_2}$ (15 mL) added. The $\mathrm{CH_2Cl_2}$ solution was filtered over Celite. Volume was reduced to ca. 5 mL and hexanes added to afford a precipitate. The precipitate was filtered, dried in vacuo, and recrystallized from $\mathrm{CH_2Cl_2}$ and hexanes (yield 250 mg, 56%). ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): 5.02 (s, 5 H, Cp); 4.4 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 3.9 (m, 8 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 3.7 (m, 4 H, THF); 3.6 (m, 4 H, THF); 1.8 (m, 8 H, THF); 1.38 (t, 6 H, $\mathrm{OCH_2C}H_3$); 1.32 (m, 12 H, $\mathrm{OCH_2C}H_3$). ^{13}C NMR (62.98 MHz, $\mathrm{CDCl_3}$): 209.9 (CO); 90.1 (Cp); 74.5 ($\mathrm{O}C\mathrm{H_2}$); 61 (b, $\mathrm{PO}C\mathrm{H_2}$); 24.9 ($\mathrm{OCH_2}C\mathrm{H_2}$); 16.0 ($\mathrm{CH_3}$). ^{31}P NMR (202.45 MHz, $\mathrm{CDCl_3}$): 128.0 (d, 2 P, $J_{\mathrm{P-P}}$ = 140 Hz); 114.2 (t, 1 P). IR (Nujol): 1939 cm^{-1} (CO); 1159, 1103 cm^{-1} ($\mathrm{P{=}O}$). Anal. Calcd for $\mathrm{C_{26}H_{51}CoF_6O_{12}P_3RuSb}$: C, 29.90; H, 4.92; P, 8.89. Found: C, 30.11; H, 4.97; P, 9.24.

[(Cyclopentadienyl)tris(diethyl phosphonato-*P*)cobaltato-*O*,*O′*,*O″*]carbonylbis(dioxane)ruthenium(II) Hexafluoroantimonate (10b). The reaction was performed as **10a** from **9** (100 mg, 0.103 mmol), trimethylamine oxide (24 mg, 0.25 mmol), and dioxane (10 mL). Recrystallization from $\mathrm{CH_2Cl_2/Et_2O}$ and hexanes yielded **10b** (35 mg, 33%). ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$): 5.04 (s, 5 H, Cp); 4.5 (m, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 4.4 (m, 2 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 3.9 (m, 8 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 3.7 (m, 8 H, dioxane); 3.6 (m, 8 H, dioxane); 1.39 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$); 1.25 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$); 1.23 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$). ^{31}P NMR (202.45 MHz, $\mathrm{CDCl_3}$): 129.6 (d, 2 P, $J_{\mathrm{P-P}}$ = 139 Hz); 114.1 (t, 1 P). IR (Nujol): 1954 (CO); 1162, 1126, 1105 cm^{-1} ($\mathrm{P{=}O}$). Anal. Calcd for $\mathrm{C_{26}H_{51}CoF_6O_{14}P_3RuSb{\cdot}3H_2O}$: C, 27.62; H, 4.95. Found: C, 27.45; H, 4.62.

[(Cyclopentadienyl)tris(diethyl phosphonato-*P*)cobaltato-*O*,*O′*,*O″*]dicarbonylmethoxyruthenium(II) (11a). A Schlenk tube was charged with **9** (100 mg, 0.10 mmol), methanol (20 mL), and trimethylamine oxide (13 mg, 0.11 mmol); the mixture was stirred at 25 °C for 2 h. Methanol was removed in vacuo. Ether was added, and the mixture was filtered over Celite to remove salts. The volume was reduced to ca. 1 mL, and a minimal amount of hexanes was added to afford a yellow precipitate (38 mg, 54% yield). ^{1}H NMR (250 MHz, $\mathrm{C_6D_6}$): 4.81 (s, 5 H, Cp); 4.34 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 4.14 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 3.94 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 3.67 (s, 3 H, $\mathrm{OC}H_3$); 1.27 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$); 1.17 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$); 1.11 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$). ^{13}C NMR (62.98 MHz, $\mathrm{C_6D_6}$): 198.7 (CO); 89.5 (Cp); 62.3 (b, $\mathrm{PO}C\mathrm{H_2}$); 61.0 (m, $\mathrm{PO}C\mathrm{H_2}$); 53.8 ($\mathrm{OCH_3}$); 16.6 ($\mathrm{OCH_2}C\mathrm{H_3}$). ^{31}P NMR (202.45 MHz, $\mathrm{C_6D_6}$): 122.9 (t, 1 P, $J_{\mathrm{P-P}}$ = 157 Hz); 113.8 (d, 2 P). IR (Nujol): 2047, 1966 cm^{-1} (CO); 1164, 1105 cm^{-1} ($\mathrm{P{=}O}$). Anal. Calcd for $\mathrm{C_{20}H_{38}CoO_{12}P_3Ru}$: C, 33.15; H, 5.29. Found: C, 32.71; H, 5.06.

[(Cyclopentadienyl)tris(diethyl phosphonato-*P*)cobaltato-*O*,*O′*,*O″*]dicarbonyl(η^1-acetato)ruthenium(II) (11b). A Schlenk tube was charged with **9** (207 mg, 0.22 mmol), acetic acid (10 mL), and trimethylamine oxide (24 mg, 0.22 mmol); the mixture was stirred at 25 °C for 2 h. Acetic acid was removed in vacuo (to dryness), ether was added, and the mixture was filtered over Celite to remove salts. The volume was reduced to ca. 1 mL and a minimal amount of hexanes added until the solution was turbid. After the mixtures was cooled for 5 h at −10 °C, yellow crystals formed, which were filtered and dried to yield **11b** (80 mg, 58% yield). ^{1}H NMR (250 MHz, $\mathrm{C_6D_6}$): 4.80 (s, 5 H, Cp); 4.3 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 4.1 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 3.9 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 2.18 (s, 3 H, $\mathrm{O_2CC}H_3$); 1.26 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$); 1.18 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$); 1.11 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$). ^{13}C NMR (62.98 MHz, $\mathrm{C_6D_6}$): 198.7 (CO); 171.3 ($\mathrm{O}C\mathrm{CH_3}$); 89.5 (Cp); 61.5 (b, $\mathrm{PO}C\mathrm{H_2}$); 60.8 ($\mathrm{PO}C\mathrm{H_2}$); 21.9 ($\mathrm{O_2C}C\mathrm{H_3}$); 16.6 (b, $\mathrm{OCH_2}C\mathrm{H_3}$). ^{31}P NMR (202.45 MHz, $\mathrm{C_6D_6}$): 121.3 (t, 1 P, $J_{\mathrm{P-P}}$ = 140 Hz); 114.0 (d, 2 P). IR (Nujol): 2044, 1964 cm^{-1} (CO); 1635 cm^{-1} ($\mathrm{C{=}O}$); 1158, 1113 cm^{-1} ($\mathrm{P{=}O}$). Anal. Calcd for $\mathrm{C_{21}H_{39}CoO_{13}P_3Ru}$: C, 33.52; H, 5.22; P, 12.48. Found: C, 33.60; H, 5.20; P, 12.26.

[(Cyclopentadienyl)tris(diethyl phosphonato-*P*)cobaltato-*O*,*O′*,*O″*]dicarbonyl(isopropoxy)ruthenium(II) (10c). A Schlenk tube was charged with **9** (112 mg, 0.112 mmol), 2-propanol (5 mL), and trimethylamine oxide (13 mg, 0.11 mmol); the mixture was stirred at 25 °C for 30 min. 2-Propanol was removed in vacuo (to dryness), ether was added, and the mixture was filtered over Celite to remove salts. The volume was reduced to ca. 1 mL, and a minimal amount of hexanes was added until the solution was turbid. After the mixture was cooled, a precipitate formed, which was filtered and dried to yield **11c** (40 mg, 46% yield). Two recrystallizations from hexanes were required to remove all of the $\mathrm{Me_3NH[SbF_6]}$. ^{1}H NMR (250 MHz, toluene-d_8): 4.83 (sp, 1 H, $\mathrm{C}H\mathrm{(Me)_2}$); 4.79 (s, 5 H, Cp); 4.25 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 4.12 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 3.89 (m, 4 H, $\mathrm{OC}H_2\mathrm{CH_3}$); 1.33 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$); 1.27 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$); 1.24 (d, 6 H, $\mathrm{OCH(C}H_3\mathrm{)_2}$); 1.10 (t, 6 H, $J_{\mathrm{H-H}}$ = 7 Hz, $\mathrm{OCH_2C}H_3$); 3.30 ($\mathrm{Me_3NH[SbF_6]}$). ^{13}C NMR (62.98 MHz, toluene-d_8): 198.4 (CO); 89.8 (Cp); 62.2 (b, $\mathrm{PO}C\mathrm{H_2}$); 61.1 ($\mathrm{PO}C\mathrm{H_2}$); 58.0 ($\mathrm{O}C\mathrm{H(Me)_2}$); 22.53 ($\mathrm{CH(}C\mathrm{H_3)_2}$); 16.8 ($\mathrm{OCH_2}C\mathrm{H_3}$). ^{31}P NMR (202.45 MHz, $\mathrm{C_6D_6}$): 124.1 (t, 1 P, $J_{\mathrm{P-P}}$ = 145 Hz); 114.5 (d, 2 P). IR ($\mathrm{CH_2Cl_2}$): 2054, 1975 cm^{-1} (CO); 1150, 1110 cm^{-1} ($\mathrm{P{=}O}$). Anal. Calcd for $\mathrm{C_{23}H_{42}CoO_{12}P_3Ru{\cdot}2H_2O{\cdot}(Me_3NHSbF_6)}$: C, 28.51; H, 5.15. Found: C, 28.60; H, 4.76.

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Supplementary Material Available: Full experimental crystallographic details for $\mathrm{RuPO_3C_{28}H_{27}}$ (**2b**) and listings of crystal data, positional parameters, anisotropic thermal parameters, and all bond lengths and angles (6 pages); a table of F_o and F_c (38 pages). Ordering information is given on any current masthead page.