

# Synthesis and Complexation Properties of the Anions $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PR}_2\text{O})_3^{2-}$ as Ligands

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Reaction of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{OMe})_2]$  (**2**) with  $\text{HP}(\text{O})(\text{OR})_2$  gave the novel tripod ligands  $\text{H}_2(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{PO}(\text{OR})_2\}_3$  ( $\text{R} = \text{Me, Et, } ^i\text{Pr, H}_2\text{I}$ ).  $\text{H}_2(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{PO}(\text{Ph}_2)\}_3$  was formed with  $\text{HP}(\text{O})\text{Ph}_2$ .  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2]_2$  (**3**) with  $\text{NaP}(\text{O})(\text{OEt})_2$  similarly gave  $\text{Na}_2(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{PO}(\text{OEt})_2\}_3$  ( $\text{Na}_2\text{1}$ ;  $\text{Na}_2\text{L}$ ). Either the hydrogen form or the sodium salt was reacted with main group and transition metal halides to yield complexes  $[\text{ML}_2]^{n-}$  ( $\text{M} = \text{Si}^{\text{IV}}, \text{Ti}^{\text{IV}}, \text{Nb}^{\text{IV}}, n = 0; \text{Co}^{\text{II}}, n = 2; \text{Cr}^{\text{III}}, \text{Fe}^{\text{III}}, n = 1$ ), or complexes of the form  $\text{LMX}$  with  $\text{MX} = \text{BPh, VO}$ . Reaction of  $\text{Na}_2(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{PO}(\text{Ph}_2)\}_3$  with  $\text{TiCl}_4$  gave intermediately  $[\text{LTiCl}_2]_2$  which readily hydrolyzed on chromatography over  $\text{Al}_2\text{O}_3$  to trinuclear  $(\text{LTiO})_3(\mu_3\text{-O})\text{H}_2$ . The latter was characterized by X-ray structure analysis. It crystallizes in the cubic space group  $Pa\bar{3}$  (No. 205),  $z = 8$ ,  $a = 30.83(1) \text{ \AA}$ ,  $V = 29300(30) \text{ \AA}^3$ . From the reaction of  $\text{Na}_2\text{1}$  and **3** under appropriate conditions, the mixed valence complex  $\text{LRu}(\eta^5\text{-C}_5\text{Me}_5)$  (**4**) was isolated. Compounds were characterized by spectroscopy and electrochemistry. From absorption spectra of the  $\text{Co}^{\text{II}}$  and the  $\text{Cr}^{\text{III}}$  complex ligand field parameters  $\Delta_o = 902$  and  $1450 \text{ cm}^{-1}$ , respectively, were derived, placing **1** near  $\text{F}^-$  in the spectrochemical series.

## Introduction

The coordination chemistry of the ligand  $\text{CpCo}\{\text{PO}(\text{OR})_2\}_3^-$  ( $\text{L}_{\text{Co}}$ ) first discovered in 1977<sup>1</sup> and broadly developed in the decade thereafter forms octahedral complexes  $\text{M}(\text{L}_{\text{Co}})_2^{n+}$  which are exceptional in that this hard tripodal oxygen ligand combines low ligand field splitting parameter  $\Delta_o$  with high complex formation constants for transition as well as main group elements.<sup>2</sup> Apart from octahedral complexes an extensive chemistry of half-sandwich complexes  $\text{M}(\text{L}_{\text{Co}})\text{L}'_n$  has been developed where  $\text{L}'$  could be typical  $\pi$ -acceptor ligands and  $\text{L}_{\text{Co}}$  or similarly  $\text{L}_{\text{Rh}}$  to some extent mimic  $(\eta^5\text{-C}_5\text{H}_5)/(\eta^5\text{-C}_5\text{Me}_5)$ .<sup>3</sup> In some instances  $\text{L}_{\text{Co}}/\text{L}_{\text{Rh}}$  allowed stabilization of complexes where no Cp analogue is known.<sup>4</sup>

When it became evident from redox investigations<sup>5</sup> that the rather uniform shift of about 1 V in redox potentials of related transitions between  $\text{Maq}^{n+}$  and  $\text{M}(\text{L}_{\text{Co}})_2^{(n-2)+}$  (the latter being reduced at more negative potential) as well as the complexing properties of  $\text{L}_{\text{Co}}$  is at least in part due to the uninegative charge of the ligand it seemed desirable to vary the carrier metal, up to then Co, Rh, or Ir in their +3 oxidation states. Incorporation of a +2 carrier metal would enhance the ligand charge by one and thus alter the properties of complexes accordingly. Since the carrier metal has to be substitutionally as inert as possible with high preference for octahedral coordination to soft as well

as hard ligands,  $\text{Ru}^{2+}$  (apart from possibly  $\text{Os}^{2+}$ ) appeared as a rational choice. Our first attempts to synthesize the target molecule  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{PO}(\text{OMe})_2\}_3^{2-}$  (**1**) along the routes established for the group 9 congeners  $\text{L}_{\text{Co,Rh,Ir}}$ , i.e., by successive Arbuzhov rearrangements of the respective phosphite complexes, Scheme 1, failed, due to the reluctance of coordinated  $\text{P}(\text{OMe})_3$  to undergo this reaction more than once.<sup>6</sup> Direct substitution of OMe in  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{OMe})_2]$  (**2**) with phosphonic acid esters or of Cl in  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2]_2$  (**3**) with the Na phosphonates led to the desired ligand. Different from Co and Rh analogues, nucleophilic exchange of OR groups at phosphorus is quite facile in the Ru tripod ligands which can in principle be used for the preparation of complexes with different OR groups.

The new ligand proved to be a versatile complexing agent just as  $\text{L}_{\text{Co}}$ . Results for main group elements as well as for transition metals are detailed below. An account of part of this work has appeared in preliminary form.<sup>7</sup>

## Experimental Section

All manipulations were performed under pure nitrogen. Solvents were dried and nitrogen-saturated. Spectra were recorded on Bruker WP 80 and Varian Unity 300 and 500 (NMR), Perkin-Elmer 842 (IR), Polytech xdap (UV/vis), and Finnigan MAT 95 (MS) spectrometers. Analyses were from Analytische Laboratorien, Engelskirchen.

Preparation and analytical data for compounds **5a**,  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{PO}(\text{OMe})_2\}_3]_2\text{Nb}$  (**6**),  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{PO}(\text{OEt})_2\}_3]_2\text{Si}$  (**7**), and **11** are given in ref 7.

$\text{H}_2(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{PO}(\text{OR})_2\}_3$ , **H<sub>2</sub>I** (**a**,  $\text{R} = \text{Me}$ ; **b**,  $\text{R} = \text{Et}$ ; **c**,  $\text{R} = ^i\text{Pr}$ ).  $\text{HPO}(\text{OR})_2$  (7.08 mmol) was injected into a solution of 1.18 mmol **2**<sup>8</sup> in 60 mL of ether. The mixture was stirred for 4 h at ambient temperature, the solvent was evaporated in vacuo, and the brown oily

(1) (a) Kläui, W.; Neukomm, H.; Werner, H.; Huttner, G. *Chem. Ber.* **1977**, *110*, 2283. (b) Kläui, W.; Otto, H.; Eberspach, W.; Buchholz, E. *Chem. Ber.* **1982**, *115*, 1922.

(2) Kläui, W. *Angew. Chem.* **1990**, *102*, 66; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 627.

(3) (a) Goldberg, I.; Shinar, H.; Navon, G.; Kläui, W. *J. Incl. Phenom.* **1987**, *5*, 181. (b) Kläui, W.; Müller, A.; Herbst, R.; Eger, E. *Organometallics* **1987**, *6*, 1824. (c) Kläui, W.; Müller, A.; Scotti, M. *J. Organomet. Chem.* **1983**, *253*, 45.

(4) (a) Kläui, W.; Lenders, B.; Hessner, B.; Evertz, K. *Organometallics* **1988**, *7*, 1357. (b) Lenders, B.; Kläui, W.; Irmeler, M.; Meyer, G. *J. Chem. Soc., Dalton Trans.* **1990**, 2069.

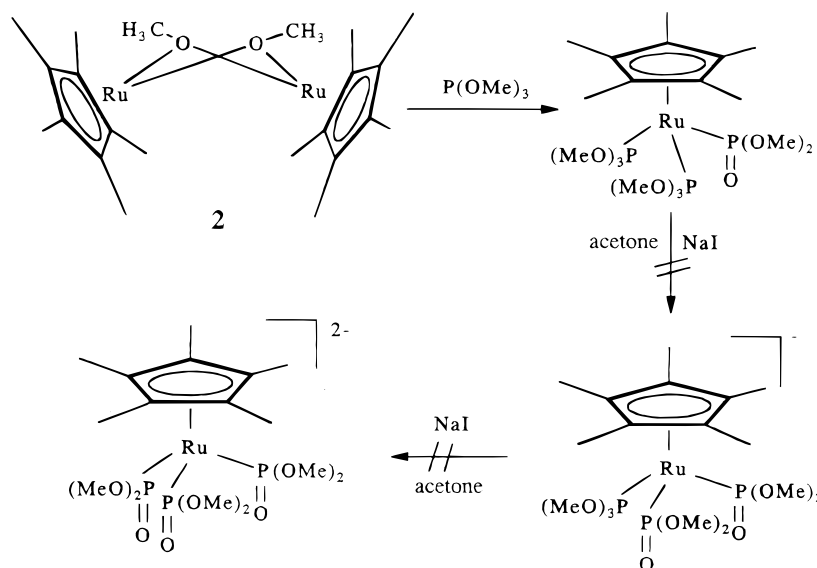
(5) Kläui, W.; Müller, A.; Eberspach, W.; Boese R.; Goldberg, I. *J. Am. Chem. Soc.* **1987**, *109*, 164.

(6) Koelle, U.; Rütther, Th.; Kläui, W. *J. Organomet. Chem.* **1992**, *426*, 99.

(7) Koelle, U.; Rütther, Th.; Englert, U.; Le Navror, N.; Kläui, W. *Angew. Chem.* **1994**, *106*, 1028; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 991.

(8) Koelle, U.; Kossakowski, J. *Inorg. Synth.* **1992**, *29*, 225.

Scheme 1



residue was extracted with 50 mL of pentane. From the pentane solution impurities and excess  $\text{HPO}(\text{OR})_2$  was frozen out by cooling to  $-78\text{ }^\circ\text{C}$  for 24 h. The pentane solution was warmed to  $0\text{ }^\circ\text{C}$ , decanted, and filtered over Celite, and products were isolated by evaporating the solvent as light brown solids in 85% (**a**), 70% (**b**), and 70% (**c**) yield.

**H<sub>2</sub>1a.**  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): ( $\eta^5\text{-C}_5\text{Me}_5$ ) 1.87 (q,  $^4J_{\text{H,P}}$  2.2 Hz), OMe 3.55 (vq,  $^3J_{\text{H,P}}$  11.2 Hz), POH 10.8 (br s).  $^{31}\text{P NMR}$ : 144.7. MS ( $m/z$ ,  $I_{\text{rel}}$  (%): 566 (5,  $\text{M}^+$ ), 534 (25,  $\text{M} - \text{MeOH}$ ), 502 (23,  $\text{M} - \text{PO}(\text{OMe})_2\text{H}_2$ ), 424 (38,  $\text{M} - \text{PO}(\text{OMe})_3\text{H}$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{35}\text{O}_9\text{P}_3\text{Ru}$  ( $M_r$  565.5): C, 33.98; H, 6.24. Found: C, 32.97; H, 6.33.

**H<sub>2</sub>1b.**  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): ( $\eta^5\text{-C}_5\text{Me}_5$ ) 1.91 (q,  $^4J_{\text{H,P}}$  2.1 Hz), OEt 1.18, 4.07, POH 9.4 (br s).

**H<sub>2</sub>1c.**  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): ( $\eta^5\text{-C}_5\text{Me}_5$ ) 1.89 (q,  $^4J_{\text{H,P}}$  2.1 Hz), O $^i$ Pr 1.0, 4.86, POH 10.2 (br s).

**Na<sub>2</sub>1a from 1a.** To a solution of 360 mg (0.673 mmol) **H<sub>2</sub>1a** in 20 mL of THF was added at  $-78\text{ }^\circ\text{C}$  a 100% excess of NaH. The mixture was warmed to ambient temperature with vigorous stirring. Gas evolution was visible from about  $-30\text{ }^\circ\text{C}$ . After 20 h excess NaH was removed by filtration over Celite. The solution was concentrated to 3 mL, 30 mL of pentane was added, and the resulting solution was cooled to  $-30\text{ }^\circ\text{C}$ , whence impurities separated as a white solid. Evaporation of the brown supernatant to dryness left 396 mg (88%) of product as light brown powder.

**Na<sub>2</sub>1b from 3.** To a solution of 2.45 mmol of freshly prepared  $\text{NaPO}(\text{OEt})_2$  (from  $\text{HPO}(\text{OEt})_2$  and NaH) in 50 mL of THF was added 0.05 mL of EtOH and in small portions 240 mg (0.34 mmol) of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2]_2$  (**3**). The color slowly changed from brown yellow into olive green. After 6 h at ambient temperature, the solvent was removed in vacuo and the oily residue was extracted with 60 mL of pentane and filtered over Celite. The product was purified by chromatography over  $\text{Me}_3\text{SiCl}$ -treated silica eluting with hexane/ether 5:1. Removing the solvent left 205 mg (40%) of product as a light brown oil.

**H<sub>2</sub>1d.** To a solution of 300 mg (0.56 mmol) of **2** in 30 mL of  $\text{Et}_2\text{O}$  was added 680 mg (3.36 mmol) of  $\text{HPOPh}_2$ . A creme solid separated within some min from the solution. After 20 h at ambient temperature, the solvent was removed in vacuo and the oily residue was washed three times with 10 mL methanol and finally with a few milliliters of pentane. Drying in a high vacuum gave 804 mg (84%) of a yellowish powder.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): ( $\eta^5\text{-C}_5\text{Me}_5$ ) 1.38 (q,  $^4J_{\text{H,P}}$  1.3 Hz), *m*-Ph 6.87 (t,  $J$  7.6 Hz), *p*-Ph 6.94 (t,  $J$  7.3 Hz), *o*-Ph 7.42 (m), POH 13.3 (br s).  $^{31}\text{P NMR}$ : 118.7. IR ( $\text{KBr}/\text{cm}^{-1}$ ): 1431 ( $\nu(\text{P}-\text{Ph})$ ), 916 ( $\nu(\text{P}=\text{O})$ ), 522 ( $\delta(\text{P}=\text{O})$ ). MS ( $m/z$ ,  $I_{\text{rel}}$ ): 764 (2,  $\text{M}-\text{PhH}$ ), 361 (29, ( $\eta^5\text{-C}_5\text{Me}_5$ )- $\text{RuPOPh}$ ). Anal. Calcd for  $\text{C}_{46}\text{H}_{47}\text{O}_3\text{P}_3\text{Ru}$  ( $M_r$  841.9): C, 65.63; H, 5.63. Found: C, 65.99; H, 5.78.

**Na<sub>2</sub>1d.** As for **Na<sub>2</sub>1a** from **H<sub>2</sub>1d**: on workup, removal of the solvent after filtration over Celite gave the product in 60% yield as a yellowish

powder. Anal. Calcd for  $\text{C}_{46}\text{H}_{45}\text{Na}_2\text{O}_3\text{P}_3\text{Ru}$  ( $M_r$  885.9): C, 62.38; H, 5.13. Found: C, 62.56; H, 5.34.

**( $\eta^5\text{-C}_5\text{Me}_5$ )Ru{PO(OEt)<sub>2</sub>}<sub>3</sub>Ru( $\eta^5\text{-C}_5\text{Me}_5$ ) (**4**).** To a slurry of 210 mg (0.34 mmol) of **3** in 30 mL of THF was added a solution of 2.05 mmol of freshly prepared  $\text{NaPO}(\text{OEt})_2$  in THF, whence the reaction mixture turned green. After 5 h at ambient temperature, the solvent was removed in vacuo and the residue was extracted with several portions of pentane. From the combined pentane extracts was obtained 290 mg (96%) product as a green powder.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): ( $\eta^5\text{-C}_5\text{Me}_5$ )  $-3.03$  (br s), Me 1.3 (br t), ( $\eta^5\text{-C}_5\text{Me}_5$ ) 2.08 (br s). IR ( $\text{KBr}/\text{cm}^{-1}$ ): 1080 ( $\nu(\text{P}=\text{O})$ ), 602 ( $\delta(\text{P}=\text{O})$ ); FAB/MS ( $m/z$ ,  $I_{\text{rel}}$ ): 885 (100,  $\text{M}^+$ ), 838 (20,  $\text{M} - \text{PO}$ ), 467 (40,  $\text{M} - (\text{PO}(\text{OEt})_3\text{Ru}(\eta^5\text{-C}_5\text{Me}_5))$ ).

**[( $\eta^5\text{-C}_5\text{Me}_5$ )Ru(PO(Ph)<sub>2</sub>)<sub>3</sub>Ti]<sub>3</sub>( $\mu_2\text{-O}$ )<sub>3</sub>( $\mu_3\text{-O}$ )H<sub>2</sub> (**9**).** To a solution of 110 mg (0.124 mmol) of **Na<sub>2</sub>1d** in 10 mL of THF was added an excess of  $\text{TiCl}_4 \cdot 2\text{THF}$ , whence the solution turned red. After removing the solvent and drying in high vacuo, we were left with 80 mg (67%) of an orange solid. Orange crystals of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PO}(\text{Ph})_2)_3\text{TiCl}_2]_3 \cdot 2\text{C}_7\text{H}_8$  (**8**· $\text{C}_7\text{H}_8$ ) were obtained by cooling a concentrated toluene solution to  $-78\text{ }^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): ( $\eta^5\text{-C}_5\text{Me}_5$ ) 1.47 (q), Ph 6.75, 7.30 (m). IR ( $\text{KBr}/\text{cm}^{-1}$ ): 907 ( $\nu(\text{P}=\text{O})$ ), 576 ( $\delta(\text{P}=\text{O})$ ). Anal. Calcd for  $(\text{C}_{53}\text{H}_{53}\text{Cl}_2\text{TiP}_3\text{O}_3\text{Ru})_3$  ( $M_r$  1050.8): C, 60.58; H, 5.08. Found: C, 60.04; H, 4.83.

The product was then chromatographed over alumina (5% water) using 2:1 toluene/hexane as eluent. Diffusion of pentane into a concentrated toluene solution gave orange crystals of  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{PO}(\text{Ph})_2)_3\text{Ti}(\mu_2\text{-O})_3(\mu_3\text{-O})\text{H}_2]$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): ( $\eta^5\text{-C}_5\text{Me}_5$ ) 1.41 (br s), Ph 6.9, 7.3 (m). Anal. ( $M_r$  2635) Calcd: C, 62.26; H, 5.06. Found: C, 63.76; H, 5.86.

**( $\eta^5\text{-C}_5\text{Me}_5$ )Ru{PO(OMe)<sub>2</sub>}<sub>3</sub>VO (**10**).** Into a solution of 360 mg (0.636 mmol) of **H<sub>2</sub>1a** in 20 mL of ether cooled to  $-78\text{ }^\circ\text{C}$  was injected 3 mL of a DMF solution containing 90 mg of  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  and 72 mg of  $\text{Et}_3\text{N}$  (0.72 mL), whence  $(\text{Et}_3\text{NH})_2\text{SO}_4$  precipitates. The olive green mixture was warmed to ambient temperature and stirred for 2 h more. From the (now clear) solution ether was removed in a high vacuum. To the oily residue was added MeOH to precipitate the product. This was filtered and washed twice with 10 mL of MeOH and with a few milliliters of ether. Drying in vacuo left 125 mg (31%) of blue powder.  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): ( $\eta^5\text{-C}_5\text{Me}_5$ ) 1.3 (br s), *POMe* 3.4 (br s). IR ( $\text{KBr}/\text{cm}^{-1}$ ): 925 ( $\nu(\text{V}=\text{O})$ ). MS ( $m/z$ ,  $I_{\text{rel}}$ ): 631 (5,  $\text{M}^+$ ), 600 (17,  $\text{M} - \text{OMe}$ ), 237 (2, ( $\eta^5\text{-C}_5\text{Me}_5$ )Ru), 133 (100, RuP). Anal. Calcd for  $\text{C}_{16}\text{H}_{33}\text{O}_{10}\text{P}_3\text{RuV}$  ( $M_r$  630.4): C, 30.48; H, 5.28. Found: C, 30.40; H, 5.35.

**Na[( $\eta^5\text{-C}_5\text{Me}_5$ )Ru(PO(OEt)<sub>2</sub>)<sub>3</sub>Cr<sup>III</sup>] (**12**).** On addition of 78 mg (0.336 mmol) of  $\text{CrCl}_3 \cdot 3\text{THF}$  to a solution of 0.50 g (0.672 mmol) of **Na<sub>2</sub>1b** in 25 mL of THF the mixture turned rapidly green. After stirring for 12 h at ambient temperature the solvent was evaporated in vacuo, the green residue was then stirred with 40 mL pentane, the solution

**Table 1.**  $\nu(\text{P}=\text{O})$  and  $\delta(\text{P}=\text{O})$  of Ligands and Complexes

compound		$\nu(\text{P}=\text{O})$	$\delta(\text{P}=\text{O})$
$\text{L}_{\text{OMe}}\text{Na}_2$	<b>1a</b>	1178	534
$\text{L}_{\text{Ph}}\text{Na}_2$	<b>1b</b>	916	522
$(\text{L}_{\text{OMe}})_2\text{M}$			
$\text{S}_i^{\text{IV}}$	<b>7</b>	1090	555
$\text{Ti}^{\text{IV}}$		1060	649
$\text{Nb}^{\text{IV}}$	<b>6</b>	1070	619
$\text{Cr}^{\text{III}}$	<b>12</b>	1098	625
$\text{Fe}^{\text{III}}$	<b>13</b>	—	600
$(\text{L}_{\text{OEt}})_2\text{Co}^{\text{II}}$	<b>11</b>	1096	584
LML'			
$\text{L}_{\text{OMe}}\text{BPh}$	<b>5a</b>	1070	
$\text{L}_{\text{Ph}}\text{BPh}$	<b>5c</b>	898	519
VO	<b>10</b>	—	652
$\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)$	<b>4</b>	1080	602

**Table 2.** Crystallographic Data for **9**

$\text{C}_{149}\text{H}_{159}\text{O}_{13}\text{P}_9\text{Ti}_3$	fw = 2883.6
$a = 11.309(7) \text{ \AA}$	$Pa\bar{3}$
$V = 29\,302(28) \text{ \AA}^3$	$T = 258 \text{ }^\circ\text{C}$
$Z = 8$	$\lambda = 0.7107 \text{ \AA}$
$R^a = 0.071$	$d_{\text{calcd}} = 1.307 \text{ g cm}^{-3}$
$R_w^b = 0.073$	$\mu = 6.01 \text{ cm}^{-1}$

<sup>a</sup>  $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$ ;  $w^{-1} = \sigma^2(F_o)$ .

filtered over Celite, the solvent evaporated, and the residue dried in a high vacuum to yield 380 mg (82%) of a light gray green powder. IR (KBr/cm<sup>-1</sup>): 1055, 1020 ( $\nu(\text{P}-\text{O}-\text{C})$ ). FAB-MS ( $m/z$ ,  $I_{\text{rel}}$ ): 1395 (100,  $\text{M} + \text{H} + \text{Na} = \text{M}' + \text{Na}$ ), 1372 (81,  $\text{M}'$ ), 1327 (29,  $\text{M}'\text{-OEt}$ ).

**Na**[( $\eta^5\text{-C}_5\text{Me}_5$ )**Ru**(**PO**(**OMe**)<sub>2</sub>)<sub>3</sub>]<sub>2</sub>**Fe**<sup>III</sup>] (**13**). To a solution of 116 mg (0.19 mmol) of **Na**<sub>2</sub>**1a** in 7 mL of THF was added a stoichiometric amount of **FeCl**<sub>3</sub>. After stirring for 12 h at ambient temperature the solvent was removed in vacuo and the oily residue washed with small portions of pentane until the pentane washings were almost colorless. Drying of the residue gave 95 mg (83%) of product as a red brown powder. Anal. Calcd for **Fe**: 4.63. Found: 4.57.

**Electrochemical Measurements.** Cyclic voltammetry was performed with EG&G equipment using a Pt inlay electrode of 0.2 cm<sup>2</sup> area in  $\text{CH}_2\text{Cl}_2$  or THF. The supporting electrolyte was 0.1 M  $\text{Bu}_4\text{-NPF}_6$ , the sweep rate 100 mV/s, and the reference electrode was an aqueous saturated calomel electrode (SCE). The ferrocene potential in this system is 0.4 V or measured potentials when deviating were corrected to fit this value.

**Crystal Structure Determination of 9.** Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a solution of **9** in toluene. An orange crystal of approximately octahedral shape and 0.5 mm diameter was studied at 258 K on an ENRAF Nonius CAD4 diffractometer with graphite monochromator. Crystal data, parameters of data collection, and convergence results are compiled in Table 2. The structure was solved with direct methods<sup>9</sup> and refined with the local version of the SDP program system.<sup>10</sup> On the basis of the three check reflections, data were corrected for an anisotropic loss of ca. 25% of diffraction intensity due to evaporation of the clathrated solvent. An empirical absorption correction<sup>11</sup> was applied (min. transmission 0.68).

The molecules occupy the 3-fold axis in the cubic space group  $Pa\bar{3}$ . After successful refinement of the trimeric complexes, solvent molecules could be located in the interstitials. A systematic grid search in the unit cell revealed three symmetrically independent voids of remarkable size ( $>70 \text{ \AA}^3$ ), which were large enough to accommodate solvent molecules. The highest peaks of a difference Fourier map were found in these regions. Each asymmetric unit contains one atom close to a 3 position thus forming a regular six-membered ring. The methyl group

of this toluene molecule is disordered over six symmetry equivalent positions and could not be located. The electron density in the other two voids was attributed to disordered pentane. These peaks were refined with isotropic displacement parameters; when their occupancy was adjusted to match the C,H analysis, their  $B_{\text{iso}}$  converged to mostly high but acceptable values (max.  $11 \text{ \AA}^2$ ).

In the final least-squares full-matrix refinement with 532 variables and 4231 symmetry independent observations with  $I > 2\sigma(I)$  hydrogen atoms were included in fixed positions. No hydrogen atoms were considered for the disordered solvent regions. All crystal data refer to a composition of 0.5 molecule of toluene and 1.5 molecules of pentane per trimeric complex.

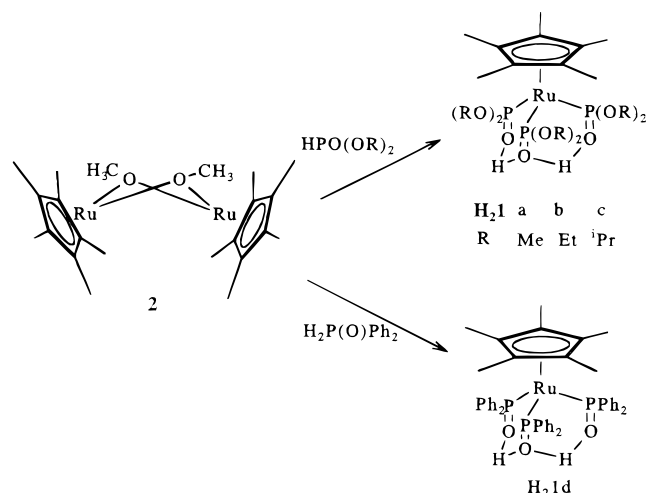
## Results

**Ligand Syntheses.** Synthesis of the ligand **1** can be achieved from either  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\text{OMe})_2]$  (**2**) or  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2]$  (**3**). In the first case the methoxo dimer<sup>8</sup> is reacted with the phosphites  $\text{HPO}(\text{OR})_2$  and gives by addition and **MeOH** substitution the tripod complex **1** in the neutral diprotonated form (**H**<sub>2</sub>**1**). The reaction is performed in ether, and the products are transferred into pentane solution from where impurities and excess  $\text{HPO}(\text{OR})_2$  are frozen out at  $-78 \text{ }^\circ\text{C}$ . The complex **1** remains as a creme solid after evaporation of the solvent and is spectroscopically pure. ( $\eta^5\text{-C}_5\text{Me}_5$ ) protons in the NMR ( $\text{C}_6\text{D}_6$ ) are quartets by coupling to three equivalent phosphorus atoms ( $J_{\text{P,H}} \approx 2.2 \text{ Hz}$ ) at 1.6–2 ppm. Protons of the **POCH** group are pseudoquartets by virtual phosphorus coupling. The **OH** protons form a broadened singlet between 9 and 11 ppm. The <sup>31</sup>P NMR spectrum shows one singlet.

In variance to group 9 tripods the lower charge of the carrier metal in **1** imposes facile nucleophilic exchange of **OR** groups on phosphorus. Thus, if the NMR spectrum of **H**<sub>2</sub>**1a** is recorded in  $\text{CD}_3\text{OD}$ , the pseudoquartet at 3.55 ppm of the **OMe** protons disappears due to formation of the **POCD**<sub>3</sub> ligand. Compounds **H**<sub>2</sub>**1** are similarly obtained with different **OR** groups by dissolving e.g. **H**<sub>2</sub>**1a** in the respective alcohol. On the other hand makes this facile substitution at phosphorus the free ligand (in the protonated form or as alkali metal salt) sensitive toward nucleophilic solvents. Decomposition occurs in media like acetone, acetonitrile or water. The isolated ligands decompose at ambient temperature within some days and have to be stored at low temperature.

Apart from  $\text{HPO}(\text{OR})_2$  **2** was reacted with  $\text{HPO}(\text{Ph})_2$  to give the **PPh**<sub>2</sub> derivative **H**<sub>2</sub>**1d**. This latter has much higher thermal stability than the **OR** derivatives and has not been observed to undergo nucleophilic substitution at phosphorus.

## Scheme 2

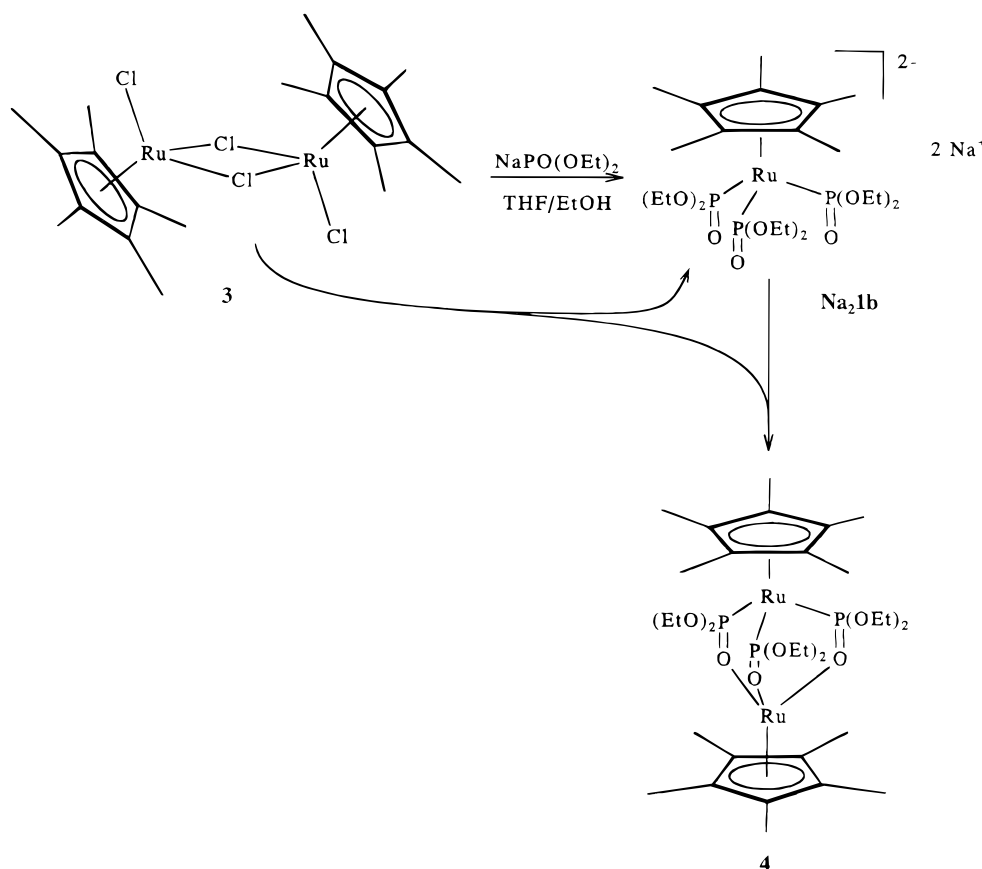


(9) Sheldrick, G. M. *SHELXS86: Program for structure solution*; University of Göttingen: Germany, 1986.

(10) Frenz, B. *SDP*, Version 5; Enraf-Nonius: Delft, The Netherlands, 1989.

(11) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, A39, 158.

Scheme 3



Attempts were made to synthesize complex **1b** directly from  $[(\eta^5\text{-C}_5\text{Me}_5)\text{RuCl}_2]_2$  (**3**) which is the precursor for the preparation of **2**. It has been found that **3** reacts with  $\text{NaPO}(\text{OEt})_2$  to yield the desired complexes, however, the reaction course is complicated. The reaction was performed in THF to which some EtOH has been added as reducing agent for  $\text{Ru}^{\text{III}}$ . During reaction the development of a green color indicated the formation of the mixed valence  $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$  complex **4** from **1** and the starting  $\text{Ru}^{\text{III}}$  chloro dimer (Scheme 3). Formation of **4** can be suppressed to some extent by adding **3** in portions to an excess of  $\text{NaPO}(\text{OR})_2$  but cannot be completely eliminated. Therefore this procedure necessitates chromatographic purification of the reaction mixture (see experimental) to isolate pure **1b** in 40% yield. Like  $\text{LCo}$  alkali metal salts also  $\text{Na}_2\mathbf{1}$  is soluble in nonpolar solvents and even hydrocarbons.

Alternatively the sodium salts of **1** are obtained from the acid  $\text{H}_2\mathbf{1}$  by deprotonation with  $\text{NaH}$ . It has been found that e.g.  $\text{NaOMe}$  as a base leads only to partial deprotonation leaving a mixture of mono- and diprotonated form. Thus the second  $\text{p}K_s$  value of  $\text{H}_2\mathbf{1}$  must be comparable to that of the alcohol  $\text{ROH}$ .

Whereas for  $\text{H}_2\mathbf{1}$  the NMR spectra are sharp and of highest possible symmetry, this is not the case for e.g. Na salts. All three signals in the  $^1\text{H}$  NMR of  $\text{Na}_2\mathbf{1a}$  in  $\text{C}_6\text{D}_6$  are broad, indicating some unsymmetrical structure. There is no clear temperature variation of line width within the limited temperature range accessible in the system. A trimeric structure with unsymmetrical oxygen coordination has been found in crystalline  $\text{Na}[\text{CpCo}\{\text{PO}(\text{OEt})_2\}_3]_3^5$  and as indicated by the NMR spectra such unsymmetrical coordination also pertains to  $\text{Na}_2\mathbf{1}$ . Obviously, coordinative exchange between oxygen sites in solvents such as benzene is slow enough to prevent symmetrization.

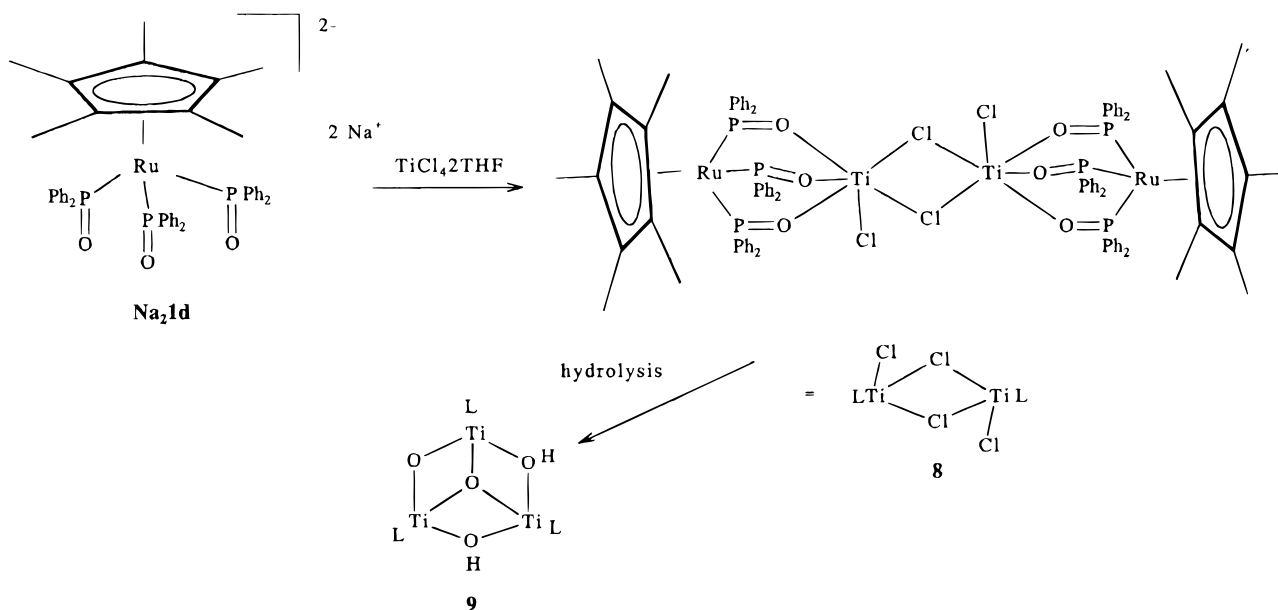
**Complex Formation.** As has been shown<sup>7</sup> tripod ligands are acting as efficient complexing agents toward main group

as well as transition elements. One of the most straightforward reactions is the one with  $\text{PhBCl}_2$  leading to thermally and air stable **1BPh** (**5**). This reaction has been used in fact to prove the formation of **1** under various conditions and to determine yields from reaction mixtures. The OMe derivative **5a** was characterized by an X-ray structure determination showing ideal symmetrical ( $\text{C}_{3v}$ ) coordination of the BPh group to three oxygen atoms similar as had been previously determined for  $\text{CpCo}\{\text{PO}(\text{OEt})_2\}_3\text{BF}$ .<sup>1a</sup> Central metals in the +IV oxidation state that were complexed by **1** were Si, Ti, and Nb through the respective chlorides  $\text{SiCl}_4$ ,  $\text{TiCl}_4$  and  $\text{NbCl}_5$ . In the latter case complexation is accompanied by a reduction to  $\text{Nb}^{\text{IV}}$ . Since no  $\text{Nb}^{\text{V}}$  oxidation wave (before the  $\text{Ru}^{\text{III}}$  oxidation see below) could be detected in the cyclic voltammogram of the Nb complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{P}(\text{O})(\text{OMe})_2\}_3]_2\text{Nb}$  (**6**), we conclude that a possible  $\text{Nb}^{\text{V}}$  complex would be a rather strong oxidant and could thus be reduced by e.g. excess ligand. The silicon complex  $[\text{Cp}^{\wedge}\text{Ru}\{\text{P}(\text{O})(\text{OMe})_2\}_3]_2\text{Si}$  ( $\text{Cp}^{\wedge} = \eta^5\text{-C}_5\text{Me}_4\text{Et}$ ) (**7**) is one of the yet rare examples of a structurally characterized hexa-oxygen-coordinated silicon in a molecular compound. As for the BPh derivative **5**, Si and Nb derivatives are also air-stable compounds, insensitive to solvents, and of good thermal stability.

The product formed from  $\text{H}_2\mathbf{1d}$  (with phenyl groups at P) and  $\text{PhBCl}_2$  was **1dBPh** (**5c**), which was, as expected, largely analogous to the OR derivatives. A somewhat different course took the reaction between  $\text{TiCl}_4 \cdot 2\text{THF}$  and  $\text{Na}_2\mathbf{1d}$  (Scheme 4). In this case no  $\text{L}_2\text{Ti}$  complex was found in the reaction mixture. NMR and IR spectra show the formation of a tripod complex with  $\nu(\text{P}=\text{O})$  and  $\delta(\text{P}=\text{O})$  both shifted to smaller ( $907\text{ cm}^{-1}$ ) and greater ( $576\text{ cm}^{-1}$ ) wavenumbers respectively compared to the free ligand (Table 1) indicative of complexation of **1** to an electrophilic cation fragment. The product contains chloride,



## Scheme 4



and elemental analysis of the orange crystals separated from toluene were in accord with the—presumably dimeric—formula  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{PO}(\text{Ph})_2\}_3\text{TiCl}_2]_2 \cdot \text{C}_7\text{H}_8$  (**8**). Attempted purification through chromatography over alumina deactivated with 5% water, however, yielded a hydrolysis product, the trinuclear titanyl complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{PO}(\text{Ph})_2\}_3\text{Ti}]_3(\mu_2\text{-O})_3(\mu_3\text{-O})\text{H}_2$  (**9**) which was identified and characterized by X-ray structure analysis.

Complex **9** crystallizes in the space group  $Pa\bar{3}$  with 8 molecules of the complex and two different solvent molecules (toluene, pentane) in the unit cell. A view of the molecule is given in Figure 1. Three  $\text{LTiO}_3$  units form a regular triangle combined by three doubly and one triply bridging oxygen atom. The 3-fold axis runs through the central oxygen O2 and is thus the principal axis of the molecular point group  $C_{3v}$ . Triply

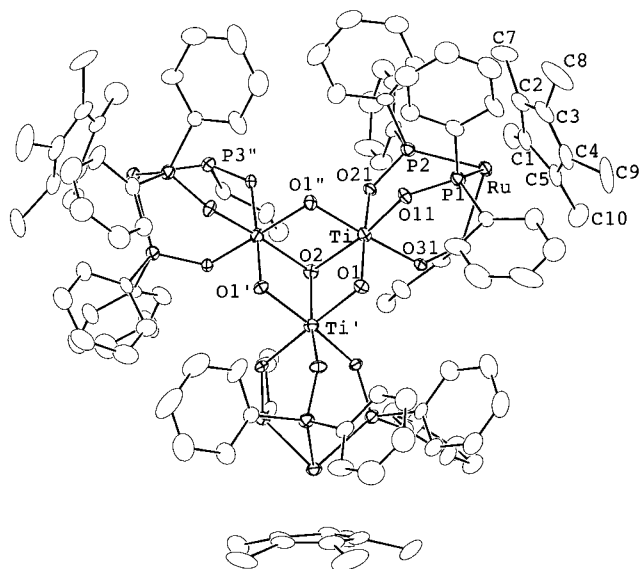
bridging oxygen in a Ti–O cluster molecule has hitherto only been found in  $(\text{CpTiO})_6(\mu_3\text{-O})_8$ <sup>12</sup> where oxygen atoms are bridging faces of a  $(\text{CpTiO})_6$  octahedron. The coordination environment of Ti in **9** is a slightly compressed oxygen octahedron with inner ligand O–Ti–O angle of  $102.0(3)^\circ$  and bridging oxygen O–Ti–O angle of  $98.9(2)^\circ$ . Ti–O distances to P–O and bridging oxygen atoms are equal within error limits. Ti–Ti distances are  $3.035(3)$  Å and are considered nonbonding.

Since in the yellow crystals of **9** all Ti are of oxidation state IV the molecular formula require two more protons for electroneutrality which, however, were not located in the crystal structure and did not show up in the elemental analysis either. They are most probably bound to bridging oxygen atoms and are disordered as to conserve molecular  $C_{3v}$  symmetry.

The reason no  $\text{L}_2\text{M}$  complex was formed in this case lies in a severe steric congestion. When Ru–C( $\eta^5\text{-C}_5\text{Me}_5$ ) distances in **9** are compared with those in **5a** and **7** (and in a wealth of other  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}$  complexes<sup>13</sup>), it becomes evident that they are longer than in any previously investigated case by about 0.09 Å. The structure of **9** shows severe steric interference of PPh with  $(\eta^5\text{-C}_5\text{Me}_5)$  group. The latter are displaced by 0.32–0.4 Å from the Cp plane in the direction away from Ru. Close contacts between phenyl and methyl groups are documented by intergroup C···C distances of e.g. 3.56 and 3.58 Å.

In the group 9 tripod series  $\text{L}_2\text{Ti}$  complexes have been isolated with  $\text{Ti}^{\text{IV}}$  and  $\text{Ti}^{\text{III}}$  where in particular  $\text{Ti}^{\text{IV}}$  should not be smaller in size than e.g. Si in **7**. Steric interference of phenyl with  $(\eta^5\text{-C}_5\text{Me}_5)$ -methyl groups prevents formation of  $\text{L}_2\text{Ti}$  and offer a general route to half-sandwich complexes  $\text{L}_{\text{Ru}}\text{MX}$  with  $\text{L} = \mathbf{1d}$ . The easy formation of the (P)Ph-substituted BPh complex **5c** is a further proof of this prediction.

Likewise, a half-sandwich type complex was obtained from the reaction of **H21** with vanadyl sulfate using  $\text{Et}_3\text{N}$  as proton scavenger. The blue vanadyl complex  $\text{Na}[\mathbf{1aVO}]$  (**10**) was prepared either from the protonated ligand or from the sodium salt. In particular it was found in this reaction that starting from

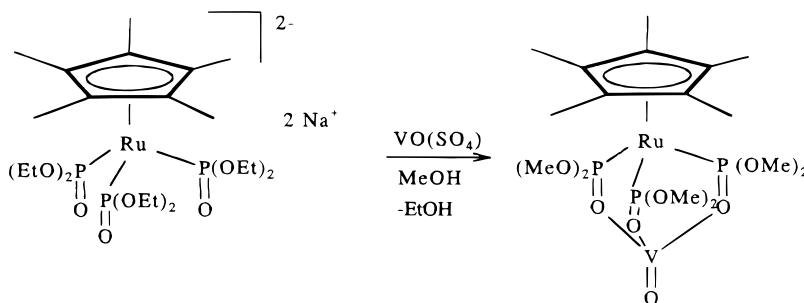


**Figure 1.** ORTEP (SCHAKAL) of complex **9**. Bond distances (Å) and angles (deg): Ru–P (mean), 2.318(2); Ti–O1, 1.951(5); Ti–O2, 1.998(6); Ti–O11, 1.918(5); Ti–O21, 1.955(5); Ti–O31, 1.942(5); P–O (mean), 1.581(6); P–Ru–P (mean), 85.4(1); O1–Ti–O11, 96.0(2); O1–Ti–O31, 86.6(2); O1–Ti–O21, 171.7(2); O11–Ti–O21, 89.2(2); O11–Ti–O31, 88.4(2); O21–Ti–O31, 87.1(2); Ti–O1–Ti', 102.0(3); Ti–O2–Ti', 98.9(2).

(12) Huffman, J. C.; Stone, J. G.; Caulton, W. G. *J. Am. Chem. Soc.* **1977**, *99*, 5829.

(13) Wang, M. H.; Englert, U.; Koelle, U. *J. Organomet. Chem.* **1993**, *453*, 127.

## Scheme 5



**Na1b** isolation of the complex from MeOH yielded exclusively the OMe derivative **1aVO**. Thus exchange of OR groups at P occurs in the complexed ligand as well. The vanadyl complex is characterized by a V=O vibration at  $925\text{ cm}^{-1}$  in the IR. The paramagnetism leads to somewhat broad signals in the NMR. The compound is air sensitive and of moderate stability in solution and also as a solid.

A further example of a first-row transition metal cation with electron configuration  $d^{n>0}$  complexed by two molecules **1** in addition to previously reported  $[\text{I}_2\text{Co}^{\text{II}}]^{2-}$  (**11**)<sup>7</sup> is the  $\text{Cr}^{\text{III}}$  complex **12** prepared by reaction of  $\text{CrCl}_3 \cdot 3\text{THF}$  with **Na21b**. Since absorption spectra of  $\text{Cr}^{\text{III}}$  for most cases are readily interpreted in terms of ligand field parameters, we hoped to extract these latter from the UV/vis spectrum of **12**. The visible region of the spectrum in pentane consists of a band with maximum  $16\,700\text{ cm}^{-1}$  ( $\epsilon = 34$ ) with a shoulder at  $14\,510\text{ cm}^{-1}$  ( $\epsilon = 19\text{ L/mol cm}$ ). Assigning the bands to the  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$  and  ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$  transitions, respectively,  $Dq$  is evaluated as  $1450\text{ cm}^{-1}$ . The respective value that has been determined for the  $\text{Co}^{\text{II}}$  complex **11** was  $902\text{ cm}^{-1}$  the difference being the normal shift from a dipositive to a tripositive ion. The value of  $Dq$  ranges  $1^2-$ , despite its doubly negative charge and similarly to group 9 tripods,<sup>1b,14</sup> near  $\text{F}^-$  (cf.  $\text{CrF}_6^{3-}$ ,  $Dq = 1490\text{ cm}^{-1}$ <sup>15</sup>) in the spectrochemical series as one of the very weak ligands.

**Redox Properties.** As one of the key parameters to characterize a ligand system has been identified its influence on the redox potential of the central metal.<sup>16</sup> Unfortunately none of the  $\text{L}_2\text{M}$  complexes of **1** allowed unambiguous location of a central metal electron transition in cyclic voltammetry. This may be due to the fact that the ligand itself by its carrier metal  $\text{Ru}^{\text{II}}$  is more sensitive to redox changes than the rather inert  $\text{Co}^{\text{III}}$  and  $\text{Rh}^{\text{III}}$  tripods.<sup>17</sup>

$\text{Ru}^{\text{II/III}}$  oxidation was studied in the PhB complexes  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{P}(\text{O})\text{R}_2\}_3\text{BPh}$ , **5a,c** ( $\text{R} = \text{OMe}, \text{Ph}$ ). The cyclic voltammograms for both compounds are very similar, showing one chemically reversible oxidation wave at  $E_{1/2} = 0.97$  (**5a**) and  $0.84$  (**5c**) V vs SCE, respectively, which is assigned a  $\text{Ru}^{\text{II/III}}$  oxidation. A second oxidation at about  $1.3\text{ V}$  is irreversible and may be attributed to a  $\text{Ru}^{\text{III/IV}}$  transition since no other redox active atoms are present.

Two chemically reversible oxidation waves were found in  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{P}(\text{OMe})_2\}_3]_2\text{Si}$  (**7**) at  $0.64$  and  $0.85\text{ V}$ . They are assigned to the two Ru centers oxidized from II to III in sequence. The potential shift of about  $200\text{ mV}$  between these chemically identical electron transitions shows the interaction between Ru centers in  $\text{L}_2\text{M}$  tripod complexes over a distance of more than  $7\text{ \AA}$ . Since a mere electrostatic effect would not

be expected to act over such a long distance, electronic coupling of the carrier metal centers across the Si atom is the only viable explanation.

An idea of the influence of  $\text{L}_{\text{Ru}}$  on the redox transitions of the complexed metal can be gathered from the compound  $\text{LVO}$ , **10**. A partly reversible wave with a peak separation of  $240\text{ mV}$  and a mean potential of  $-0.25\text{ V SCE}$  was observed at the reductive scan. The oxidative scan gave a mostly irreversible peak at  $0.63\text{ V}$ . Whereas the latter could be either  $\text{Ru}^{\text{II/III}}$  or  $\text{V}^{\text{IV/V}}$  oxidation the reduction peak clearly refers to  $\text{V}^{\text{IV/III}}$  with, however, possibly some chemical transformation at the reduced V. The measured potential means a stabilization of  $\text{V}^{\text{IV}}$  vs  $\text{V}^{\text{III}}$  by about  $0.6\text{ V}$  through  $\text{L}_{\text{Ru}}$  as compared to the aqua ion  $\text{VOaq}^{2+}$ . ( $E^\circ$  for  $\text{VOaq}^{2+}/\text{V}^{3+}$  in water is  $0.34\text{ V NHE}$ . Since ferrocene<sup>+0</sup> in water is  $0.4\text{ V vs NHE}$  and in e.g.  $\text{CH}_2\text{Cl}_2$  has the same value vs an aqueous SCE separated by a frit from the organic solution, under these conditions NHE potentials in water can be roughly equated to SCE potentials in organic solvents of low to medium polarity for large ions such as the complexes dealt with herein.)

Pertinent results were further borne out by the electrochemistry of the mixed valence complex  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}\{\text{P}(\text{OEt})_2\}_3\text{-Ru}(\eta^5\text{-C}_5\text{Me}_5)$ , **4**. The neutral compound showed an irreversible reduction at  $-1.1\text{ V}$  and two irreversible oxidation peaks at  $0.36$  and  $1.35\text{ V}$ , respectively. The  $0.36\text{ V}$  peak is assigned  $\text{Ru}^{\text{II/III}}$  oxidation and the  $-1.1\text{ V}$  peak to  $\text{Ru}^{\text{III/II}}$  reduction. By comparison with Ru-based potentials in  $\text{L}_{\text{Co}}\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)$  ( $-0.31\text{ V}^{18}$ ) and  $\text{L}_{\text{Ru}}$ , oxidation states in **4** should be partitioned as  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}^{\text{II}}\{\text{P}(\text{OEt})_2\}_3\text{Ru}^{\text{III}}(\eta^5\text{-C}_5\text{Me}_5)$ . Note that  $\text{Ru}^{\text{II}}$  resides in the *softer* and  $\text{Ru}^{\text{III}}$  in the *harder* ligand environment. The value of  $-1.1\text{ V}$  for reduction of  $\text{Ru}^{\text{III}}$ , albeit the peak potential of an irreversible reduction, can nevertheless be compared to the same transition in  $(\eta^5\text{-C}_5\text{Me}_5)\text{RuL}_{\text{Co}}$ . The considerably more negative  $\text{Ru}^{\text{III/II}}$  potential signalizes a significant stabilization of the  $\text{Ru}^{\text{III}}$  oxidation state in a  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}$  moiety by  $\text{L}_{\text{Ru}}$  as compared to  $\text{L}_{\text{Co}}$ .

Despite this unambiguous assignment of oxidation states to the two chemically different Ru centers in **4** a certain degree of electronic interaction placing the complexes between Robin-Day class III and class II is evident from the properties of the compound.  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}^{\text{III}}$  complexes are all brown to dark in color and do not show transitions beyond  $450\text{ nm}$  in their electronic absorption spectra. In contrast is the green color of **4** reminiscent of the symmetrical  $\text{Ru}^{\text{II/III}}$  mixed valence complex  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)^{19}$  (and similarly other mixed valence Ru complexes of the same type such as  $(\text{NH}_3)_3\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{NH}_3)_3^{20}$ ) which are considered class III complexes. The

(14) Kläui, W.; Eberspach, W.; Gütlisch, P. *Inorg. Chem.* **1987**, *26*, 3977.

(15) Lever, A. B. P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984; p. 419.

(16) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.

(17) ElMurr, N.; Chaloyard, A.; Kläui, W. *Inorg. Chem.* **1979**, *18*, 2629.

(18) Koelle, U.; Kläui, W. *Z. Naturforsch.* **1991**, *B36*, 75.

(19) Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383.

(20) Anillo, A.; Rosete, R. O.; Cole-Hamilton, D. J. *Polyhedron* **1987**, *6*, 1709.

high stabilization of the  $\text{O}_3\text{Ru}^{\text{III}}(\eta^5\text{-C}_5\text{Me}_5)$  center toward reduction could then be interpreted in terms of partial charge transfer from the carrier metal  $\text{Ru}^{\text{II}}$  to  $\text{Ru}^{\text{III}}$ . The rather cathodic oxidation potential of the carrier  $\text{Ru}^{\text{II}}$  in **4** as compared to complexes **5** and **7** with redox invariant complexed atoms may in turn be explained by a diminished charge density of  $\text{Ru}^{\text{II}}$  induced through transfer to  $\text{Ru}^{\text{III}}$ . From the hardness of the PO  $\pi/\sigma$ -donor in  $\text{L}_{\text{Co,Rh}}$  it was concluded that there is very little if any electronic interaction between the  $\text{Co}^{\text{III}}$ ,  $\text{Rh}^{\text{III}}$  carrier metal and the oxygen-complexed inner metal ions.<sup>2</sup> In particular the redox chemistry of **4** as well as that of **7** clearly shows that in case of a  $\text{Ru}^{\text{II}}$  carrier metal the  $-\text{P}(\text{OR})_2\text{O}-$  moieties linking three metals in these complexes not only act as geometrical spacers but also as an electronic link between metal centers.

### Conclusion

Replacement of  $(\text{Co}, \text{Rh}, \text{Ir})^{\text{III}}$  by  $\text{Ru}^{\text{II}}$  as the carrier metal in tripod ligands  $(\eta^5\text{-C}_5\text{Me}_5)\text{M}\{\text{PR}_2\text{O}\}_3^-$  drastically changes the properties of the ligands as well as the complexes. Whereas the free ligands in their protonated form or as the alkali metal salts are less stable than their  $\text{L}_{\text{Co}}$  counterparts being particularly sensitive toward nucleophiles, stable complexes are formed with higher valent metals and nonmetals. In contrast to  $\text{L}_{\text{Co}}$  where exchange of substituents at P has proven rather difficult and is achieved only for  $\text{R} = \text{OR}'$  in some special instances<sup>21</sup> such a reaction seems to be facile and general at  $\text{L}_{\text{Ru}}$ . No quantitative parameters are yet available concerning complex formation

constants, but qualitatively complexing properties of  $\text{L}_{\text{Ru}}$  seem to compare to those of  $\text{L}_{\text{Co}}$ . The spectroscopic data place  $\text{L}_{\text{Ru}}$  similar to  $\text{L}_{\text{Co}}$  among the weak ligands near fluoride in the spectrochemical series. With the chemically more stable ligand  $\text{L}_{\text{Ru}}$  with  $\text{R} = \text{Ph}$  only one  $\text{L}_{\text{Ru}}$  unit complexes to a metal or metal fragment, thus leading easily to mixed ligand complexes. This facet may prove useful for the future development of a  $\text{L}_{\text{Ru}}$  half-sandwich chemistry in analogy to complexes  $\text{L}_{\text{Co}}\text{M}(\text{CO})_n$  and others<sup>3</sup> where  $\text{L}_{\text{Ru}}$  is a strong  $\sigma$ -donor well suited for stabilizing a variety of organometallic fragments featuring strong acceptor ligands. Nucleophilic exchange at P can be employed if groups OR different from those of the starting phosphinic acid are desired. The most noticeable feature of  $\text{L}_{\text{Ru}}$ , however, appears to be the ability to stabilize high-oxidation state metals and nonmetals. Ensuing complexes are chemically inert and provide a pseudotetrahedral or octahedral oxygen environment in highly soluble molecular compounds as was demonstrated with e.g.  $(\text{L}_{\text{Ru}})_2\text{Si}$ .

**Acknowledgment.** Financial support from the Fonds der Chemischen Industrie, Frankfurt am Main, and a loan of  $\text{RuCl}_3$  from Johnson Matthey, Reading, England, is gratefully acknowledged.

**Supporting Information Available:** An X-ray crystallographic file, in CIF format, for the structure determination of **9** is available on the Internet only. Access information is given on any current masthead page.

(21) Kläui, W. Personal communication.