

symmetry (neglecting the *o*-methyl substituent of the tolyl group). This effect should also be operative for an arsenic analogue, but preparative experiments have so far been unsuccessful, probably owing to a further increase of the radius of the central element, which renders Au...Au contacts more difficult.

Arylphosphinidene groups RP bridging four metal atoms are not completely unknown in the structural chemistry of metal clusters. A very good example in case is the tetranuclear rhodium(I) complex  $\{\text{Rh}_4(\text{CO})_4[\mu\text{-P}(\text{C}_6\text{H}_{11})_2]_4(\mu_4\text{-PC}_6\text{H}_{11})\}$  with 4-fold symmetry.<sup>28</sup> It should be noted, however, that the open-shell configuration of electrons of the Rh(I) centers ( $4d^8$ ) suggests metal-metal bonding in classical terms for these clusters, while for gold(I) with its formally closed-shell configuration ( $5d^{10}$ ) such bonding interactions are ruled out, unless a mixing with empty 6s states<sup>29</sup> through relativistic contraction of the latter provides a new basis for such bonding contacts. It is this point which makes

the title compounds interesting novel species in cluster chemistry, and the almost complete absence of similar phenomena with the neighboring elements platinum and mercury once more distinguishes gold as a unique element.

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**Registry No.** 1, 132157-62-1; 2, 141088-89-3; 2- $4\text{C}_6\text{H}_6$ , 141088-92-8; 3, 141088-91-7;  $[(\text{C}_6\text{H}_5)_3\text{PAu}]_3\text{O}^+\text{BF}_4^-$ , 53317-87-6;  $[\text{Ph}_3\text{PAu}]^+[\text{BF}_4]^-$ , 67215-70-7; phenyltris[(triphenylphosphine)aurio(I)]phosphonium(+) tetrafluoroborate, 132157-66-5.

**Supplementary Material Available:** For complexes 1 and 2, tables of crystallographic data and anisotropic thermal parameters (12 pages); tables of observed and calculated structure factor amplitudes (122 pages). Ordering information is given on any current masthead page.

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## Synthesis, Characterization, and Reactivity of Ruthenium Carbonyl Complexes Containing a Chelating Triphosphine Ligand and Two Weakly Coordinated Anions

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Protonation of *cis-mer*- $\text{RuH}_2(\text{CO})(\text{Cytpp})$  ( $\text{Cytpp} = \text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)_2$ ) with excess HX ( $X = \text{BF}_4, \text{O}_3\text{SCF}_3$ ) in benzene/diethyl ether produces air-stable complexes with two weakly coordinated anions, viz., *cis-mer*- $\text{RuX}_2(\text{CO})(\text{Cytpp})$  ( $X = \text{BF}_4$  (2),  $\text{O}_3\text{SCF}_3$  (3)). A single-crystal X-ray diffraction analysis at 223 K shows that 3 crystallizes in the space group  $P2_1/c$  with cell parameters  $a = 11.712$  (2) Å,  $b = 15.338$  (2) Å,  $c = 27.072$  (3) Å,  $\beta = 98.58$  (1)°,  $Z = 4$ ,  $V = 4809$  (1) Å<sup>3</sup>,  $R = 0.041$ , and  $R_w = 0.046$  for the 7036 intensities with  $F_o^2 > 3\sigma(F_o^2)$  and the 539 variables. The molecules contain two *cis*-oriented monodentate  $\text{O}_3\text{SCF}_3^-$  ligands. The structural behavior of 2 and 3 in both  $\text{CD}_2\text{Cl}_2$  and acetone- $d_6$  was investigated by variable-temperature  $^31\text{P}\{\text{H}\}$  and  $^19\text{F}\{\text{H}\}$  NMR spectroscopies in the range 178–303 K; a complex behavior involving species with coordinated and free  $\text{BF}_4^-$  and  $\text{O}_3\text{SCF}_3^-$  ions was observed. 2 and 3 are useful synthons for a variety of coordination and organometallic complexes. 2 undergoes substitution reactions with acetonitrile and organic isocyanides to afford disubstituted complexes *cis-mer*- $[\text{Ru}(\text{CO})\text{L}_2(\text{Cytpp})][\text{BF}_4]_2$  ( $L = \text{MeCN}, \text{CNBu-}t, \text{CNCy}$ ). New Ru-F complexes  $[\text{Ru}(\text{F})(\text{CO})(\text{L})(\text{Cytpp})][\text{BF}_4]$  ( $L = \text{H}_2\text{O}, \text{CO}, \text{CNBu-}t$ ) have also been synthesized from 2. The absence of fluoride abstraction from triflate and the solubility of 3 in THF render this a more versatile starting material than 2. Substitution reactions with acetonitrile and ammonia produce disubstituted complexes *cis-mer*- $[\text{Ru}(\text{CO})\text{L}_2(\text{Cytpp})][\text{O}_3\text{SCF}_3]_2$  ( $L = \text{MeCN}, \text{NH}_3$ ). The reaction of 3 with an excess of trimethyl phosphite leads only to the monosubstituted phosphite products  $[\text{Ru}(\text{CO})(\text{P}(\text{OMe})_3)(\text{Cytpp})][\text{O}_3\text{SCF}_3]_2$  (11a, 11b), which probably differ by the orientation of the Ph group of Cytpp. Complexes with the cations  $[\text{Ru}(\text{X})(\text{CO})(\text{P}(\text{OMe})_3)(\text{Cytpp})]^+$  ( $X = \text{Cl}, \text{OMe}$ ) are generated from reactions of mixtures of 11a and 11b with the appropriate anion. 3 also reacts with selected anions ( $X^- = \text{Me}^-, \text{I}^-, \text{and H}^-$ ) to afford complexes *cis-mer*- $\text{RuX}_2(\text{CO})(\text{Cytpp})$ .

### Introduction

In recent years, transition-metal complexes with weakly coordinated anions have been the focus of many studies and several reviews.<sup>1</sup> These complexes have been recognized for their utility as starting materials that readily undergo substitution reactions even with weakly nucleophilic ligands under mild conditions.<sup>2</sup> Although some ruthenium complexes with multiple phosphine ligands and weakly coordinated anions have been isolated,<sup>3,4</sup> we found no examples that contain a chelated triphosphine ligand. The advantages of using chelated triphosphine ligands over monodentate phosphine ligands in the synthesis of transition-metal

complexes have been enumerated.<sup>5</sup> One advantage in particular, viz., the added control on the coordination number and geometry of products, was utilized in this study to prepare complexes with weakly coordinated anions that do not lose phosphine ligands.

A variety of reactions of ruthenium dihydridophosphine complexes with hydride abstracting reagents<sup>6</sup> or with strong acids containing poorly coordinating anions<sup>7,8</sup> have failed to produce ruthenium phosphine complexes with weakly ligated anions. In particular, the reaction of *cis-mer*- $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$  with  $\text{HBF}_4$  (aq) gives *mer*- $[\text{RuH}(\text{CO})(\text{H}_2\text{O})(\text{PPh}_3)_3][\text{BF}_4]$ , which upon carbonylation loses phosphine to yield  $[\text{RuH}(\text{CO})_2(\text{H}_2\text{O})(\text{PPh}_3)_2][\text{BF}_4]$ .<sup>8</sup> However, the reactions of *cis-mer*- $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$  with sulfonic acids,  $\text{HO}_3\text{SR}$  ( $R = \text{Me}, \text{CF}_3$ , and

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Table I. Phosphorus-31, Fluorine-19, and Proton NMR Data for the New *mer*-Ru(Cyttp) Complexes<sup>a</sup>

complex	<sup>31</sup> P{ <sup>1</sup> H} NMR <sup>b</sup>			<sup>19</sup> F{ <sup>1</sup> H} NMR <sup>c</sup>			<sup>1</sup> H NMR features <sup>d</sup>
	δ(P <sub>C</sub> )	δ(P <sub>W</sub> )	J <sub>PC<sub>W</sub></sub>	δF	J <sub>PC<sub>F</sub></sub>	J <sub>P<sub>W</sub>F</sub>	
<i>cis-anti</i> -RuCl <sub>2</sub> (CO)(Cyttp) (1) <sup>e</sup>	18.4	4.4	31.9				
<i>cis</i> -Ru(BF <sub>4</sub> ) <sub>2</sub> (CO)(Cyttp) (2)	22.7	8.2	30.5				
<i>cis</i> -Ru(OSO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub> (CO)(Cyttp) (3) <sup>f</sup>	22.7	7.4	31.0				
<i>cis-anti</i> -[Ru(CO)(NCMe) <sub>2</sub> (Cyttp)][BF <sub>4</sub> ] <sub>2</sub> (4a)	11.6	6.8	29.7				2.85 (s); 2.86 (s)
<i>cis-anti</i> -[Ru(CO)(NCMe) <sub>2</sub> (Cyttp)][O <sub>3</sub> SCF <sub>3</sub> ] <sub>2</sub> (4b)	11.6	6.8	29.5				2.90 (s); 2.94 (d, 1)
<i>cis</i> -[Ru(CO)(CNBu- <i>t</i> ) <sub>2</sub> (Cyttp)][BF <sub>4</sub> ] <sub>2</sub> (5)	-11.1	10.0	28.7				1.80 (s); 1.83 (s)
<i>cis</i> -[Ru(CO)(CNCy) <sub>2</sub> (Cyttp)][BF <sub>4</sub> ] <sub>2</sub> (6)	-10.5	10.4	28.8				[4.5-4.6 (m); 2 H]
[RuF(CO)(H <sub>2</sub> O)(Cyttp)][BF <sub>4</sub> ] (7a)	33.2	12.3	34	-318.8 <sup>g</sup>	16	24	
[RuF(CO)(H <sub>2</sub> O)(Cyttp)][BF <sub>4</sub> ] (7b)	29.9	11.0	34		0	22	
<i>cis</i> -[RuF(CO) <sub>2</sub> (Cyttp)][BF <sub>4</sub> ] (8a)	-0.8	14.8	36	-410.7	44	24	
<i>cis</i> -[RuF(CO) <sub>2</sub> (Cyttp)][BF <sub>4</sub> ] (8b)	-16.6	13.2	36	-417.3 <sup>g</sup>	14	21	
[RuF(CO)(CNBu- <i>t</i> )(Cyttp)][BF <sub>4</sub> ] (9a)	4.0	12.3	36	-401.6	44	23	1.79 (s)
[RuF(CO)(CNBu- <i>t</i> )(Cyttp)][BF <sub>4</sub> ] (9b)	-11.2	13.7	35	-391.7 <sup>g</sup>	11	20	1.75 (s)
<i>cis</i> -[Ru(CO)(NH <sub>3</sub> ) <sub>2</sub> (Cyttp)][O <sub>3</sub> SCF <sub>3</sub> ] <sub>2</sub> (10)	10.9	3.9	31.8				[3.35 (br), 3.58 (br), 3.63 (t); 6 H]
[Ru(CO)(P(OMe) <sub>3</sub> )(Cyttp)][O <sub>3</sub> SCF <sub>3</sub> ] <sub>2</sub> (11a) <sup>h</sup>	-13.2	7.9	36.0				4.26 (d, 10.7)
[Ru(CO)(P(OMe) <sub>3</sub> )(Cyttp)][O <sub>3</sub> SCF <sub>3</sub> ] <sub>2</sub> (11b) <sup>i</sup>	-14.1	6.0	36.4				4.21 (d, 10.7)
[RuCl(CO)(P(OMe) <sub>3</sub> )(Cyttp)][BPh <sub>4</sub> ] <sub>2</sub> (12) <sup>j,k</sup>	-11.7	4.7	36.4				3.73 (d, 10.5)
[Ru(OMe)(CO)(P(OMe) <sub>3</sub> )(Cyttp)][O <sub>3</sub> SCF <sub>3</sub> ] <sub>2</sub> (13) <sup>l,m</sup>	-7.1	7.3	38.7				[3.74 (d, 10.0); 9 H] [3.18 (s); 3 H]
<i>cis</i> -RuMe <sub>2</sub> (CO)(Cyttp) (14) <sup>k</sup>	4.4	11.7	30.9				-0.12 (td, 6.1, 4.0); -0.43 (dt, 9.3, 7.1)

<sup>a</sup>Solvent is acetone-*d*<sub>6</sub> unless otherwise stated. Carbon-13 NMR and IR data are included in the Experimental Section. <sup>b</sup>Chemical shifts are in δ with respect to external 85% H<sub>3</sub>PO<sub>4</sub> (δ 0.0); positive values are downfield; coupling constants are in Hz. P<sub>C</sub> is the central phosphorus, and P<sub>W</sub> represents the two terminal phosphorus atoms of Cyttp. <sup>c</sup>Value given is for the fluoride ligand. Chemical shifts are in δ with respect to external CFCl<sub>3</sub> (δ 0.0); positive values are downfield. <sup>d</sup>Chemical shifts are in δ with respect to Me<sub>4</sub>Si (δ 0.0); br = broad; d = doublet; m = multiplet; s = singlet; t = triplet; numbers in parentheses are coupling constants in Hz; resonances for Cyttp are not included. <sup>e</sup>In CD<sub>2</sub>Cl<sub>2</sub>. <sup>f</sup>These are the major signals for the fluxional complex at 300 K. An additional broad <sup>31</sup>P resonance at δ 8.2 (d) is observed. <sup>g</sup>Broad signal; J<sub>PF</sub> determined solely by <sup>31</sup>P{<sup>1</sup>H} NMR. <sup>h</sup>δ(P(OMe)<sub>3</sub>) 119.9, J<sub>PCP</sub> = 380.6 Hz, J<sub>PWP</sub> = 37.1 Hz. <sup>i</sup>δ(P(OMe)<sub>3</sub>) 117.9, J<sub>PCP</sub> = 396.7 Hz, J<sub>PWP</sub> = 36.4 Hz. <sup>j</sup>δ(P(OMe)<sub>3</sub>) 119.1, J<sub>PCP</sub> = 423.9 Hz, J<sub>PWP</sub> = 38.9 Hz. <sup>k</sup>In CDCl<sub>3</sub>. <sup>l</sup>δ(P(OMe)<sub>3</sub>) 96.4, J<sub>PCP</sub> = 440.0 Hz, J<sub>PWP</sub> = 42.0 Hz. <sup>m</sup>In C<sub>6</sub>D<sub>6</sub>.

*p*-Tol), afford the complexes *cis-cis*-Ru(OSO<sub>2</sub>R)<sub>2</sub>(CO)(H<sub>2</sub>O)(PPh<sub>3</sub>)<sub>2</sub>.<sup>4</sup>

Herein we report the protonation of an analogous complex that contains the chelated triphosphine Cyttp (Cyttp = PhP(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PCy<sub>2</sub>)<sub>2</sub>). Protonation of *cis-mer*-RuH<sub>2</sub>(CO)(Cyttp) with excess HX (X = BF<sub>4</sub>, O<sub>3</sub>SCF<sub>3</sub>) in benzene/diethyl ether produces air-stable complexes with two weakly coordinated anions, viz., *cis-mer*-RuX<sub>2</sub>(CO)(Cyttp) (X = BF<sub>4</sub> (2), O<sub>3</sub>SCF<sub>3</sub> (3)). A single-crystal X-ray diffraction analysis of 3 confirms the coordination of both triflate anions. The utility of 2 and 3 as starting materials for the preparation of a variety of coordination and organometallic complexes is reported.

### Experimental Section

All reactions and manipulations of air-sensitive compounds were carried out under an atmosphere of Ar by use of standard procedures.<sup>9</sup> Air-sensitive solids were handled and transferred in a Vacuum Atmosphere HE43 inert-atmosphere box equipped with a Mo-40 catalyst system. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Infrared (IR) spectra were recorded on a Perkin-Elmer 283B grating spectrophotometer from 4000 to 200 cm<sup>-1</sup> as Nujol mulls between NaCl or CsI plates unless otherwise specified and were calibrated with polystyrene. A Bruker AM-250 or WM-300 spectrometer was used to obtain proton, phosphorus-31, fluorine-19, and carbon-13 NMR spectra in 5-mm tubes. Residual solvent proton or carbon-13 resonances were used as internal standards for the proton or carbon-13 NMR spectra. Phosphorus chemical shifts were determined relative to 85% H<sub>3</sub>PO<sub>4</sub> at 0.00 ppm as an external standard. Fluorine chemical shifts are relative to CFCl<sub>3</sub> at 0.00 ppm as an external standard. Phosphorus-31, fluorine-19, and selected proton NMR data for new Ru(Cyttp) complexes are presented in Table I.

Reagent grade solvents were distilled under Ar from appropriate drying agents prior to use. Reagent grade chemicals were used as purchased from Aldrich Chemical Co., Inc., unless stated otherwise. Carbon monoxide was obtained from AGA Gas, Inc., and used without further purification. Ruthenium trichloride hydrate was loaned by Johnson Matthey, Inc. *cis-mer-syn*-RuH<sub>2</sub>(CO)(Cyttp) was prepared by the literature method.<sup>10</sup>

***cis-mer-anti*-RuCl<sub>2</sub>(CO)(Cyttp).** Concentrated hydrochloric acid (0.5 mL, 6 mmol) was added to a stirred solution of *cis-mer-syn*-RuH<sub>2</sub>(CO)(Cyttp) (0.279 g, 0.389 mmol) in 30 mL of CH<sub>2</sub>Cl<sub>2</sub>. The mixture

was stirred for 5 min, 10 mL of hexane was added, and the volume of solution was reduced to ca. 5 mL. The resulting white powder was collected on a filter frit, washed twice with 10-mL portions of hexane, and dried under vacuum overnight. Yield, 0.235 g, 77%. Anal. Calcd for C<sub>37</sub>H<sub>61</sub>Cl<sub>2</sub>OP<sub>3</sub>Ru: C, 56.48; H, 7.81; Cl, 9.01. Found: C, 56.27; H, 7.64; Cl, 8.89. IR (CCl<sub>4</sub>, cm<sup>-1</sup>) ν(CO) 1943. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>) δ 202.5 (q, <sup>2</sup>J<sub>PC</sub> = 11.5 Hz, CO).

***cis-mer*-Ru(BF<sub>4</sub>)<sub>2</sub>(CO)(Cyttp).** A solution of 85% tetrafluoroboric acid in diethyl ether (2.0 mL, 12 mmol) was added to a stirred solution of *cis-mer-syn*-RuH<sub>2</sub>(CO)(Cyttp) (1.31 g, 1.83 mmol) in 125 mL of benzene and 25 mL of diethyl ether. Effervescence commenced immediately and lasted approximately 1 min. After several minutes a pale yellow precipitate began to form, and the solution was stirred for an additional 30 min at 0 °C. The powder was collected on a filter frit, washed twice with 20-mL portions of hexane, and dried under vacuum overnight. Yield, 1.43 g, 88%. Anal. Calcd for C<sub>37</sub>H<sub>61</sub>B<sub>2</sub>F<sub>8</sub>OP<sub>3</sub>Ru: C, 49.96; H, 6.91. Found: C, 48.78; H, 7.07. IR (cm<sup>-1</sup>) ν(CO) 1982 (vs), (BF<sub>4</sub>) 1100-950 (s).

***cis-mer*-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cyttp).** Neat trifluoromethanesulfonic acid (0.26 mL, 2.9 mmol) was added to a stirred solution of *cis-mer-syn*-RuH<sub>2</sub>(CO)(Cyttp) (0.998 g, 1.39 mmol) in 50 mL of benzene and 10 mL of diethyl ether. Effervescence commenced immediately, and the clear colorless solution became slightly yellow. Effervescence stopped after approximately 1 min, and after several more minutes a pale yellow solid began to precipitate. The solution was stirred for an additional 15 min, and then solvent was removed under vacuum. Approximately 200 mL of CH<sub>2</sub>Cl<sub>2</sub> was introduced with stirring to fully dissolve the sample, and then 100 mL of hexane was added. The volume of the solution was reduced to 50 mL, and the resulting pale yellow powder was collected on a filter frit, washed twice with 20-mL portions of hexane, and dried for several days under vacuum. It was sometimes necessary to wash the product with H<sub>2</sub>O to remove excess triflic acid. Yield, 1.29 g, 91%. Anal. Calcd for C<sub>39</sub>H<sub>61</sub>F<sub>6</sub>O<sub>7</sub>P<sub>3</sub>RuS<sub>3</sub>: C, 46.20; H, 6.06. Found: C, 46.04; H, 6.19. IR (cm<sup>-1</sup>) ν(CO) 1982 (m), 1970 (s), 1960 (m).

***cis-mer-anti*-[Ru(CO)(NCMe)<sub>2</sub>(Cyttp)][BF<sub>4</sub>]<sub>2</sub>.** A solution of *cis-mer*-Ru(BF<sub>4</sub>)<sub>2</sub>(CO)(Cyttp) (0.150 g, 0.169 mmol) in 1 mL of MeCN was stirred for 5 min, and then 30 mL of diethyl ether was added to precipitate a white powder. The powder was collected on a filter frit, washed with 5 mL of diethyl ether, and dried under vacuum overnight. Yield, 0.151 g, 92%. Anal. Calcd for C<sub>41</sub>H<sub>67</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub>OP<sub>3</sub>Ru: C, 50.68; H, 6.95; N, 2.88. Found: C, 50.68; H, 6.87; N, 2.68. IR (cm<sup>-1</sup>) ν(CN) 2310 (w), 2280 (m), 2240 (w), ν(CO) 1970 (s), (BF<sub>4</sub>) 1130-980 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>) δ 202.0 (q, <sup>2</sup>J<sub>PC</sub> = 11 Hz, CO), 4.2 (s, MeCN), 3.7 (s, MeCN), MeCN obscured by phenyl signals of Cyttp.

***cis-mer-anti*-[Ru(CO)(NCMe)<sub>2</sub>(Cyttp)][O<sub>3</sub>SCF<sub>3</sub>]<sub>2</sub>.** A solution of *cis-mer*-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cyttp) (0.057 g, 0.056 mmol) in 1 mL of MeCN and 1 mL of benzene was slowly evaporated to dryness under a

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stream of argon yielding effluorescent crystals. Yield, 0.058 g, 96%. Anal. Calcd for  $C_{43}H_{67}F_9N_2O_7P_3RuS_2$ : C, 47.12; H, 6.16; N, 2.56. Found: C, 47.32; H, 6.36; N, 2.51. IR (hexachloro-1,3-butadiene,  $cm^{-1}$ )  $\nu(CN)$  2300 (vw), 2275 (w),  $\nu(CO)$  1985 (s).

**cis-mer-[Ru(CO)(CNBu-t)<sub>2</sub>(Cytpp)]BF<sub>4</sub>·2**. Approximately 0.1 mL of *tert*-butyl isocyanide (0.9 mmol) was added to a stirred solution of *cis-mer*-Ru(BF<sub>4</sub>)<sub>2</sub>(CO)(Cytpp) (0.210 g, 0.236 mmol) in 10 mL of acetone. After 5 min all solvent was removed, 20 mL of hexane was added, and the mixture was stirred overnight. The resulting pale yellow precipitate was collected on a filter frit and dried under vacuum. The yellowish product was recrystallized by layering hexane on top of its solution in acetone at -23 °C. Colorless crystals formed and were collected by filtration. Yield, 0.210 g, 84%. Anal. Calcd for  $C_{47}H_{79}B_2F_8N_2OP_3Ru$ : C, 53.47; H, 7.54; N, 2.65. Found: C, 53.49; H, 7.55; N, 2.48. IR ( $cm^{-1}$ )  $\nu(CN)$  2195 (sh), 2175 (s),  $\nu(CO)$  2015 (s), (BF<sub>4</sub>) 1150–950 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>)  $\delta$  198.7 (q, <sup>2</sup>J<sub>PC</sub> = 10 Hz, CO), 137.5 (br, CNBu-*t* trans to CO), 134.0 (br, d, <sup>2</sup>J<sub>PC</sub> = 75 Hz, CNBu-*t* trans to P), 63.2 (s, CMe<sub>3</sub>), 62.2 (s, CMe<sub>3</sub>), 30.0 (s, CMe<sub>3</sub>), 29.3 (s, CMe<sub>3</sub>).

**cis-mer-[Ru(CO)(CNCy)<sub>2</sub>(Cytpp)]BF<sub>4</sub>·2**. A procedure analogous to that for *cis-mer*-[Ru(CO)(CNBu-*t*)<sub>2</sub>(Cytpp)]BF<sub>4</sub>·2 was followed, with cyclohexyl isocyanide replacing *tert*-butyl isocyanide. Yield, 0.194 g, 78%. Anal. Calcd for  $C_{51}H_{83}B_2F_8N_2OP_3Ru$ : C, 55.29; H, 7.55; N, 2.53. Found: C, 55.04; H, 7.40; N, 2.76. IR ( $cm^{-1}$ )  $\nu(CN)$  2205 (s, sh), 2185 (s),  $\nu(CO)$  2015 (vs), (BF<sub>4</sub>) 1150–950 (s).

**mer-[RuF(CO)(H<sub>2</sub>O)(Cytpp)]BF<sub>4</sub>·2**. A solution of *cis-mer*-Ru(BF<sub>4</sub>)<sub>2</sub>(CO)(Cytpp) (0.500 g, 0.562 mmol) and NaF (0.150 g, 3.60 mmol) in 50 mL of acetone and 15 mL of degassed distilled H<sub>2</sub>O was stirred for 30 min. Solvent was removed under vacuum, and the solid was scraped loose from the sides of the flask; then 20 mL of H<sub>2</sub>O was added, and the mixture was stirred for 1 h. The white solid was collected on a filter frit, washed twice with 10-mL portions of H<sub>2</sub>O and then twice with 10-mL portions of hexane, and dried under vacuum for 24 h. Upon drying the solid turns yellow but regains the original white color when stored in air for several hours. These color changes are reversible and reproducible. Yield, 0.390 g, 96%. Anal. Calcd for  $C_{37}H_{63}BF_5O_2P_2Ru$ : C, 52.92; H, 7.56. Found: C, 52.88; H, 7.57. IR ( $cm^{-1}$ )  $\nu(CO)$  1935 (vs), (BF<sub>4</sub>) 1150–950 (s).

**cis-mer-[RuF(CO)<sub>2</sub>(Cytpp)]BF<sub>4</sub>·2**. A solution of *mer*-[RuF(CO)(H<sub>2</sub>O)(Cytpp)]BF<sub>4</sub>·2 (0.120 g, 0.143 mmol) in 10 mL of acetone was stirred for 1 h under an atmosphere of carbon monoxide. Solvent was then removed under vacuum, and solid material was scraped loose from the sides of the flask; then 20 mL of hexane was added, and the mixture was stirred overnight. The resulting very fine white precipitate was collected on a filter frit and dried under vacuum overnight. Yield, 0.083 g, 69%. Anal. Calcd for  $C_{38}H_{61}BF_5O_2P_2Ru$ : C, 53.72; H, 7.24. Found: C, 53.59; H, 7.28. IR ( $cm^{-1}$ )  $\nu(CO)$  2030 (s), 1965 (s), (BF<sub>4</sub>) 1150–1000 (s). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone-*d*<sub>6</sub>, major isomer **8a** only)  $\delta$  200.3 (ddt, <sup>2</sup>J<sub>PC</sub> = 12, 9 Hz, <sup>2</sup>J<sub>FC</sub> = 65 Hz, CO trans to F), 194.1 (dtd, <sup>2</sup>J<sub>PC</sub> = 94, 11 Hz, <sup>2</sup>J<sub>FC</sub> = 4 Hz, CO trans to P).

**mer-[RuF(CO)(CNBu-*t*)(Cytpp)]BF<sub>4</sub>·2**. Approximately 0.1 mL of *tert*-butyl isocyanide (0.9 mmol) was added to a stirred solution of *mer*-[RuF(CO)(H<sub>2</sub>O)(Cytpp)]BF<sub>4</sub>·2 (0.070 g, 0.083 mmol) in 10 mL of acetone. After 5 min, solvent was removed under vacuum, 20 mL of hexane was added, and the mixture was stirred overnight. The white solid was collected on a filter frit, washed twice with 10-mL portions of hexane, and dried under vacuum overnight. Yield, 0.050 g, 71%. Anal. Calcd for  $C_{42}H_{70}BF_5NOP_3Ru$ : C, 55.75; H, 7.80. Found: C, 55.65; H, 7.66. IR ( $cm^{-1}$ )  $\nu(CN)$  2165 (s),  $\nu(CO)$  1945 (vs), (BF<sub>4</sub>) 1150–1000 (s).

**cis-mer-[Ru(CO)(NH<sub>3</sub>)<sub>2</sub>(Cytpp)]O<sub>3</sub>SCF<sub>3</sub>·2**. Ammonia was bubbled through a stirred solution of *cis-mer*-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cytpp) (0.134 g, 0.132 mmol) in 25 mL of THF for 1 h. All volatiles were then removed under vacuum, 40 mL of hexane was added, and the mixture was stirred overnight to yield a white precipitate. The solid was collected on a filter frit and dried under vacuum overnight. Yield, 0.116 g, 84%. Anal. Calcd for  $C_{39}H_{67}F_6N_2O_7P_3RuS_2$ : C, 44.69; H, 6.44; N, 2.67. Found: C, 44.81; H, 6.38; N, 2.88. IR ( $cm^{-1}$ )  $\nu(NH)$  3350–3150 (s),  $\nu(CO)$  1970 (vs),  $\delta(NH)$  1535 (s).

**mer-[Ru(CO)(P(OMe)<sub>3</sub>(Cytpp)]O<sub>3</sub>SCF<sub>3</sub>·2**. Trimethyl phosphite (0.050 mL, 0.42 mmol) was added to a stirred solution of *cis-mer*-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cytpp) (0.207 g, 0.204 mmol) in 30 mL of THF. After the mixture was stirred for 15 min, all volatiles were removed under vacuum. A 30-mL portion of hexane was added, and the mixture was stirred for 3 h to yield a light tan precipitate. The precipitate was collected on a filter frit, washed with 10 mL of hexane, and dried overnight under vacuum. Yield, 0.190 g, 82%. Anal. Calcd for  $C_{42}H_{70}F_6O_{10}P_4RuS_2$ : C, 44.33; H, 6.20. Found: C, 44.54; H, 6.44. IR ( $cm^{-1}$ )  $\nu(CO)$  1970.

**mer-[RuCl(CO)(P(OMe)<sub>3</sub>(Cytpp)]BPh<sub>4</sub>·2**. Trimethyl phosphite (0.050 mL, 0.42 mmol) was added to a stirred solution of *cis-mer*-Ru-

(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cytpp) (0.154 g, 0.152 mmol) in 40 mL of THF. The mixture was stirred for 15 min, and LiCl (0.050 g, 1.2 mmol) was added as a solid. After an additional 15 min of stirring, solvent was removed under vacuum, and 15 mL of methanol was added to completely dissolve the sample. A solution of NaBPh<sub>4</sub> (0.200 g, 0.584 mmol) in 10 mL of methanol was added to the reaction mixture to produce a white precipitate. After 15 min of stirring the white solid was collected on a filter frit and dried under vacuum overnight. Yield, 0.107 g, 59%. Anal. Calcd for  $C_{64}H_{90}BClO_4P_4Ru$ : C, 64.35; H, 7.59; Cl, 2.97. Found: C, 64.55; H, 7.46; Cl, 3.16. IR ( $cm^{-1}$ )  $\nu(CO)$  1960.

**mer-[Ru(OMe)(CO)(P(OMe)<sub>3</sub>(Cytpp)]O<sub>3</sub>SCF<sub>3</sub>·2**. A solution of sodium methoxide (0.014 g, 0.264 mmol) in 2 mL of methanol was added to a stirred solution of *mer*-[Ru(CO)(P(OMe)<sub>3</sub>(Cytpp)]O<sub>3</sub>SCF<sub>3</sub>·2 (0.200 g, 0.176 mmol) in 30 mL of THF. After 5 min of stirring solvent was removed, 40 mL of benzene was added, and the mixture was stirred vigorously for 30 min. The mixture was filtered through a frit, and the filtrate was evaporated to dryness. Upon addition of 20 mL of hexane and stirring for 3 h, a pale yellow precipitate was obtained. The product was collected on a filter frit and dried under vacuum overnight. Yield, 0.086 g, 48%. IR ( $cm^{-1}$ )  $\nu(CH)$  for OMe ligand 2725 (m),  $\nu(CO)$  1925 (vs).

**cis-mer-RuMe<sub>2</sub>(CO)(Cytpp)**. A 1.4 M solution of methyl lithium in diethyl ether (0.520 mL, 0.728 mmol) was added to a solution of *cis-mer*-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cytpp) (0.325 g, 0.320 mmol) in 50 mL of THF at 0 °C. The colorless solution became intensely purple within 2 min. After 20 min of stirring, solvent was removed, 10 mL of hexane was added at room temperature, and the mixture was stirred for 1 h. The resulting white solid was collected on a filter frit while the purple filtrate was discarded. The white solid was extracted with 10 mL of benzene. The extracts were slowly evaporated almost to dryness, and colorless, air-sensitive crystals that formed were collected on a filter frit and dried under vacuum overnight. Yield, 0.128 g, 53%. Anal. Calcd for  $C_{39}H_{67}OP_3Ru$ : C, 62.80; H, 9.05. Found: C, 62.75; H, 8.82. IR ( $cm^{-1}$ )  $\nu(CO)$  1895. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  206.6 (q, <sup>2</sup>J<sub>PC</sub> = 4.9 Hz, CO), -6.3 (q, <sup>2</sup>J<sub>PC</sub> = 11.2 Hz, Me trans to CO), -14.7 (dt, <sup>2</sup>J<sub>PC</sub> = 58.1, 11.4 Hz, Me trans to P).

**cis-mer-syn-RuH<sub>2</sub>(CO)(Cytpp)**. A mixture of *cis-mer*-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cytpp) (0.200 g, 0.197 mmol) and NaH (0.019 g, 0.79 mmol) was stirred in 40 mL of THF for 2 h. Solvent was then removed, and the residue was extracted twice with 20-mL portions of benzene. The extracts were combined and reduced in volume to ca. 1 mL, and then 10 mL of ethanol was added to induce the precipitation of a white solid. The precipitate was collected on a filter frit, washed with 10 mL of hexane, and dried under vacuum overnight. Yield, 0.131 g, 93%. The spectroscopic data are identical with those of an authentic sample of *cis-mer-syn*-RuH<sub>2</sub>(CO)(Cytpp).<sup>10</sup>

**cis-mer-anti-RuI<sub>2</sub>(CO)(Cytpp)**. A mixture of *cis-mer*-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cytpp) (0.111 g, 0.109 mmol) and NaI (0.146 g, 0.974 mmol) was dissolved in 10 mL of acetone and 2 mL of H<sub>2</sub>O and the contents were stirred for 15 min. Solvent was removed, and 10 mL of H<sub>2</sub>O was added to the residue. After the suspension was stirred for 5 min, the bright yellow solid was collected on a filter frit, washed once with 10 mL of H<sub>2</sub>O and twice with 10-mL portions of hexane, and dried under vacuum. Yield, 0.102 g, 96%. <sup>13</sup>P{<sup>1</sup>H} NMR and IR spectra are identical with those of an authentic sample of *cis-mer-anti*-RuI<sub>2</sub>(CO)(Cytpp).<sup>11</sup>

**Crystallographic Analysis of cis-mer-anti-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cytpp)**. The crystal used for data collection was a pale yellow, hexagonal rod. Examination of the diffraction pattern on a Rigaku AFC5S diffractometer indicated a monoclinic crystal system with systematic absences  $h0l$ ,  $l = 2n + 1$  and  $0k0$ ,  $k = 2n + 1$ . The space group is uniquely determined as  $P2_1/c$ . The cell constants were determined at 223 K by a symmetry restricted least-squares fit of the diffractometer setting angles for 25 reflections in the  $2\theta$  range 20 to 30° with Mo K $\alpha$  radiation ( $\lambda(K\alpha) = 0.71069 \text{ \AA}$ ).

Data were collected with  $\omega$  scans at 223 K. Six standard reflections were measured after every 150 reflections and indicated that a small amount of decomposition had occurred. The standards decreased in intensity by an average value of 1.4%, and a linear decay correction was applied during data reduction. The data were not corrected for absorption.

The position of the ruthenium atom was located on a Patterson map and then used as a phasing model in the direct methods program DIRDIF.<sup>12</sup> All of the non-hydrogen atoms of the ruthenium complex were located on the resulting electron density map. During the course of least-squares refinement it became evident that there was some residual electron

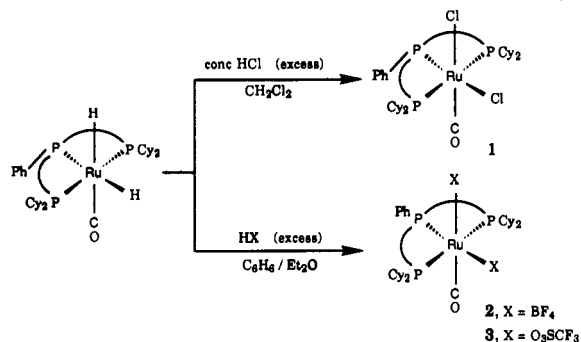
(11) Jia, G. Ph.D. Dissertation, The Ohio State University, 1989.

(12) Parthasarathi, V.; Beurskens, P. T.; Slot, H. J. B. *Acta Crystallogr.* 1983, **A39**, 860–864.

**Table II.** Crystallographic Data for *cis-mer*-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cyttp) (3)

C <sub>39</sub> H <sub>61</sub> F <sub>6</sub> O <sub>7</sub> P <sub>3</sub> RuS <sub>2</sub> ·1.15H <sub>2</sub> O	formula weight = 1034.74
<i>a</i> = 11.712 (2) Å	space group <i>P2</i> <sub>1</sub> / <i>c</i> (No. 14)
<i>b</i> = 15.338 (2) Å	<i>T</i> = 223 K
<i>c</i> = 27.072 (3) Å	$\lambda$ = 0.71069 Å
$\beta$ = 98.58 (1)°	$\mu$ = 5.67 cm <sup>-1</sup>
<i>V</i> = 4809 (1) Å <sup>3</sup>	<i>R</i> ( <i>F</i> ) = 0.041 <sup>a</sup>
<i>Z</i> = 4	<i>R</i> <sub>w</sub> ( <i>F</i> ) = 0.046 <sup>b</sup>
$\rho_{\text{calc}}$ = 1.43 g cm <sup>-3</sup>	

$$^a R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \quad ^b R_w(F) = \frac{[\sum w(|F_o| - |F_c|)^2]}{\sum w|F_o|^2} \text{ with } w = 1/\sigma^2(F_o).$$

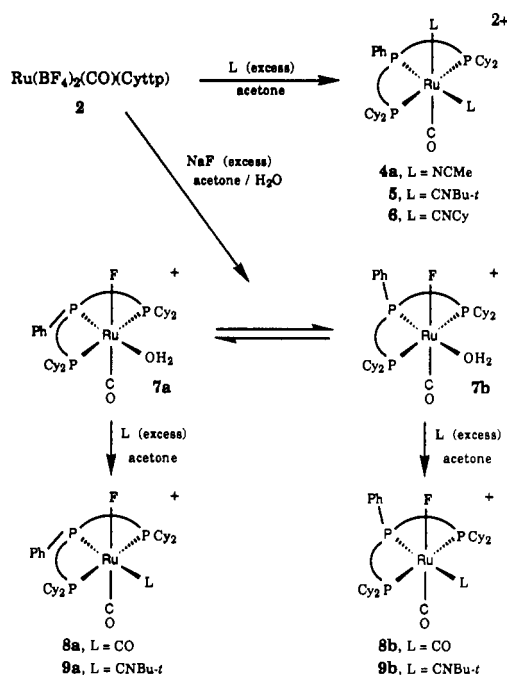
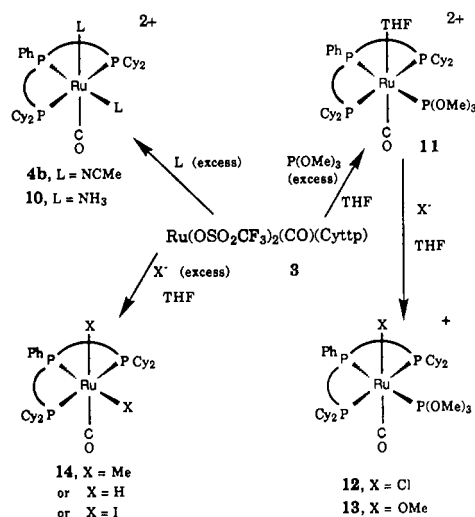
**Scheme I**

density in the regions of the unit cell between the ruthenium complexes (but not bonded to the ruthenium complex). This electron density, which ranged from 0.73 to 1.11 e/Å<sup>3</sup>, was modeled in terms of four water molecules with variable occupancy factors. The occupancy factors and isotropic thermal parameters for these oxygen atoms of the disordered water molecules were refined in alternate cycles until the model converged. The following occupancy factors were obtained: O(8) 0.32 (2), O(9) 0.27 (2), O(10) 0.32 (2), and O(11) 0.24 (2). From this it follows that there are 1.15 molecules of water per molecule of ruthenium complex. After anisotropic refinement of the ruthenium complex, the hydrogen atoms were included in the model as fixed contributions in calculated positions at C-H = 0.98 Å and with *B*(H) = *B*<sub>eq</sub>(attached carbon atom)·1.2. No hydrogen atoms were added to the disordered water molecules, and these water molecules were kept at the isotropic refinement stage. The final refinement cycle for the 7036 intensities with *I* > 3σ(*I*) and 539 variables resulted in agreement indices of *R* = 0.041 and *R*<sub>w</sub> = 0.046. The final difference electron density map has maximum and minimum peaks of 0.51 and -0.40 e/Å<sup>3</sup>. The (102) reflection was removed from the data set because of asymmetric backgrounds. Neutral atom scattering factors and anomalous dispersion terms were used and are from the usual sources.<sup>13</sup> All calculations were done with the TEXSAN package of crystallographic programs.<sup>14</sup>

Further crystallographic details are given in Table II. Final positional and equivalent isotropic thermal parameters are presented in Table III. Lists of anisotropic thermal parameters, hydrogen atom coordinates, and structure factors are available as supplementary material.<sup>15</sup>

## Results

The protonation of *cis-mer*-RuH<sub>2</sub>(CO)(Cyttp) with an excess of HCl, HO<sub>3</sub>SCF<sub>3</sub>, or HBF<sub>4</sub> results in the loss of 2 equiv of H<sub>2</sub> and the formation of the *cis-mer* complexes RuCl<sub>2</sub>(CO)(Cyttp) (1), Ru(BF<sub>4</sub>)<sub>2</sub>(CO)(Cyttp) (2), or Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cyttp) (3), respectively, as shown in Scheme I. An X-ray diffraction analysis was performed on 3, and the structure and selected bond distances and angles are presented in Figure 1 and Table IV, respectively. The structures of 2 and 3 in both dichloromethane and acetone solutions were probed by variable-temperature <sup>19</sup>F{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies. The variable-temperature <sup>19</sup>F{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 3 in CD<sub>2</sub>Cl<sub>2</sub> from 188 to 303

**Scheme II****Scheme III**

K are reproduced in Figure 2 as evidence for the presence of the complex mixture of species in solution. Partial <sup>19</sup>F{<sup>1</sup>H} and full <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 2 in CD<sub>2</sub>Cl<sub>2</sub> in the temperature range 188–303 K are shown in Figure 3. The full <sup>19</sup>F{<sup>1</sup>H} NMR spectrum of 2 at 188 K and <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F{<sup>1</sup>H} NMR spectra of 2 and 3 in acetone-*d*<sub>6</sub> at 243 and 303 K are fully described in the discussion and are available as supplementary material.

As shown in Scheme II, 2 undergoes substitution reactions with acetonitrile and organic isocyanides to afford disubstituted dicationic complexes *cis-mer*-[Ru(CO)L<sub>2</sub>(Cyttp)][BF<sub>4</sub>]<sub>2</sub> (4a, L = MeCN; 5, L = CNBu-*t*; 6, L = CNCy). The syn and anti isomers of *mer*-[RuF(CO)(H<sub>2</sub>O)(Cyttp)][BF<sub>4</sub>]<sub>2</sub> are generated by the reaction of 2 with NaF in an acetone/H<sub>2</sub>O mixed-solvent system as major (7a) and minor (7b) inseparable products. 7a and 7b readily substitute CO or CNBu-*t* for H<sub>2</sub>O to produce syn and anti isomers of complexes *mer*-[RuF(CO)L(Cyttp)][BF<sub>4</sub>]<sub>2</sub> (8a, 8b, L = CO; 9a, 9b, L = CNBu-*t*).

The reactions of 3 are set out in Scheme III. Substitution reactions with acetonitrile and ammonia produce disubstituted complexes *cis-mer*-[Ru(CO)L<sub>2</sub>(Cyttp)][O<sub>3</sub>SCF<sub>3</sub>]<sub>2</sub> (4b, L = MeCN; 10, L = NH<sub>3</sub>). The reaction of 3 with an excess of trimethyl phosphite leads only to monosubstituted products in which the phosphite is trans to the central phosphorus atom of Cyttp. Two isomers of [Ru(CO)(P(OMe)<sub>3</sub>)(Cyttp)][O<sub>3</sub>SCF<sub>3</sub>]<sub>2</sub>

(13) Scattering factors for the non-hydrogen atoms, including terms for anomalous dispersion, are from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 71 and 148. The scattering factor for the hydrogen atom is from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* 1965, 42, 3175–3187.

(14) *TEXSAN, Single Crystal Structure Analysis Software, Version 5.0*; Molecular Structure Corporation: The Woodlands, TX, 1989.

(15) See paragraph at end of paper regarding supplementary material.

**Table III.** Final Positional Parameters for *cis-mer*-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cytpp) (3)<sup>a</sup>

atom	x	y	z	B <sub>eq</sub> or B, Å <sup>2</sup>	atom	x	y	z	B <sub>eq</sub> or B, Å <sup>2</sup>
Ru	0.72213 (3)	0.08963 (2)	0.66290 (1)	1.50 (1)	C(13)	0.5296 (3)	0.2625 (3)	0.6114 (1)	2.0 (2)
S(1)	0.7167 (1)	-0.10882 (7)	0.59336 (4)	2.51 (4)	C(14)	0.6112 (3)	0.3409 (3)	0.6224 (1)	2.3 (2)
S(2)	0.94947 (9)	0.21743 (7)	0.64895 (4)	2.36 (4)	C(15)	0.5522 (4)	0.4158 (3)	0.6452 (2)	3.2 (2)
P(1)	0.60762 (8)	0.16450 (7)	0.59222 (4)	1.77 (4)	C(16)	0.4415 (4)	0.4422 (3)	0.6123 (2)	3.5 (2)
P(2)	0.55654 (8)	0.02832 (7)	0.68366 (4)	1.77 (4)	C(17)	0.3608 (4)	0.3650 (3)	0.6009 (2)	3.2 (2)
P(3)	0.84410 (9)	0.01526 (7)	0.73275 (4)	1.80 (4)	C(18)	0.4179 (3)	0.2900 (3)	0.5772 (2)	2.6 (2)
F(1)	0.8014 (3)	-0.0762 (2)	0.5112 (1)	6.1 (2)	C(19)	0.4783 (3)	0.0899 (3)	0.7258 (1)	2.0 (1)
F(2)	0.7977 (3)	-0.2081 (2)	0.5296 (1)	6.8 (2)	C(20)	0.5295 (4)	0.1066 (3)	0.7747 (2)	2.8 (2)
F(3)	0.9234 (3)	-0.1266 (3)	0.5690 (1)	6.6 (2)	C(21)	0.4711 (4)	0.1502 (3)	0.8078 (2)	3.4 (2)
F(4)	1.0018 (3)	0.2267 (4)	0.5592 (1)	9.4 (3)	C(22)	0.3595 (4)	0.1799 (3)	0.7932 (2)	3.4 (2)
F(5)	1.1262 (3)	0.2767 (3)	0.6135 (2)	9.2 (3)	C(23)	0.3079 (4)	0.1648 (3)	0.7449 (2)	3.1 (2)
F(6)	1.1070 (4)	0.1477 (3)	0.6061 (2)	11.1 (3)	C(24)	0.3658 (4)	0.1204 (3)	0.7118 (2)	2.7 (2)
O(1)	0.6915 (3)	0.2374 (2)	0.7299 (1)	3.0 (1)	C(25)	0.8580 (4)	0.0719 (3)	0.7953 (1)	2.4 (2)
O(2)	0.7455 (2)	-0.0207 (2)	0.6115 (1)	2.3 (1)	C(26)	0.9536 (4)	0.1414 (3)	0.8017 (2)	2.8 (2)
O(3)	0.7458 (3)	-0.1754 (2)	0.6302 (1)	4.1 (2)	C(27)	0.9558 (5)	0.1917 (3)	0.8503 (2)	4.1 (2)
O(4)	0.6061 (3)	-0.1153 (3)	0.5632 (1)	4.6 (2)	C(28)	0.9648 (5)	0.1316 (3)	0.8955 (2)	4.5 (3)
O(5)	0.8802 (2)	0.1383 (2)	0.6358 (1)	2.3 (1)	C(29)	0.8680 (5)	0.0651 (4)	0.8887 (2)	4.1 (2)
O(6)	0.8877 (3)	0.2969 (2)	0.6378 (1)	4.5 (2)	C(30)	0.8689 (4)	0.0116 (3)	0.8413 (2)	3.1 (2)
O(7)	1.0227 (3)	0.2129 (2)	0.6959 (1)	4.0 (2)	C(31)	0.9948 (3)	-0.0044 (2)	0.7224 (1)	1.9 (1)
C(1)	0.4938 (3)	0.0946 (3)	0.5601 (1)	2.4 (2)	C(32)	1.0016 (3)	-0.0473 (3)	0.6718 (1)	2.2 (2)
C(2)	0.4033 (3)	0.0663 (3)	0.5917 (2)	2.6 (2)	C(33)	1.1269 (4)	-0.0556 (3)	0.6629 (2)	3.1 (2)
C(3)	0.4458 (3)	-0.0017 (3)	0.6313 (1)	2.3 (2)	C(34)	1.1996 (4)	-0.1058 (3)	0.7051 (2)	3.2 (2)
C(4)	0.5727 (3)	-0.0799 (3)	0.7122 (1)	2.1 (2)	C(35)	1.1913 (4)	-0.0650 (3)	0.7551 (2)	2.8 (2)
C(5)	0.6660 (3)	-0.0951 (3)	0.7568 (1)	2.3 (2)	C(36)	1.0667 (4)	-0.0581 (3)	0.7641 (2)	2.6 (2)
C(6)	0.7888 (3)	-0.0932 (3)	0.7444 (1)	2.1 (1)	C(37)	0.7048 (3)	0.1805 (3)	0.7037 (1)	2.0 (2)
C(7)	0.6882 (3)	0.1988 (3)	0.5413 (1)	2.1 (2)	C(38)	0.8166 (4)	-0.1296 (3)	0.5488 (2)	3.0 (2)
C(8)	0.7376 (4)	0.1186 (3)	0.5180 (2)	2.9 (2)	C(39)	1.0501 (4)	0.2135 (4)	0.6038 (2)	4.3 (3)
C(9)	0.8031 (5)	0.1421 (3)	0.4747 (2)	3.8 (2)	O(8)	0.377 (3)	0.099 (2)	0.946 (1)	16 (1) <sup>b</sup>
C(10)	0.7293 (5)	0.1970 (3)	0.4354 (2)	4.1 (2)	O(9)	0.281 (5)	0.091 (3)	0.924 (2)	25 (2) <sup>b</sup>
C(11)	0.6883 (4)	0.2782 (3)	0.4589 (2)	3.6 (2)	O(10)	0.267 (3)	0.015 (2)	0.973 (1)	21 (1) <sup>b</sup>
C(12)	0.6178 (4)	0.2555 (3)	0.5006 (1)	2.7 (2)	O(11)	0.169 (3)	-0.035 (2)	0.942 (1)	15 (1) <sup>b</sup>

<sup>a</sup> B<sub>eq</sub> = (8/3)π<sup>2</sup>∑<sub>i</sub>U<sub>ij</sub>a<sub>i</sub>\*a<sub>j</sub>\*a<sub>i</sub>a<sub>j</sub>. <sup>b</sup> Refined isotropically.

(11a, 11b) are detected by proton and phosphorus-31 NMR spectroscopies. The complex [RuCl(CO)(P(OMe)<sub>3</sub>)(Cytpp)]-[BPh<sub>4</sub>] (12) is produced by treatment of a mixture of 11a and 11b with chloride followed by metathesis of the anion. The unusual ruthenium methoxide complex [Ru(OMe)(CO)(P(OMe)<sub>3</sub>)(Cytpp)][O<sub>3</sub>SCF<sub>3</sub>] (13) is obtained by the reaction of a mixture of 11a and 11b with sodium methoxide. 3 also reacts with selected anions (X<sup>-</sup> = Me<sup>-</sup>, I<sup>-</sup>, and H<sup>-</sup>) to afford complexes *cis-mer*-RuX<sub>2</sub>(CO)(Cytpp) (14, X = Me).

### Discussion

The protonation of *cis-mer*-RuH<sub>2</sub>(CO)(Cytpp) with HCl results in the evolution of hydrogen gas and the formation of *cis-mer*-RuCl<sub>2</sub>(CO)(Cytpp) (1). The meridional orientation of the Cytpp ligand is indicated by both the A<sub>2</sub>X pattern in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum and the <sup>13</sup>C{<sup>1</sup>H} NMR resonances for the ipso cyclohexyl carbon atoms which appear as virtual triplets<sup>16</sup> at 40.1 ppm (t, J<sub>PC</sub> = 10.8 Hz) and 32.5 ppm (t, J<sub>PC</sub> = 10.9 Hz). In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum the downfield shift of the signal for the central phosphorus atom (18.4 ppm) relative to the terminal phosphorus atoms (4.4 ppm) indicates that a weak trans-influence ligand, viz., chloride, is trans to the central phosphorus atom.<sup>5</sup> The equal coupling of the carbonyl carbon to the three phosphorus atoms (11.5 Hz) in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum is consistent with a structure in which the CO is *cis* to all phosphorus donors of Cytpp. Through a different route we were able to isolate another complex *cis-mer*-RuCl<sub>2</sub>(CO)(Cytpp) the spectroscopic properties of which, like those of 1, are consistent with the assigned geometry.<sup>17</sup> The two isomers presumably differ by the orientation of the phenyl group of the central phosphorus atom. The term *syn* is used to represent the stereoisomer in which the phenyl group is on the same side as the higher atomic number ligand *cis* to the three donor atoms of Cytpp.<sup>18</sup> The term *anti* refers to the other stereoisomer. *Syn* and *anti* isomers have been previously reported for chelated

triphosphine complexes.<sup>10,19</sup> On the basis of empirical relationships which will be published later,<sup>17</sup> we formulate 1 as *cis-mer-anti*-RuCl<sub>2</sub>(CO)(Cytpp), in which the phenyl ring is on the side of the carbonyl ligand, as it is in the starting material *cis-mer-syn*-RuH<sub>2</sub>(CO)(Cytpp).<sup>10</sup> The other possible meridional isomer, i.e. *trans-mer*-RuCl<sub>2</sub>(CO)(Cytpp), was previously reported by Meek et al.<sup>20</sup>

The protonation of *cis-mer*-RuH<sub>2</sub>(CO)(Cytpp) with the superacids HBF<sub>4</sub> and HO<sub>3</sub>SCF<sub>3</sub> leads to products that analyze as Ru(BF<sub>4</sub>)<sub>2</sub>(CO)(Cytpp) (2) and Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cytpp) (3), respectively. 2 is isolated as a white powder that is insoluble in hexane, diethyl ether, benzene, toluene, and THF. We found 2 to be soluble in CH<sub>2</sub>Cl<sub>2</sub> and acetone but observe slow abstraction of fluoride from the BF<sub>4</sub><sup>-</sup> anion when the solutions in acetone are stored for extended periods of time. 3 is isolated as a pale yellow powder that exhibits solubility properties similar to those of 2, with the advantage of being soluble in THF. This and the lack of propensity for fluoride abstraction from the anions make 3 a very attractive synthon for various ruthenium(II) complexes.

Pale yellow crystals of 3 suitable for a low-temperature X-ray diffraction analysis were grown from CH<sub>2</sub>Cl<sub>2</sub>. The ORTEP drawing in Figure 1 shows the meridional orientation of the triphosphine around ruthenium and the *cis* geometry of two monodentate triflate ligands in the essentially octahedral complex. The Ru-O bond distances of 2.233 (3) Å for Ru-O(2) and 2.221 (3) Å for Ru-O(5) are notably longer than those of the only other structurally characterized σ-bound ruthenium sulfonate complex *cis-cis*-Ru(OSO<sub>2</sub>Tol-*p*)<sub>2</sub>(H<sub>2</sub>O)(CO)(PPh<sub>3</sub>)<sub>2</sub>, in which the Ru-O bond distances for the tosylates are 2.165 (5) and 2.162 (6) Å.<sup>4</sup> The ruthenium(II)-oxygen bond distances for anionic ligands in other

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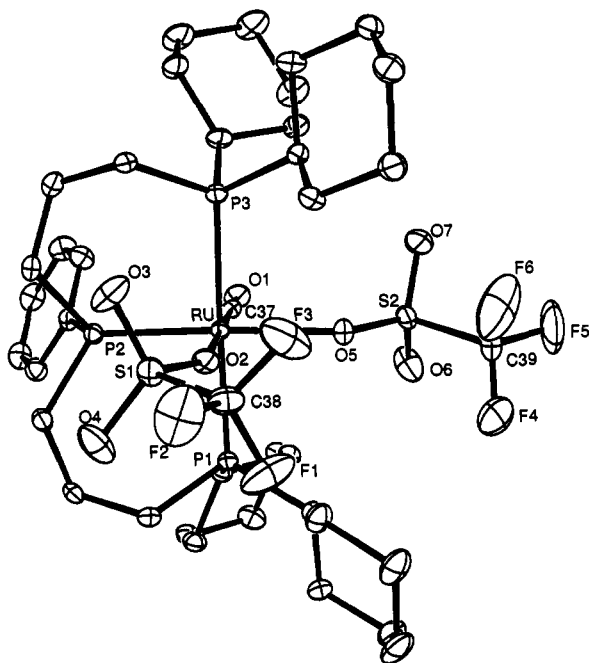


Figure 1. ORTEP drawing of 3, showing atom numbering scheme. The non-hydrogen atoms are represented by 30% probability thermal ellipsoids, and the hydrogen atoms are omitted for clarity.

Table IV. Selected Bond Lengths and Angles for *cis-mer*-Ru(OSO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>(CO)(Cytpt) (3)

Bond Lengths, Å					
Ru-P(1)	2.452 (1)	S(1)-O(3)	1.433 (3)	F(1)-C(38)	1.299 (5)
Ru-P(2)	2.299 (1)	S(1)-O(4)	1.428 (3)	F(2)-C(38)	1.318 (5)
Ru-P(3)	2.472 (1)	S(1)-C(38)	1.829 (5)	F(3)-C(38)	1.289 (5)
Ru-O(2)	2.233 (3)	S(2)-O(5)	1.474 (3)	F(4)-C(39)	1.273 (6)
Ru-O(5)	2.221 (3)	S(2)-O(6)	1.426 (3)	F(5)-C(39)	1.317 (6)
Ru-C(37)	1.808 (4)	S(2)-O(7)	1.424 (3)	F(6)-C(39)	1.284 (7)
S(1)-O(2)	1.461 (3)	S(2)-C(39)	1.820 (5)	O(1)-C(37)	1.151 (5)
Bond Angles, deg					
P(1)-Ru-P(2)	89.95 (4)	O(2)-S(1)-O(3)	113.9 (2)		
P(1)-Ru-P(3)	177.87 (4)	O(2)-S(1)-O(4)	113.7 (2)		
P(1)-Ru-O(2)	88.43 (7)	O(2)-S(1)-C(38)	104.2 (2)		
P(1)-Ru-O(5)	88.32 (8)	O(3)-S(1)-O(4)	116.7 (2)		
P(1)-Ru-C(37)	91.0 (1)	O(3)-S(1)-C(38)	103.0 (2)		
P(2)-Ru-P(3)	92.09 (4)	O(4)-S(1)-C(38)	103.1 (2)		
P(2)-Ru-O(2)	91.64 (8)	O(5)-S(2)-O(6)	114.2 (2)		
P(2)-Ru-O(5)	173.56 (8)	O(5)-S(2)-O(7)	114.3 (2)		
P(2)-Ru-C(37)	89.4 (1)	O(5)-S(2)-C(39)	101.4 (2)		
P(3)-Ru-O(2)	90.92 (7)	O(6)-S(2)-O(7)	116.7 (2)		
P(3)-Ru-O(5)	89.58 (8)	O(6)-S(2)-O(39)	104.1 (3)		
P(3)-Ru-C(37)	89.6 (1)	O(7)-S(2)-C(39)	103.5 (2)		
O(2)-Ru-O(5)	82.1 (1)	Ru-O(2)-S(1)	150.2 (2)		
O(2)-Ru-C(37)	178.8 (1)	Ru-O(5)-S(2)	130.7 (2)		
O(5)-Ru-C(37)	96.8 (1)	Ru-C(37)-O(1)	178.4 (3)		

similar complexes are also shorter than those found for 3. For example, Ru(OC(O)CF<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)(PMe<sub>3</sub>)<sub>3</sub> shows η<sup>1</sup>-trifluoroacetato Ru-O bond lengths of 2.158 (4) and 2.179 (4) Å,<sup>21</sup> Ru(OC(O)Ph)<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> exhibits η<sup>1</sup>-benzoato Ru-O bond lengths of 2.083 (7) and 2.086 (5) Å,<sup>22</sup> and Ru(SO<sub>4</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> displays η<sup>2</sup>-sulfato Ru-O bond lengths of 2.111 (5) Å.<sup>23</sup> Various other ruthenium(II) η<sup>1</sup>-carboxylato,<sup>24</sup> sulfato,<sup>25</sup> salicylaldehydato,<sup>26</sup>

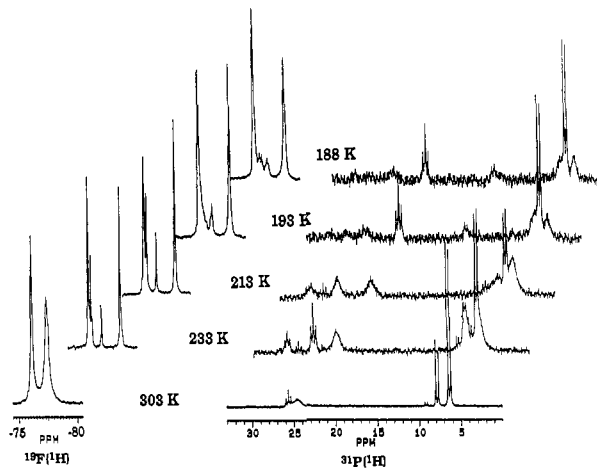


Figure 2. Variable-temperature <sup>19</sup>F{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 3 in CD<sub>2</sub>Cl<sub>2</sub>.

oxalato,<sup>27</sup> μ-trifluoromethanesulfonato,<sup>28</sup> acetylacetonato,<sup>29</sup> and Ru(II)-Ru(II) μ-carboxylato<sup>30</sup> complexes all have shorter Ru-O bond lengths for the anionic oxygen-donor ligands than does 3. These long Ru-O bond distances in 3 are a good indication of the weak nature of the bonding between the triflate ligands and ruthenium.

The ruthenium-central phosphorus, Ru-P(2), bond distance of 2.299 (1) Å is relatively short compared to the ruthenium-terminal phosphorus bond distances of 2.452 (1) Å for Ru-P(1) and 2.472 (1) Å for Ru-P(3). The former is comparable to the Ru-P bond distances for other ruthenium-chelated polyphosphine complexes with a meridional geometry of the polyphosphine ligand in which weakly bound substrates are trans to the central phosphorus.<sup>19f,31</sup>

The ruthenium-terminal phosphorus bond distances are longer than in other meridional Cytpt or ttp neutral complexes of ruthenium in which distances range from 2.298 (1) to 2.442 (1) Å.<sup>10,19f,31</sup> These longer bonds may be the result of steric repulsions between the cyclohexyl groups and triflate ligands. The Ru-C bond distance of 1.808 (4) Å is comparable to that in similar neutral ruthenium carbonyl complexes.<sup>4,24a</sup> The X-ray structure determination also reveals that the phenyl group on the central phosphorus atom points to the carbonyl ligand, as it does in both 1 and the starting material RuH<sub>2</sub>(CO)(Cytpt). Hence 3 is the anti isomer in the solid.

Structures of 2 and 3 in solution are of interest since both compounds contain weakly coordinated ligands. We utilized variable-temperature <sup>19</sup>F{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopies and CD<sub>2</sub>Cl<sub>2</sub> and acetone-*d*<sub>6</sub> solvents in an effort to learn more about the structural behavior of 2 and 3 in solution. The variable-temperature <sup>19</sup>F{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 3 in CD<sub>2</sub>Cl<sub>2</sub> solution are presented in Figure 2. A variety of fluxional processes are suggested by the complexity of these spectra. Ludi and Bailey<sup>3c</sup> reported a similar study on Ru(dppe)<sub>2</sub>(tos)<sub>2</sub> (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, tos = O<sub>3</sub>Stol-*p*) and proposed equilibria involving an octahedral complex containing chelated tosylate, a five-coordinate complex with one monodentate tosylate, and an octahedral complex with two tosylates. The room-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of their complex shows only one set of

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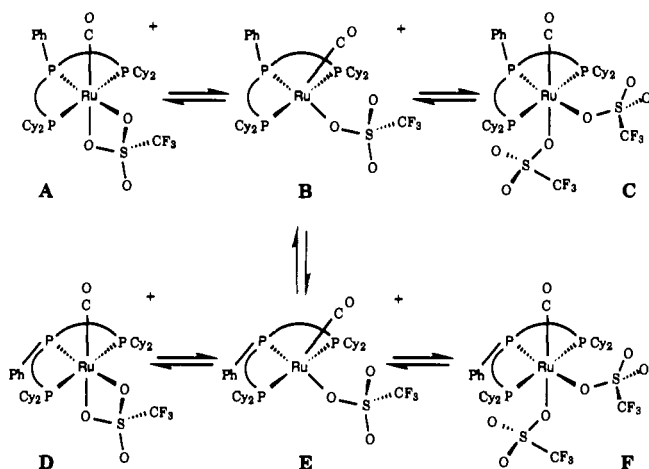
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Scheme IV



sharp coalescence signals. The two sets of signals in the room-temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** are apparently due to two parallel fluxional processes, most likely those of the syn and anti isomers. If so, we might expect these signals to coalesce at a higher temperature into one set consisting of a doublet and a triplet for the terminal and central phosphorus atoms, respectively, owing to syn-anti isomerization. The boiling point of the solvent precludes such a study in this case. The equilibria given in Scheme IV are consistent with the existence of the aforementioned complexes in solution. The presence of the four species A, C, D, and F seems to be indicated by the four signals between 20 and 30 ppm at 233 or 213 K in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **3**. This is consistent with the observation of two sets of signals for the Ludi-Bailey complex<sup>36</sup> at similar temperatures. However, distinct resonances for the proposed five-coordinate species B and E are not observed for **3**. The  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra indicate a variety of species involving triflate, but the assignment of signals, even the assignment of free triflate which is expected in this region, is not possible. The limiting low-temperature spectrum for these exchange processes could not be obtained owing to the freezing point of  $\text{CD}_2\text{Cl}_2$ .

The variable-temperature  $^{19}\text{F}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **2** in  $\text{CD}_2\text{Cl}_2$  solution, which are reproduced in Figure 3, are more complex than those of **3**. The partial  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra given in Figure 3 show signals from -141 to -155 ppm. In this region of the spectra, signals for free  $\text{BF}_4^-$  and the terminal F atoms of coordinated  $(\mu\text{-F})\text{BF}_3^-$  are typically observed in  $\text{CD}_2\text{Cl}_2$ .<sup>32,33</sup> Complete interpretation of these spectra is not possible; however, there is significant evidence that  $\text{BF}_4^-$  is bound to the metal. At 188 K, two doublets (-146.3 ppm ( $J = 91$  Hz) and -149.7 ppm ( $J = 83$  Hz)) and a broad signal (-147.5 ppm) are observed. The doublets exhibit splittings that are similar to values of 90–100 Hz reported by others<sup>32</sup> for  $^2J_{\text{FF}}$  of coordinated  $\text{BF}_3^-$ . Therefore, the doublets are assigned to the terminal F atoms of two inequivalent coordinated  $\text{BF}_3^-$  ions, the splitting being due to coupling with the bridging fluorine in each case. We can only speculate that the broad signal at -147.5 ppm is due to intramolecular and/or intermolecular exchange processes that may involve both coordinated and free  $\text{BF}_4^-$ . A detailed study by Hersh et al.<sup>34</sup> considers possible fluxional processes, which may also occur for **2** in  $\text{CD}_2\text{Cl}_2$  solution. Two broad signals at -261 and -251 ppm are observed at 188 K with relative intensities of 4:1. The upfield shift of these broad signals is typical for the bridging F atom of coordinated  $\text{BF}_4^-$ .<sup>32,33a</sup> The combined intensity of these upfield broad signals is approximately 10% of the overall intensity

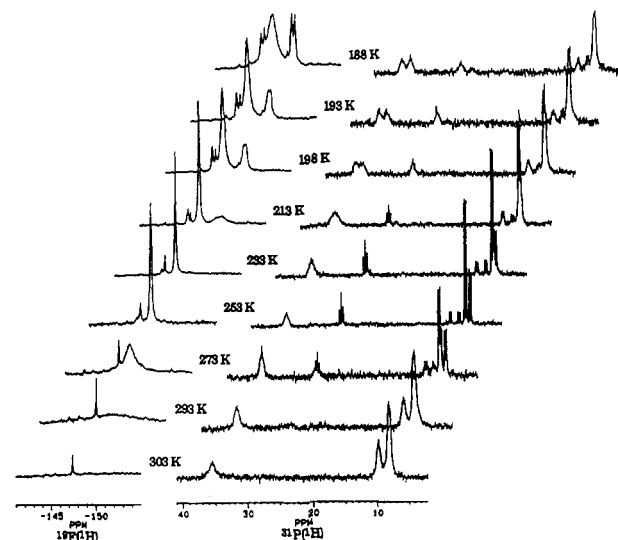


Figure 3. Variable-temperature  $^{19}\text{F}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **2** in  $\text{CD}_2\text{Cl}_2$ .

of the signals in the partial  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum at 188 K in Figure 3. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **2** offer additional evidence for coordinated  $\text{BF}_4^-$ . The most downfield signal at 233 K gradually splits into a broad doublet as the temperature is lowered to 188 K. This phenomenon occurs simultaneously with the gradual growth of the doublets discussed above in the  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra. These observations are likely the result of  $\text{BF}_4^-$  coordination trans to the central phosphorus. The  $^2J_{\text{PF}}$  coupling constant of 136 Hz is significantly larger than  $^2J_{\text{PF}}$  values of 19–58 Hz observed in other complexes in which the bridging F couples to a cis phosphorus atom.<sup>32a,b,35</sup> The phosphorus to fluorine coupling is not observed in the  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra, possibly owing to complex splitting of the bridging F signal by interaction with  $^{10}\text{B}$ ,  $^{11}\text{B}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  nuclei. Complex **2** appears to be a rare example of a low-valent carbonyl/phosphine complex with more than one weakly coordinating  $\text{BF}_4^-$  anion.<sup>36</sup> However, the possibility that the inequivalent coordinated  $\text{BF}_4^-$  ions described above are associated with different metal centers, such as those in syn and anti isomers, cannot be dismissed.

The variable temperature study of **2** and **3** in acetone- $d_6$  showed more straightforward behavior. At 303 K the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** consists of major (8.3 (d), 23.2 (br) ppm) and minor (7.4 (d), 26.5 (br) ppm) sets of signals. As the temperature is lowered, these signals sharpen, and at 243 K very sharp  $\text{A}_2\text{X}$  patterns are observed for two species in solution. The major (8.0 (d), 22.5 (t) ppm;  $^2J_{\text{PP}} = 31$  Hz) and minor (7.8 (d), 26.4 (t) ppm;  $^2J_{\text{PP}} = 31$  Hz) species are observed in an approximately 2:1 ratio. The  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum at 303 K consists of two singlets at -77.1 and -75.2 ppm in an approximate 6:1 ratio. The more intense signal is assigned to free triflate in solution, but the weaker signal remains unexplained. The intensity ratio substantially increases upon lowering the temperature, and the weaker signal splits into two very weak signals both around -75 ppm. These results are consistent with the presence of syn and anti isomers of disolvento metal complexes in solution and strongly indicate that acetone is a better ligand than triflate. The possibility of an equilibrium involving coordinated triflate cannot however be ruled out because of the presence of extraneous, weak  $^{19}\text{F}\{^1\text{H}\}$  NMR signals in the spectra.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** in acetone- $d_6$  at 303 K consists of a slightly broadened  $\text{A}_2\text{X}$  pattern at 8.2 (d) and 22.9 (t) ppm. As the temperature is lowered, a secondary set of peaks grows in until, at 243 K, a spectrum with sharp signals at almost identical

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chemical shifts as those observed for **3** in acetone- $d_6$  at 243 K is observed. The  $^{19}\text{F}\{^1\text{H}\}$  NMR signals at  $-148.1$  ppm ( $^{11}\text{BF}_4^-$ ) and  $-148.0$  ppm ( $^{10}\text{BF}_4^-$ ) with relative intensities of 4:1 remain sharp throughout the temperature range indicating that  $\text{BF}_4^-$  does not coordinate. The slight downfield shift of the  $^{10}\text{BF}_4^-$  (19.7% natural abundance) isotopomer relative to the  $^{11}\text{BF}_4^-$  (80.3% natural abundance) isotopomer has been previously observed.<sup>32a,c</sup> As expected, acetone is a better ligand than  $\text{BF}_4^-$ , and therefore **2** exists in solution as a mixture of syn and anti isomers of disolvento complexes.

The utility of **2** as a starting material for the synthesis of *cis-mer*-substituted products was explored by use of a variety of neutral ligands and acetone as solvent. Acetonitrile, *tert*-butyl isocyanide, and cyclohexyl isocyanide readily react with **2** to form the corresponding *cis-mer*- $[\text{Ru}(\text{CO})\text{L}_2(\text{Cytpp})][\text{BF}_4]_2$  complexes (**4a**, L = MeCN; **5**, L = CNBu-*t*; **6**, L = CNCy). The *cis-mer* geometry for **4a** is indicated by the spectroscopic data. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum the downfield shift of the central phosphorus signal relative to the terminal phosphorus signal shows that MeCN is trans to the former phosphorus atom.<sup>5</sup> Signals for two coordinated acetonitrile ligands are observed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum along with the expected quartet ( $^2J_{\text{PC}} = 11$  Hz) for the CO, which is *cis* to all three phosphorus atoms. The acetonitrile ligands in **4a** are apparently tightly bound to ruthenium, since they cannot be removed under vacuum even upon prolonged treatment. The fact that syn-anti isomerization is not observed for **4a** in acetone also suggests that the acetonitrile ligands remain tightly coordinated in solution. This statement is based upon our observations, reported here and elsewhere,<sup>17</sup> that syn-anti isomerization apparently occurs only when a five-coordinate intermediate is generated in solution. From empirical relationships<sup>37</sup> we assign the orientation of the phenyl ring in **4a** as anti to the acetonitrile ligand that is *cis* to all three phosphorus atoms.

The isocyanide complexes **5** and **6** appear to adopt the same geometry as **4a**. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra the central phosphorus signals are more than 20 ppm upfield from the corresponding terminal phosphorus signals, as expected from the trans labeling effect of isocyanides.<sup>38</sup> The *cis* geometry of the isocyanides is further indicated by two strong  $\nu(\text{CN})$  absorptions in the IR spectrum of each complex.<sup>39</sup> The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **5** shows a quartet signal ( $^2J_{\text{PC}} = 10$  Hz) for the CO to indicate its *cis* position with respect to the three phosphorus atoms. Additional  $^{13}\text{C}\{^1\text{H}\}$  NMR assignments for **5** are given in the Experimental Section. The  $^1\text{H}$  NMR spectrum of **6** shows a multiplet at 4.5–4.6 ppm of the relative intensity 2; it is assigned to the protons attached to the ipso carbon atoms of the isocyanide cyclohexyl groups.

No reaction was observed between **2** and  $\text{PPh}_3$  by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. This is attributed to the large cone angle of  $\text{PPh}_3$  and the steric demands of Cytpp.<sup>40</sup> Other ruthenium Cytpp complexes failed to react with  $\text{PPh}_3$ , presumably for the same reasons.<sup>10</sup> Surprisingly, we also found that **2** failed to react with 2,2'-bipyridine in acetone. The reaction of **2** with CO leads to a mixture of products that abstract  $\text{F}^-$  from  $\text{BF}_4^-$  to yield **8a** and **8b** after several days in acetone solution. Abstraction of  $\text{F}^-$  from  $\text{BF}_4^-$  has been reviewed.<sup>41</sup> A full account of the intriguing reactions of **2** and **3** with CO will be presented in a subsequent paper.<sup>42</sup>

The reaction of **2** with excess NaF in acetone/ $\text{H}_2\text{O}$  leads to the formation of a mixture of syn and anti isomers of  $[\text{RuF}(\text{CO})(\text{H}_2\text{O})(\text{Cytpp})][\text{BF}_4]$ , **7a** and **7b**. The white mixture of **7a** and **7b** turns yellow under vacuum at 0.1 Torr after 1 day. The

color change is reversed upon storage of the yellow mixture in air for several hours. This phenomenon can be continually reproduced on a single sample and is likely due to the loss and recapture of  $\text{H}_2\text{O}$ . The lability of the  $\text{H}_2\text{O}$  ligand in **7a** and **7b** was investigated by use of  $^2\text{D}\{^1\text{H}\}$  NMR and  $\text{D}_2\text{O}$  in place of  $\text{H}_2\text{O}$  in the synthesis of **7a** and **7b**. A  $^2\text{D}\{^1\text{H}\}$  NMR spectrum of the yellow mixture prepared by using  $\text{D}_2\text{O}$  in acetone showed only a signal due to the natural abundance of deuterium in the acetone, thus indicating that  $\text{D}_2\text{O}$  (or  $\text{H}_2\text{O}$ ) is lost under vacuum. Gradual addition of  $\text{D}_2\text{O}$  ( $\ll 1$  equiv) first resulted in the appearance of a singlet at 4.13 ppm and then of a set of broad signals with peaks at 5.07 and 4.34 ppm. Continued addition of  $\text{D}_2\text{O}$  (1–2 equiv) led to the appearance of sets of broad signals with peaks at slightly lower field strength. When a large excess of  $\text{D}_2\text{O}$  was added, a singlet at 4.60 ppm was observed. These observations indicate that exchange of free and coordinated  $\text{D}_2\text{O}$  occurs in solution. The room temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **7a** in acetone- $d_6$  consists of a signal for the central phosphorus atom at 33.2 ppm ( $^2J_{\text{PP}} = 34$  Hz,  $^2J_{\text{PF}} = 16$  Hz) and the terminal phosphorus atoms at 12.3 ppm ( $^2J_{\text{PF}} = 24$  Hz). As the temperature is lowered, these signals broaden and then sharpen until at 243 K two sets of signals for both the central phosphorus atom ( $\delta$  35.0 ppm,  $^2J_{\text{PP}} = 34$  Hz,  $^2J_{\text{PF}} = 9$  Hz;  $\delta$  31.1 ppm,  $^2J_{\text{PP}} = 34$  Hz,  $^2J_{\text{PF}} = 15$  Hz) and the terminal phosphorus atoms ( $\delta$  12.9 ppm,  $^2J_{\text{PF}} = 24$  Hz;  $\delta$  11.5 ppm,  $^2J_{\text{PF}} = 24$  Hz) are observed. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at 303 K is therefore a coalescence spectrum of two signals attributed to complexes with coordinated  $\text{H}_2\text{O}$  and without coordinated  $\text{H}_2\text{O}$ . Only one broad signal at  $-318.9$  ppm was noted in the  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum at 303 K for coordinated  $\text{F}^-$ , whereas two signals at  $-310.4$  (br) and  $-318.8$  (br) ppm were observed at 243 K. These results are also consistent with a rapid exchange of coordinated and free  $\text{H}_2\text{O}$  at 303 K.

The lability of  $\text{H}_2\text{O}$  in **7a** and **7b** is further demonstrated by the facile substitution reactions with CO and CNBu-*t* to form a mixture of syn and anti isomers of *mer*- $[\text{RuF}(\text{CO})\text{L}(\text{Cytpp})][\text{BF}_4]$  complexes (**8a** and **8b**, L = CO; **9a** and **9b**, L = CNBu-*t*). The dicarbonyl complexes **8a** and **8b** both have a meridional orientation of the Cytpp ligand as indicated by the  $^{31}\text{P}\{^1\text{H}\}$  NMR data. The upfield shift of the central phosphorus atom signal relative to the terminal phosphorus atom signal for both isomers indicates that CO rather than  $\text{F}^-$  is trans to the central phosphorus. The dramatic differences in the central phosphorus-fluorine coupling constants ( $^2J_{\text{PCF}}$ ) for **8a** and **8b** resemble the differences observed between **7a** and **7b** and between **9a** and **9b** (cf. Table I). To confirm the *cis* geometry of the fluoride relative to the central phosphorus atom for **8a** (and, by analogy, for **7a** and **9a**), a  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of a mixture of **8a** and **8b** containing  $>95\%$  **8a** was obtained. The signal for the carbonyl trans to the central phosphorus occurs at 194.1 (dtd) ppm with couplings of 94, 11, and 4 Hz to  $\text{P}_\text{C}$ ,  $\text{P}_\text{W}$ , and  $\text{F}$ , respectively. The carbonyl trans to fluoride resonates at 200.3 (ddt) ppm with couplings of 65, 12, and 9 Hz to  $\text{F}$ ,  $\text{P}_\text{C}$ , and  $\text{P}_\text{W}$ , respectively. Hence, the *cis* geometry for both isomers is confirmed, and the isomers observed for **7**, **8**, and **9** must result from the stereochemical orientation of the phenyl group on the central phosphorus atom. Scheme II provides the reactions and structures of these fluoride-containing complexes.

In each of the fluoro complexes described above, the fluoro ligand is trans to a carbonyl ligand and *not* trans to the central phosphorus of the chelated ligand. The preferential trans orientation of the  $\pi$ -donor fluoro and  $\pi$ -acceptor carbonyl ligands appears to be common for other  $d^6$  complexes.<sup>43</sup> It is worth noting that difluorination of **2** to form *cis-mer*- $\text{RuF}_2(\text{CO})(\text{Cytpp})$  does *not* occur in an acetone/water mixed-solvent system even in the presence of excess NaF. In contrast, the complexes *cis-mer*- $\text{RuX}_2(\text{CO})(\text{Cytpp})$  (X = Cl, I) form readily under analogous conditions in which NaX is substituted for NaF.

The reactions of **3** are shown in Scheme III. The absence of fluoride abstraction from triflate and the solubility of **3** in THF render **3** a more versatile starting material than **2**. Upon disso-

(37) The other stereoisomer, *cis-mer-syn*- $[\text{Ru}(\text{CO})(\text{NCMe})_2(\text{Cytpp})][\text{O}_3\text{SCF}_3]_2$ , has been prepared; see ref 17.

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lution in acetonitrile **3** forms the same cation as that in **4a** but with  $\text{O}_3\text{SCF}_3^-$  rather than  $\text{BF}_4^-$  as the counterion, namely, *cis-mer-anti*- $[\text{Ru}(\text{CO})(\text{NCMe})_2(\text{Cytpt})][\text{O}_3\text{SCF}_3]_2$  (**4b**). When ammonia is bubbled through a solution of **3** in THF, a new diammine complex *cis-mer*- $[\text{Ru}(\text{CO})(\text{NH}_3)_2(\text{Cytpt})][\text{O}_3\text{SCF}_3]_2$  (**10**), results. Absorptions for the N–H stretching ( $3350\text{--}3150\text{ cm}^{-1}$ ) and N–H bending ( $1535\text{ cm}^{-1}$ ) modes are observed in the IR spectrum. A complex set of signals in the  $^1\text{H}$  NMR spectrum at 3.35 (br), 3.58 (br), and 3.63 (t) ppm for six protons is assigned to the two  $\text{NH}_3$  ligands. The downfield shift of the central phosphorus atom resonance relative to the terminal phosphorus atoms resonance in the  $^{31}\text{P}\{\text{H}\}$  NMR spectrum indicates that  $\text{NH}_3$ , a weak trans-influence ligand, is positioned trans to the central phosphorus. Hence **10** must adopt a *cis* geometry.

As did **2**, **3** failed to react with  $\text{PPh}_3$ . However, **3** does react with  $\text{P}(\text{OMe})_3$  to form monosubstituted products. The isolated product of this reaction is tentatively formulated as *mer*- $[\text{Ru}(\text{CO})(\text{P}(\text{OMe})_3)(\text{Cytpt})][\text{O}_3\text{SCF}_3]_2$  (**11**). The  $^{31}\text{P}\{\text{H}\}$  NMR spectrum of **11** in acetone- $d_6$  shows two sets of signals in an approximate 8:1 ratio to indicate the presence of two species in solution. In both complexes, the *trans* geometry of  $\text{P}(\text{OMe})_3$  and the central phosphorus of *Cytpt* is clearly indicated by the large coupling constants of more than 400 Hz. The remaining  $^{31}\text{P}\{\text{H}\}$  NMR data for these two species, designated as **11a** (major) and **11b**, are presented in Table I. Their ratio in THF- $d_8$  is close to 1:1. It is likely that the two complexes are *syn* and *anti* stereoisomers. *Syn* and *anti* stereoisomers of similar phosphite complexes have been previously reported.<sup>10,19a</sup> It is also possible that the two species differ by the occupancy of the "sixth site", since triflate, acetone, and residual THF are all present in solution. This latter possibility appears less likely however, based on the fact that exchange of such weakly coordinating ligands is expected to be fast at room temperature and probably would not give rise to two sets of sharp signals but rather to only one set of broad or sharp signals. The  $^1\text{H}$  NMR spectrum of **11** provides additional evidence that both products contain  $\text{P}(\text{OMe})_3$  based on the appearance of two doublets for the  $\text{P}(\text{OMe})_3$  protons. The spectrum also shows signals at ca. 5.6 ppm (a multiplet corresponding to <0.5 protons) and ca. 3.7 ppm (a multiplet corresponding to >3 protons) whose intensities vary for samples from different runs of the reaction. These signals may derive from coordinated solvents (since complete removal of THF by vacuum treatment or extensive washing with hexane proved unsuccessful) or an impurity that could not be removed from the product.

The tentative formulation of **11** is supported by its reaction with  $\text{LiCl}$ . After metathesis of tetraphenylborate for triflate, the analytically pure *mer*- $[\text{RuCl}(\text{CO})(\text{P}(\text{OMe})_3)(\text{Cytpt})][\text{BPh}_4]$  (**12**) can be isolated. The  $^{31}\text{P}\{\text{H}\}$  NMR spectrum in  $\text{CDCl}_3$  shows only one set of signals, which again indicates a *trans* geometry for the  $\text{P}(\text{OMe})_3$  ligand and central phosphorus of the meridionally oriented *Cytpt*. A doublet at 3.73 ppm in the  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  is assigned to the  $\text{P}(\text{OMe})_3$  protons. Elemental analysis confirms the presence of one chloride ligand.

Complex **11** also undergoes reaction with  $\text{NaOMe}$  in THF and a small amount of methanol to form a mononuclear ruthenium alkoxide which we formulate as  $[\text{Ru}(\text{OMe})(\text{CO})(\text{P}(\text{OMe})_3)(\text{Cytpt})][\text{O}_3\text{SCF}_3]$  (**13**). The structure of **13** is shown in Scheme III. The pale yellow isolated solid is very sparingly soluble in hexane, acetone, and THF but sufficiently soluble in benzene to allow characterization by  $^{31}\text{P}\{\text{H}\}$  and  $^1\text{H}$  NMR spectroscopies. The  $^{31}\text{P}\{\text{H}\}$  and  $^1\text{H}$  NMR data are presented in Table I. The large coupling between the central phosphorus of *Cytpt* and the phosphite phosphorus of 440 Hz indicates a *trans* disposition of these atoms. A singlet at 3.18 ppm in the  $^1\text{H}$  NMR spectrum and an absorption at  $2725\text{ cm}^{-1}$  in the IR spectrum are assigned to the protons and the C–H stretch, respectively, of the coordinated methoxide ligand. The IR  $\nu(\text{CO})$  band at  $1925\text{ cm}^{-1}$  for **13** is at significantly lower energy than that in either **11** or **12**. This would appear to indicate that methoxide-to-ruthenium  $\pi$  bonding occurs to enhance  $\pi$  backbonding between Ru and the *trans* carbonyl. It is generally recognized that mononuclear ruthenium

alkoxide complexes are rare;<sup>44</sup> we found only one example of a well-characterized compound<sup>45</sup> among relatively few that have been reported.<sup>46</sup> The well-characterized methoxide complex of Gouterman et al.,<sup>45</sup> viz.,  $\text{Ru}(\text{OEP})(\text{NO})(\text{OMe})$  (OEP = octaethylporphinate), apparently gains stability from the inability of the methoxide to undergo  $\beta$ -hydrogen elimination owing to the occupancy of the equatorial plane by the porphyrin ligand.<sup>47</sup> The methoxide complex reported here may similarly derive its stability from the coordination in the equatorial plane of the meridional *Cytpt* and trimethyl phosphite ligands.

The nucleophiles  $\text{Me}^-$ ,  $\text{H}^-$ , and  $\text{I}^-$  all react with **3** to form *cis*-substituted neutral complexes. The complexes *cis-mer*- $\text{RuH}_2(\text{CO})(\text{Cytpt})$ <sup>10</sup> and *cis-mer*- $\text{RuI}_2(\text{CO})(\text{Cytpt})$ <sup>11</sup> have been previously prepared by other routes. However, the air-sensitive dimethyl complex *cis-mer*- $\text{RuMe}_2(\text{CO})(\text{Cytpt})$  (**14**) is a new compound. Its  $^{13}\text{C}\{\text{H}\}$  NMR spectrum confirms this formulation with signals for the CO at 206.6 ppm (q,  $^2J_{\text{PC}} = 4.9\text{ Hz}$ ), the methyl *trans* to the central phosphorus at  $-14.7\text{ ppm}$  (dt,  $^2J_{\text{PC}} = 58.1, 11.4\text{ Hz}$ ), and the methyl *trans* to CO at  $-6.3\text{ ppm}$  (q,  $^2J_{\text{PC}} = 11.2\text{ Hz}$ ). The resonance for the methyl *trans* to phosphorus in the  $^1\text{H}$  NMR spectrum is observed at  $-0.12\text{ ppm}$  as a triplet of doublets. A larger coupling constant to the *cis* phosphorus atoms (6.1 Hz) than to the *trans* phosphorus atom (4.0 Hz) has been noted by others.<sup>48</sup> The protons of the other methyl ligand resonate at  $-0.43\text{ ppm}$  as a doublet of triplets owing to coupling to the central phosphorus atom (9.3 Hz) and terminal phosphorus atoms (7.1 Hz).

## Conclusion

The compounds *cis-mer*- $\text{Ru}(\text{BF}_4)_2(\text{CO})(\text{Cytpt})$  (**2**) and *cis-mer*- $\text{Ru}(\text{OSO}_2\text{CF}_3)_2(\text{CO})(\text{Cytpt})$  (**3**) represent unusual examples of octahedral ruthenium(II) complexes. They display a rigid geometry imposed by the meridional orientation of a chelating triphosphine, *Cytpt*, and a tightly bound carbonyl, which remains *cis* to the three phosphorus atoms at all times. The weakly coordinated anions,  $\text{BF}_4^-$  and  $\text{O}_3\text{SCF}_3^-$ , complete the coordination environments of ruthenium(II) and provide two very labile *cis*-octahedral sites. As a result, these air-stable compounds are rare examples of labile low-spin  $d^6$  transition-metal complexes. The utility of **2** and **3** as starting materials has been shown by the synthesis of a variety of coordination and organometallic complexes of ruthenium(II).

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**Supplementary Material Available:** Figures showing complete  $^{19}\text{F}\{\text{H}\}$  NMR spectrum of **2** at 188 K in  $\text{CD}_2\text{Cl}_2$ ,  $^{19}\text{F}\{\text{H}\}$  and  $^{31}\text{P}\{\text{H}\}$  NMR spectra of complexes **2** and **3** at 303 and 243 K in acetone- $d_6$ , and a complete numbering scheme for the non-hydrogen atoms and listings of anisotropic thermal parameters, hydrogen atom coordinates, bond distances involving the hydrogen atoms, additional bond distances, intermolecular distances involving the non-hydrogen atoms, and complete crystallographic details for complex **3** (18 pages); a table of observed and calculated structure factors for complex **3** (48 pages). Ordering information is given on any current masthead page.

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