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Organometallic Compounds of Ruthenium Containing an Anionic Oxygen Tripod Ligand

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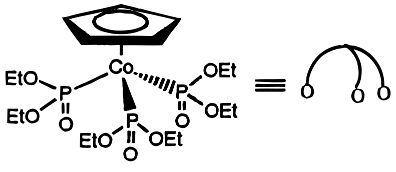
Reaction of NaL_{OEt} ($L_{OEt} = (\eta^5\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3$) with $Ru(PPh_3)_3Cl_2$, $Ru(DMSO)_4Cl_2$ (DMSO = dimethyl sulfoxide), and $Ru(PPh_3)_2(CO)Cl(CH{=}CHPh)$ afforded $L_{OEt}Ru(PPh_3)_2Cl$ (**1**), $L_{OEt}Ru(DMSO)_2Cl$ (**2**), and $L_{OEt}Ru(PPh_3)(CO)(CH{=}CHPh)$ (**3**), respectively. The structures of complexes **1** and **2** have been established by X-ray crystallography. The mean Ru−O, Ru−P, and Ru−Cl bond distances in **1** are 2.183, 2.267, and 2.393(3) Å, respectively. The mean Ru−O, Ru−S, and Ru−Cl distances in **2** are 2.118, 2.188, and 2.362(2) Å, respectively. Treatment of **3** with HBF_4 yielded the olefin complex $[L_{OEt}Ru(PPh_3)(CO)(\eta^2\text{-}PhCH{=}CH_2)]BF_4$ (**4**). Reaction of complex **1** with $PhC{\equiv}CH$ in the presence of NH_4PF_6 gave the vinylidene complex $[L_{OEt}Ru(PPh_3)_2({=}C{=}CHPh)](PF_6)$ (**6**). The mean Ru−O, Ru−P, and Ru−C distances in **6** are 2.127, 2.344, and 1.80(2) Å, respectively. Deprotonation of **6** with NaOH gave the acetylide complex $L_{OEt}Ru(PPh_3)_2(C{\equiv}CPh)$ (**7**). Reaction of complex **1** with 3-butyn-1-ol in the presence of NH_4PF_6 afforded the cyclic carbene complex $[L_{OEt}Ru(PPh_3)_2\text{-}\{{=}\overline{C(CH_2)_3O}\}]PF_6$ (**8**). The mean Ru−O, Ru−P, and Ru−C distances in **8** are 2.175, 2.335, and 1.87(1) Å, respectively. Reaction of $L_{OEt}Ru(PPh_3)_2Cl$ with I_2 afforded the cation $[L_{OEt}\text{-}Ru(PPh_3)_2Cl]^+$ ($\mathbf{1}^+$), isolated as the I_3 and PF_6 salts. The mean Ru−O, Ru−P, and Ru−Cl distances in $\mathbf{1}^+$ are 2.095, 2.380, and 2.300(3) Å, respectively. The cyclic voltammogram of **1** in CH_2Cl_2 exhibits a reversible Ru(III/II) couple at −0.021 V vs $Cp_2Fe^{+/0}$.

Introduction

Organometallic complexes of late-transition-metal-containing O-donor coligands are of interest because they are related to the active intermediates of homogeneous catalysis in aqueous media.[1] A notable example is $[Ru(OH_2)_6](OTs)_2$ (OTs = tosylate), which catalyzes ring-opening metathesis polymerization of cyclic olefins[2] and isomerization of olefins[3] in water. The anionic cobalt(III)-based oxygen tripod ligand L_{OEt} (**I**, $CpCo\{PO(OEt)_2\}_3$) first introduced by Kläui has been employed as an oxygen analog for Cp (**II,** cyclopentadienyl) and Tp (**III**, hydriotris(pyrazol-1-yl)borate)[4] and as a model for the facially disposited triaqua moiety.[5]



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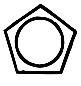

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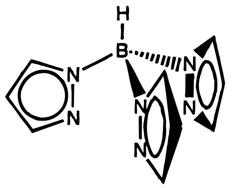

III

Owing to its high stability and π-donation capability and weak ligand field strength (similar to that for hydroxide and fluoride[6]), organometallic complexes of L_{OEt} were found to be quite different from the conventional Cp-based analogs.[4] Nevertheless, in contrast to the well-known half-sandwich complexes $(\eta^5\text{-}C_5R_5)RuL_2X$[6] and $TpRuL_2X$,[7] organoruthenium complexes of L_{OEt} have not been well explored. Kläui first synthesized the carbonyl complexes $L_{OEt}Ru(CO)_2X$, $[L_{OEt}Ru(CO)_2]_2$, and $L_{OEt}Ru(CO)(PR_3)Cl$[4] and the sandwich compound $[L_{OEt}Ru(\eta^6\text{-}C_6H_6)]PF_6$.[8] Labinger, Bercaw, and co-workers found that the oxoruthenium complexes

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(1) For reviews, see for example: (a) Herrmann, W. A.; Kohlpainter, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1524. (b) Roundhill, D. M. *Adv. Organomet. Chem.* **1995**, 155.

(2) (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542. (b) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1992**, *25*, 3345.

(3) McGrath, D. V.; Grubbs, R. H. *Organometallics* **1994**, *13*, 224.

(4) Kläui, W. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 627.

(5) For a review, see for example: Kölle, U. *Coord. Chem. Rev.* **1994**, *135*, 623.

(6) Davies, A. G.; McNally, J. P.; Smallridge, A. *Adv. Organomet. Chem.* **1990**, *30*, 1 and references cited therein.

(7) See for example: (a) Bruce, M. I.; Sharrocks, D. N., Stone. F. G. A. *J. Organomet. Chem.* **1971**, *31*, 269. (b) Bruce, M. I.; Iqbal, M. Z.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2820. (c) McNair, A. M.; Boyd, D. C.; Mann, K. R. *Organometallics* **1986**, *5*, 303. (d) Albers, M. O.; Robinson, D. J.; Shaver, A.; Singleton, E. *Organometallics* **1986**, *5*, 2199. (e) Restivo, R. J.; Ferguson, G.; O'Sullivan, D. J. ; Lalor, F. *Inorg. Chem.* **1975**, *4*, 3046. (f) Alcock, N. A.; Hill, A. F.; Melling, R. P. *Organometallics* **1991**, *10*, 3898. (g) Germel, C.; Trimmel, G.; Slugovc, C.; Mereiter, K.; Kremel, S.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 3998. (h) Gemel, C.; Wiede, P.; Mertier, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1996**, 4071. (i) Hill, A. F. *J. Organomet. Chem.* **1990**, *395*, C35.

(8) Kläui, W.; Otto, H.; Eberspach, W.; Bulcholz, E. *Chem. Ber.* **1982**, *115*, 1922.

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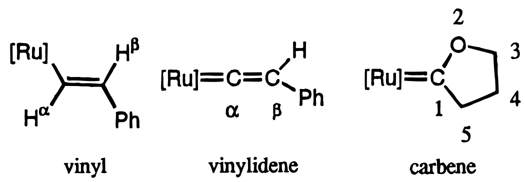

Figure 1.

$[(L_{OEt})_2Ru(OH_2)_2(\mu\text{-}O)_2](CF_3SO_3)_2$, $(L_{OEt})_2Ru_2(OH)_2(\mu\text{-}O)_2$, and $(L_{OEt})_2Ru_2(O)_2(\mu\text{-}O)_2$ are potent catalysts for alcohol oxidation.[9] More recently, the cation $[L_{OEt}Ru(COD)(OH_2)]^+$ (COD = 1,5-cycloctadiene) has been isolated and structurally characterized by Kölle and coworkers.[10] In an effort to develop new metal catalysts with oxgyen-based ligands, we here describe the synthesis of some ruthenium(II) and -(III) complexes of L_{OEt} and the crystal structures of the vinylidene and carbene derivatives.

Experimental Section

Solvents were purified and distilled prior to use. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300 and 75 MHz for ^1H and ^{13}C, respectively. Chemical shifts (δ, ppm) were reported with reference to $Si(CH_3)_4$ (^1H and ^{13}C) and H_3PO_4 (^{31}P). Hydrogen atom labeling schemes for the vinyl, vinylidene, and cyclic carbene complexes are shown in Figure 1. Infrared spectra (Nujol) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Mass spectra were obtained on a Finnigan TSQ-7000 spectrometer. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) Model 273A potentiostat. The working and reference electrodes are glassy carbon and $Ag/AgNO_3$ (0.1 M in acetonitrile), respectively. Potentials were reported with reference to $Cp_2Fe^{+/0}$. Elemental analyses were performed by Medac Ltd., Brunel University, U.K.

Materials. $Ru(PPh_3)_3Cl_2$,[11] $Ru(DMSO)_4Cl_2$[12] (DMSO = dimethyl sulfoxide), $RuCl(CO)(CH{=}CHPh)(PPh_3)_2$,[13] and NaL_{OEt}[14] were prepared according to the literature methods. $PhC{\equiv}CH$ and 3-butyn-1-ol were obtained from Aldrich and used as received.

Synthesis of $L_{OEt}Ru(PPh_3)_2Cl$ (1). A mixture of $Ru(PPh_3)_3Cl_2$ (1.2 g, 1.25 mmol) and NaL_{OEt} (0.5 g, 0.896 mmol) in THF/toluene (50 mL, 1:1) was heated at reflux overnight. The volatiles were removed in vacuo, and the residue was washed with hexane. Recrystallization from ether/hexane afforded orange crystals, which were suitable for X-ray analysis (yield 0.72 g, 68%). ^1H NMR ($CDCl_3$): δ 0.87 (t, 6H, CH_3), 1.04 (t, 6H, CH_3), 1.34 (t, 6H, CH_3), 2.87−2.98 (m, 4H, CH_2), 3.58−3.62 (m, 4H, CH_2), 4.36−4.85 (m, 4H, CH_2), 4.93 (s, 5H, C_5H_5), 6.94−7.50 (m, 30H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.12 (s, PPh_3), 102−111.4 (m, $P(O)(OEt)_2$). MS (CI): m/z 1195 (M^+). Anal. Calcd for $[RuCoC_{53}H_{65}ClO_9P_5]$: C, 53.2; H, 5.6. Found: C, 55.7; H, 5.6. $E°(CH_2Cl_2) = -0.021$ V vs $Cp_2Fe^{+/0}$.

Reaction of 1 with *t*-BuNC. To a solution of **1** (50 mg, 0.04 mmol) in toluene/THF (10 mL, 1:1) was added *t*-BuNC (0.1 mL), and the mixture was heated to 75 °C for 2 h. The solvent was pumped off and the residue extracted with hexane. Concentration and cooling at −10 °C afforded orange crystals of **1** along with a minor yellow product. The yellow product was identified as $L_{OEt}Ru(PPh_3)(t\text{-}BuNC)Cl$: ^1H NMR ($CDCl_3$): δ 0.80 (t, 3H, CH_3), 0.94 (t, 3H, CH_3), 1.24−1.38 (t, 12H, CH_3), 1.41 (s, 9H, *t*-Bu), 2.89−2.96 (m, 2H, CH_2), 3.44 (m, 1H, CH_2), 3.59 (m, 1H, CH_2), 4.00 (m, 2H, CH_2), 4.23−4.52 (m, 6H, CH_2), 4.93 (s, 5H, C_5H_5), 7.24−7.71 (m, 15H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 61.5 (s, PPh_3). MS (FAB): m/z 1016 (M^+).

Synthesis of $L_{OEt}Ru(DMSO)_2Cl$ (2). A mixture of $Ru(DMSO)_4Cl_2$ (0.5 g, 1.03 mmol) and NaL_{OEt} (0.41 g, 0.73 mmol) in THF (50 mL) was heated at reflux overnight. The volatiles were removed in vacuo, and the residue was recrystallized from CH_2Cl_2/hexane to give orange crystals (yield 0.14 g, 23%). ^1H NMR ($CDCl_3$): δ 1.24 (t, 6H, CH_3), 1.29 (t, 6H, CH_3), 1.3 (t, 6H, CH_3), 3.21 (s, 6H, $(CH_3)_2SO$), 3.37 (s, 6H, $(CH_3)_2SO$), 4.01−4.26 (overlapping q, 12H, CH_2), 4.99 (s, 5H, C_5H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 112 (s br, $P(O)(OEt)_2$). MS (CI): m/z 828 (M^+). Anal. Calcd for $[RuCoC_{21}H_{47}ClS_2O_{11}P_3]$: C, 30.5; H, 5.9. Found: C, 30.1; H, 5.8. $E°(CH_2Cl_2) = 0.386$ V vs $Cp_2Fe^{+/0}$.

Synthesis of $L_{OEt}Ru(CO)(PPh_3)(CH{=}CHPh)$ (3). A mixture of $RuCl(CO)(CH{=}CHPh)(PPh_3)_2$ (1.3 g, 1.64 mmol) and NaL_{OEt} (0.57 g, 1.03 mmol) in CH_2Cl_2 (25 mL) was stirred at room temperature for 48 h. The volatiles were removed in vacuo, and the residue was recrystallized from hexane. The yellow solid was collected and washed with cold hexane (yield 0.65 g, 62%). ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, CH_3), 1.01 (t, 3H, CH_3), 1.19 (t, 3H, CH_3), 1.28−1.35 (overlapping t, 6H, CH_3), 1.39 (t, 3H, CH_2), 3.08−3.12 (m, 2H, CH_2), 3.52−3.73 (m, 2H, CH_2), 4.04−4.34 (m, 8H, CH_2), 4.94 (s, 5H, C_5H_5), 8.36 (dd, $^3J_{HH} = 15.9$ Hz, $^3J_{HP} = 3.06$ Hz, $-CH{=}CHPh$), 6.12 (d, $J_{HH} = 15.9$ Hz, $CH{=}CHPh$), 6.86−7.73 (m, 20H, phenyl protons). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −16.1 to −16.9 (CH_3), 59.3−60.4 (CH_2), 88.9 (C_5H_5), 124−141 (PPh_3), 122.7 (C_β), 159.61 (d, $^2J_{CP} = 15.07$ Hz, C_α), 206.5 (d, $^2J_{CP} = 47.7$ Hz, CO). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 59.8 (s, PPh_3), 109.7 (m, $P(O)(OEt)_2$). IR (cm^{-1}): 1918 ν_{CO}, 1596 and 1582 $\nu_{C=C}$. MS (CI): m/z 1028 (M^+). Anal. Calcd for $[RuCoC_{44}H_{59}O_{10}P_4]$: C, 51.3; H, 5.6. Found: C, 50.9; H, 5.9.

Synthesis of $[L_{OEt}Ru(PPh_3)(CO)(\eta^2\text{-}PhCH{=}CH_2)]BF_4$ (4). To a solution of **3** (50 mg, 0.05 mmol) in Et_2O (10 mL) was added 1 equiv of HBF_4 (0.05 mL of a 1 M solution in Et_2O) at 0 °C. The yellow precipitate was collected and washed with Et_2O (yield 50%). ^1H NMR (CD_2Cl_2): δ 0.96 (t, 3H, CH_3), 1.26 (t, 3H, CH_3), 1.28 (t, 3H, CH_3), 1.29 (t, 3H, CH_3), 1.44 (t, 3H, CH_3), 1.45 (t, 3H, CH_3), 3.01−3.26 (m, 3H, OCH_2 and $CH_2{=}CHPh$), 3.77−3.98 (m, 7H, OCH_2 and $CH_2{=}CHPh$), 4.26−4.36 (m, 4H, OCH_2), 5.11 (s, 5H, C_5H_5), 5.92 (dd , $^{cis}J_{HH} = 13.9$ Hz, $^{trans}J_{HH} = 9.1$ Hz, 1H, $CH_2{=}CHPh$), 6.97−7.71 (m, 20H, phenyl protons). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 51.2 (s, PPh_3), 112.9 (m, $P(O)(OEt)_2$). ^{19}F NMR (CD_2Cl_2): δ −154.7 (BF_4). IR (cm^{-1}): 1978 ν_{CO}.

On recrystallization from CH_2Cl_2/hexane complex **4** was found to decompose to give $[L_{OEt}Ru(PPh_3)(CO)(OH_2)]BF_4$ (**5**). ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, CH_3), 1.01 (t, 3H, CH_3), 1.32 (t, 3H, CH_3), 1.34 (t, 3H, CH_3), 1.36 (t, 3H, CH_3), 1.39 (t, 3H, CH_3), 2.50 (s, 2H, H_2O), 3.20−3.43 (m, 4H, CH_2), 4.19 (m, 2H, CH_2), 4.22−4.32 (m, 6H, CH_2), 4.99 (s, 5H, C_5H_5), 7.41−7.50 (m, 15H, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 50 (s, PPh_3), 112 (m, $P(O)(OEt)_2$). IR (cm^{-1}): 1954 $\nu_{C=O}$. MS (FAB): m/z 944 $(M - BF_4)^+$, 927 $(M - BF_4 - H_2O + 1)^+$. Anal. Calcd for $[RuCoC_{36}H_{52}BF_4O_9P_5]$: C, 41.9; H, 5.0. Found: C, 42.1; H, 5.1.

Synthesis of $[L_{OEt}Ru(PPh_3)_2({=}C{=}CHPh)]PF_6$ (6). A mixture of complex **1** (70 mg, 0.06 mmol) with $PhC{\equiv}CH$ (0.1 mL, 1 mmol) and NH_4PF_6 (17 mg, 0.1 mmol) in MeOH/THF (25 mL, 1:1) was stirred at room temperature overnight. The volatiles were pumped off and the residue washed with hexane. Recrystallization from CH_2Cl_2/ether/hexane afforded yellow crystals that are suitable for X-ray analysis (yield 60 mg, 70%). ^1H NMR ($CDCl_3$): δ 0.98 (t, 6H, CH_3), 1.18 (t, 6H, CH_3), 1.24 (t, 6H, CH_3), 3.16−3.37 (m, 4H, CH_2), 3.76−4.05 (m, 8H, CH_2), 4.59 (t, $^4J_{HP} = 4.6$ Hz, 1H, ${=}C{=}CHPh$), 5.08 (s, 5H, C_5H_5), 7.06−7.34 (m, 35H, phenyl protons). $^{13}C\{^1H\}$ NMR ($CDCl_3$):

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[9] Power, J. M.; Evertz, K.; Herling, L.; Marsh, R.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1990**, *29*, 5058.

[10] Kölle, U.; Flunkert, G.; Gorissen, R.; Schmidt, M. U.; Englert, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 440.

[11] Hallman, R. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 238.

[12] Evans, I. P.; Spencer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

[13] Torres, M. R.; Vegas, A.; Santos, A.; Ros, J. *J. Organomet. Chem.* **1986**, *309*, 169.

[14] Kläui, W. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1979**, *34B*, 1043.

Table 1. Crystallographic Data and Experimental Details for $L_{OEt}Ru(PPh_3)_2Cl$ (1), $L_{OEt}Ru(DMSO)_2Cl$ (2), $[L_{OEt}Ru(PPh_3)_2(=C=CHPh)]PF_6$ (6), $[L_{OEt}Ru(PPh_3)_2\{=\overline{C(CH_2)_3O}\}](PF_6)$ (8), and $[L_{OEt}Ru(PPh_3)_2Cl](PF_6)$ (1·PF_6)

	1	**2**	**6**·$^1/_4$hexane	**8**·$^1/_2$MeOH	**1**·PF_6
empirical formula	$C_{53}H_{65}ClCoO_9P_5Ru$	$C_{42}H_{94}Cl_2Co_2O_{23}P_6Ru_2S_4$	$C_{62.5}H_{73.5}CoF_6O_9P_6$	$RuC_{57.5}H_{73}CoF_6O_{10.5}P_6Ru$	$C_{59}H_{77}ClCoF_6O_3P_6Ru$
fw	1196.3	1672.1	1428.5	1392.0	1329.54
color, habit	brown, bar	orange, plate	yellow, wedge	yellow, plate	brown, block
cryst dimens, mm	0.4 × 0.1 × 0.1	0.45 × 0.35 × 0.08	0.6 × 0.4 × 0.1	0.5 × 0.4 × 0.1	0.22 × 0.22 × 0.28
a, Å	12.875(3)	18.230(3)	44.716(12)	11.926(2)	15.637(1)
b, Å	21.570(4)	10.123(2)	24.910(4)	13.244(3)	18.704(1)
c, Å	39.070(8)	37.901(5)	46.004(5)	23.102(5)	119.990(1)
α, deg				98.83(3)	
β, deg		98.86(2)	91.66(2)	96.32(3)	106.87(2)
γ, deg				116.37(3)	
V, Å^3	10 850(4)	6911(2)	51 218(17)	3164.3(11)	5846.6(6)
Z	8	4	32	2	4
cryst syst	orthorhombic	monoclinic	monoclinic	triclinic	orthorhombic
space group	$Pbc2_1$	$P2_1/c$	$I2/a$	$P\bar{1}$	$P2_12_12_1$
D_{calcd}, g cm^{-3}	1.465	1.607	1.482	1.461	1.510
T, °C	−45	−37	−48	−45	0
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
scan type	ω	ω	ω	ω	ω
2θ range, deg	3.0−50.0	3.0−50.0	3.0−41.0	3.0−45.0	3.0−51.3
μ, cm^{-1}	8.35	13.04	7.17	7.25	8.16
no. of rflns measd	11 725	10 074	23 921	7876	5914
no. of rflns obsd	7453	6847	13 519	5102	4148
R,[a] %	4.57	4.77	7.03	7.41	6.30
R_w,[b] %	4.55	5.51	6.90	8.38	7.00
F(000)	4944	3440	23 536	1434	2748
GOF[c]	1.37	1.42	1.57	1.83	3.14

[a] $R = (\sum|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [(\sum w^2|F_o| - |F_c|)^2/\sum w^2|F_o|^2]^{1/2}$. [c] $GOF = [(\sum w|F_o| - |F_c|)^2/(N_{observn} - N_{param})]^{1/2}$.

δ 15.9−16.2 (CH_3), 60.3−61.4 (CH_2), 89.15 (C_5H_5), 116.2 (C_β), 126−134 (s, phenyl), 362.25 (t, $^2J_{CP}$ = 21 Hz, C_α). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −145 (sept, PF_6), 34.7 (s, PPh_3), 110.4 (m, $P(O)(OEt)_2$). IR (cm^{-1}): 1622, 1596 $\nu_{C=C}$. MS (DCI): m/z 1262 ($M - PF_6$)$^+$. Anal. Calcd for $[RuCoC_{60}H_{71}F_6O_9P_6]$: C, 52.0; H, 5.1. Found: C, 52.2; H, 5.1.

Synthesis of $L_{OEt}Ru(PPh_3)_2(C\equiv CPh)$ (7). To a solution of **6** (80 mg, 0.063 mmol) in THF/MeOH (20 mL, 1:1) was added NaOH (20 mg, 0.5 mmol). The resulting mixture was stirred at room temperature for 40 min. Slow evaporation in vacuo afforded a yellow microcrystalline solid (yield 40%). ^1H NMR (C_6D_6): δ 0.97 (t, 6H, CH_3), 1.20 (s, 6H, CH_3), 1.55 (s, 6H, CH_3), 3.15 (m, 4H, CH_2), 3.95 (m, 4H, CH_2), 4.82 (m, 4H, CH_2), 5.01 (s, 5H, C_5H_5), 7.02 (m, 18H, PPh_3), 7.16 (m, 1H, $PhC\equiv C$ p), 7.46 (t, 2H, $PhC\equiv C$ m), 7.83 (d, 2H, $PhC\equiv C$ o), 8.10 (m, 12H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.9 (s, PPh_3), 105.5 (m, $P(O)(OEt)_2$). IR (cm^{-1}): 2066 $\nu_{C\equiv C}$.

Synthesis of $[L_{OEt}Ru(PPh_3)_2\{=\overline{C(CH_2)_3O}\}]PF_6$ (8). This was prepared as for complex **7** from **1** (70 mg, 0.06 mmol), 3-butyn-1-ol (0.1 mL), and NH_4PF_6 (17 mg, 0.1 mmol). The product was recrystallized from CH_2Cl_2/hexane, isolated as yellow prisms (yield 40 mg, 50%). ^1H NMR ($CDCl_3$): δ 0.94 (t, 6H, CH_3), 1.12 (t, 6H, CH_3), 1.40 (t, 6H, CH_3), 1.75 (q, $^2J_{HH}$ = 6.9 Hz, 2H, C^4H_2), 3.13 (m, 2H, CH_2), 3.27 (m, 2H, CH_2), 3.46−3.78 (m, 6H, C^5H_2 and CH_2), 4.03 (t, $^2J_{HH}$ = 7.35 Hz, 2H, C^3H_2), 4.12 (m, 4H, CH_2), 5.04 (s, 5H, C_5H_5), 7.06−7.35 (m, 30H, PPh_3). $^{13}C\{^1H\}$ NMR: δ 15.9−16.3 (CH_3), 21.6 (C^4), 52.4 (C^5), 59−61 (CH_2), 80.4 (C^3), 89.07 (C_5H_5), 127−134 (phenyl carbons), 305.2 (t, $^2J_{PC}$ = 16.5 Hz, C^1). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 44.5 (s, PPh_3), 105.8−109.2 (m, $P(O)(OEt)_2$). Anal. Calcd for $[RuCoC_{57}H_{51}F_6O_9P_6]$: C, 41.0; H, 5.2. Found: C, 42.0; H, 5.6.

Synthesis of $[L_{OEt}Ru(PPh_3)_2Cl](I_3)$ (1·I_3). To a solution of complex **1** (0.50 g, 0.42 mmol) in CH_2Cl_2 (20 mL) was added 1 equiv of I_2 (0.11 g, 0.42 mmol), and the resulting mixture was stirred in air at room temperature overnight. The solvent was pumped off and the residue washed with ether. Recrystallization from CH_2Cl_2/ether afforded dark brown blocks (yield 0.53 g, 80%). MS (CI): m/z 1196 ($M - I_3$)$^+$. Anal. Calcd for $[RuCoC_{53}H_{65}ClI_3O_9P_5]$: C, 40.3; H, 4.1; I, 24.2. Found: C, 41.3; H, 4.5; I, 23.7.

Synthesis of $[L_{OEt}Ru(PPh_3)_2Cl]PF_6$ (1·PF_6). To a solution of complex **1**·I_3 (0.50 g, 0.32 mmol) in acetone (20 mL, 10:1) was added silver(I) p-toluenesulfonate (70 mg, 0.43 mmol), and the mixture was stirred at room temperature for 20 min, during which time a copious amount of silver iodide precipitated. The solvent was pumped off, and the residue was extracted with MeOH. Addition of NH_4PF_6 (70 mg) and cooling to 0 °C afforded purple crystals (yield 0.30 g, 70%). μ_{eff} (Evans method,[15] $CHCl_3$): 1.8 μ_B. Anal. Calcd for $[RuCoC_{53}H_{65}ClF_6O_9P_6]$: C, 47.4; H, 4.9. Found: C, 47.5; H, 4.9.

X-ray Diffraction Measurements. A summary of crystallographic data and experimental details are given in Table 1. Data for **1**, **2**, **6**, and **8** were collected on a Siemens P4 diffractometer with graphite-monochromated Mo Kα radiation. Data for **1**·PF_6 were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation. All the structures were solved by direct methods and refined by full-matrix least-squares analyses. The unit cell of complex **6** was unusually large, and solution revealed four independent molecular cations per asymmetric unit along with hexafluorophosphate counterions; three of these were at general positions, and two sat on special positions, contributing to half of the asymmetric unit. A single molecule of solvent, either hexane or ether, which appeared to be disordered, was also located. The large size of the structure precluded anisotropic refinement of all atoms, though atoms heavier than C were refined anisotropically. The final discrepancy index was ca. 7.0% with the largest residual peaks located in the region of the solvent. For complex **8**, solution was more straightforward. The asymmetric unit contained one molecular cation and one ordered hexafluorophosphate sitting on an inversion center. The other a general site and appeared highly disordered, possibly due to site overlap with methanol solvent. Again these problems limited the quality of the structure and the final R value was similar to that of **6**. Selected bond lengths and angles for **1**, **2**, **6**, **8**, and **1**·PF_6 are listed in Tables 2−6, respectively. Atomic coordinates are given in the Supporting Information.

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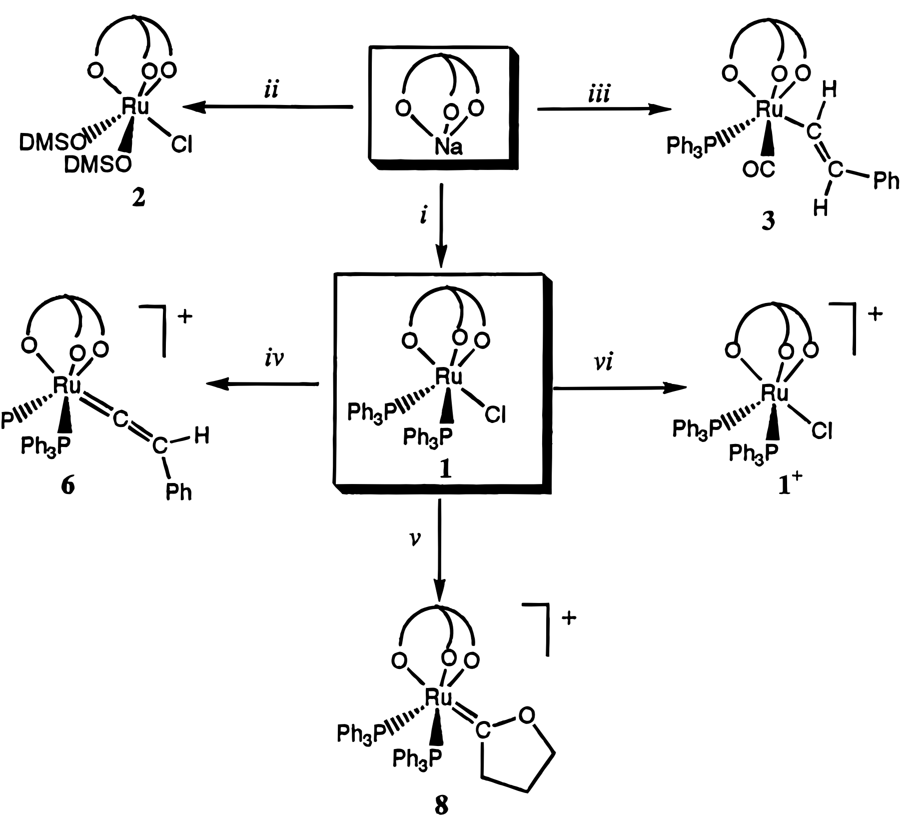
(15) Evans, D. *J. Chem. Soc.* **1959**, 2003.

Scheme 1[a]



[a] Reagents and conditions: (*i*) $Ru(PPh_3)_3Cl_2$, THF, reflux; (*ii*) $Ru(DMSO)_4Cl_2$, THF, reflux; (*iii*) $Ru(CO)(PPh_3)_2Cl(CH{=}CHPh)$, CH_2Cl_2; (*iv*) $PhC{\equiv}CH$, NH_4PF_6, CH_2Cl_2/MeOH; (*v*) 3-butyn-1-ol, NH_4PF_6, CH_2Cl_2/MeOH; (*vi*) I_2, CH_2Cl_2.

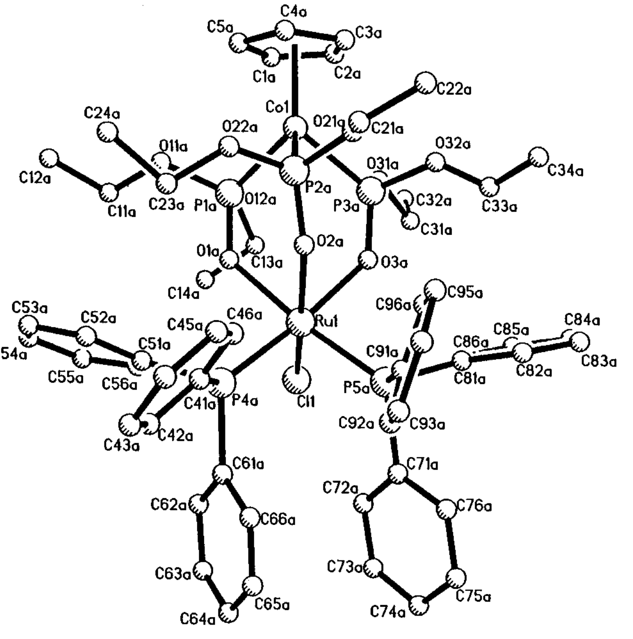


Figure 2. Perspective view of $L_{OEt}Ru(PPh_3)_2Cl$.

Results and Discussion

Synthesis. The syntheses of the Ru−L_{OEt} complexes are summarized in Scheme 1.

Reaction of $Ru(PPh_3)_2Cl_2$ with NaL_{OEt} in THF afforded $L_{OEt}Ru(PPh_3)_2Cl$ (**1**), isolated as air-stable orange crystals. Figure 2 shows a diagram of the molecule; selected bond lengths and angles are given in Table 2. The mean Ru−O distance in **1** of 2.183 Å is longer than that for the Ru^{II}−COD complex $[L_{OEt}Ru(COD)(OH_2)]^+$ (2.10 Å),[10] apparently due to the steric bulk of PPh_3.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $L_{OEt}Ru(PPh_3)_2Cl$ (1)

Ru(1)−Cl(1)	2.393(3)	Ru(1)−O(1)	2.203(6)
Ru(1)−O(2)	2.158(6)	Ru(1)−O(3)	2.189(6)
Ru(1)−P(4)	2.265(3)	Ru(1)−P(5)	2.269(3)
Cl(1)−Ru(1)−O(1)	86.2(2)	Cl(1)−Ru(1)−O(2)	166.1(2)
O(1)−Ru(1)−O(2)	83.5(2)	Cl(1)−Ru(1)−O(3)	87.4(2)
O(1)−Ru(1)−O(3)	84.7(2)	O(2)−Ru(1)−O(3)	82.3(2)
Cl(1)−Ru(1)−P(4)	93.1(1)	O(1)−Ru(1)−P(4)	89.7(2)
O(2)−Ru(1)−P(4)	96.2(2)	O(3)−Ru(1)−P(4)	174.4(2)
Cl(1)−Ru(1)−P(5)	94.6(1)	O(1)−Ru(1)−P(5)	174.4(2)
O(2)−Ru(1)−P(5)	94.7(2)	O(3)−Ru(1)−P(5)	89.8(2)
P(4)−Ru(1)−P(5)	95.7(1)		

The mean Ru−P distance in **1** of 2.267 Å is shorter than that in $CpRu(PPh_3)_2Cl$ (2.336 Å),[16] although the cone angle of L_{OEt} is expected to be larger than that of Cp, which is indicative of strong Ru−P π-bonding in **1**.

Substitution reactions of **1** with Lewis bases were found to be slow. No phosphine exchange was observed on treatment of **1** with PMe_3. Reaction of **1** with *t*-BuNC in toluene at 60 °C gave the monosubstituted product $L_{OEt}Ru(PPh_3)(t\text{-BuNC})Cl$ in low yield. Reaction of **1** with $NaBPh_4$ or NH_4PF_6 in MeOH/THF resulted in yellow solutions, presumably containing the cation $[L_{OEt}Ru(PPh_3)_2(MeOH)]^+$, from which hygroscopic solids were isolated. We have not been able to obtain analytically pure samples of these hygroscopic cationic complexes. However, this cation was found to react with acetylenes to give air-stable crystalline vinylidene and carbene species (see below).

The DMSO complex $L_{OEt}Ru(DMSO)_2Cl$ (**2**) was synthesized similarly as for **1** by the reaction of Ru-

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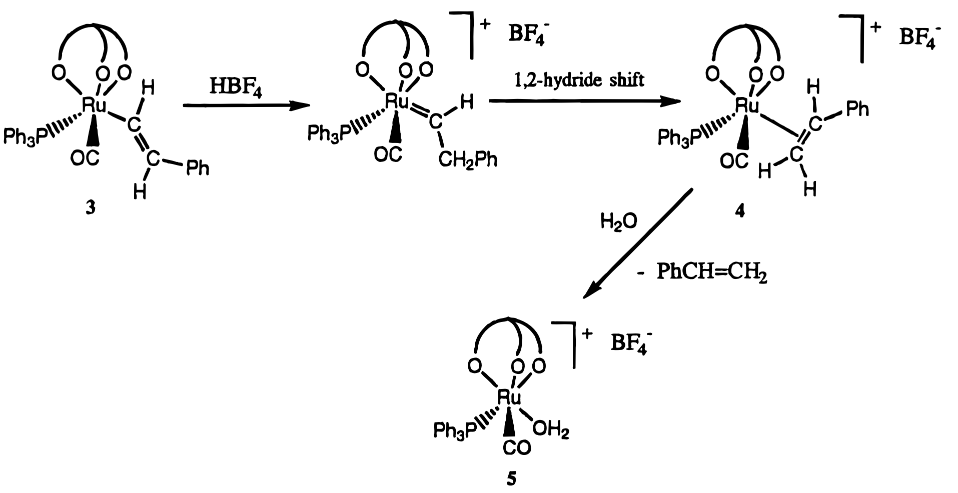
(16) Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1981**, 1398.

Scheme 2



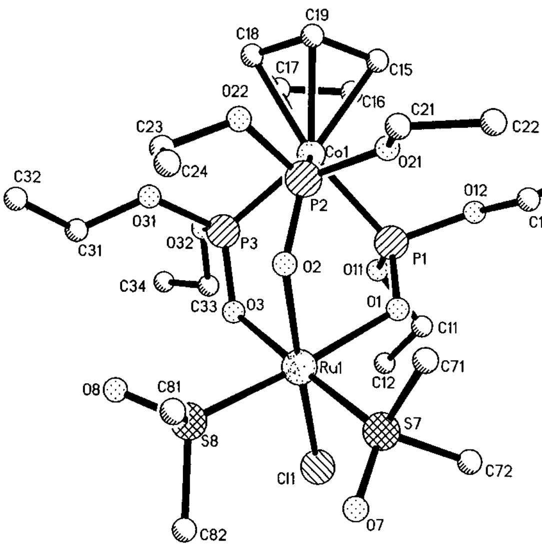


Figure 3. Perspective view of $L_{OEt}Ru(DMSO)_2Cl$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $L_{OEt}Ru(DMSO)_2Cl$ (2)

Ru(1)−Cl(1)	2.362(2)	Ru(1)−S(7)	2.186(2)
Ru(1)−S(8)	2.190(2)	Ru(1)−O(1)	2.134(4)
Ru(1)−O(2)	2.107(4)	Ru(1)−O(3)	2.112(5)
Cl(1)−Ru(1)−S(7)	90.4(1)	Cl(1)−Ru(1)−S(8)	92.8(1)
S(7)−Ru(1)−S(8)	95.4(1)	Cl(1)−Ru(1)−O(1)	90.8(1)
S(7)−Ru(1)−O(1)	87.7(1)	S(8)−Ru(1)−O(1)	175.2(1)
Cl(1)−Ru(1)−O(2)	174.3(1)	S(7)−Ru(1)−O(2)	93.4(1)
S(8)−Ru(1)−O(2)	91.1(1)	O(1)−Ru(1)−O(2)	85.0(2)
Cl(1)−Ru(1)−O(3)	87.7(1)	S(7)−Ru(1)−O(3)	176.2(1)
S(8)−Ru(1)−O(3)	87.9(1)	O(1)−Ru(1)−O(3)	89.0(2)
O(2)−Ru(1)−O(3)	88.3(2).		

$(DMSO)_4Cl_2$ with NaL_{OEt}. Figure 3 shows a perspective view of **3**; selected bond lengths and angles are given in Table 3. The Ru−Cl distance in **2** of 2.362(2) Å is similar to that in **1**. However, the Ru−O distances in **2** (2.118 Å) are slightly shorter than those in **1**, obviously because of the smaller steric demand of DMSO compared with PPh_3. The two DMSO ligands in **2** bind to Ru on the S atom with a mean Ru−S distance of ca. 2.188 Å, which is shorter than those in $Ru(DMSO)_4Cl_2$ ($d(Ru-S_{trans\ to\ O})$ = 2.252(1) Å)[17] and (η^5-C_5Me_5)$Ru(DMSO)_2Cl$ (2.302(2) and 2.299(2) Å).[18]

σ-Vinyl Complex. Interaction of $Ru(PPh_3)_2(CO)Cl(CH{=}CHPh)$ with NaL_{OEt} afforded the σ-vinyl complex $L_{OEt}Ru(PPh_3)(CO)(CH{=}CHPh)$ (**3**). The IR spectrum of **3** shows ν_{CO} at 1918 cm^{-1}, which is lower than that for $TpRu(PPh_3)(CO)(CH{=}CH_2)$ (1927 cm^{-1}),[7i] in line with the stronger donor strength of L_{OEt} relative to Tp. The $^2J_{HH}$ value for the vinyl protons (H_α and H_β) of 15.9 Hz indicates that they are *trans* to each other. H_a was also found to couple with the phosphorus of PPh_3 ($^3J_{PH}$ = 3.06 Hz). Treatment of **3** with HBF_4 in Et_2O resulted in the precipitation of a yellow solid, identified as $L_{OEt}Ru(PPh_3)(CO)(\eta^2$-$PhCH{=}CH)]BF_4$ (**4**). The ^1H NMR spectrum of **4** shows a doublets of doublets at δ 5.91 ($^{cis}J_{HH}$ and $^{trans}J_{HH}$ of 13.9 and 9.1 Hz, respectively), assignable to the α-olefinic proton of coordinated styrene. The signals for the β-olefinic protons of styrene were found to overlap with those for the methylene protons of L_{OEt}. This η^2-styrene complex was presumably formed via the protonation of the β-carbon followed by a 1,2-hydride shift (Scheme 2). A similar mechanism has been proposed for the protonation of the related iron σ-vinyl complex $CpFe(CO)(PPh_3)(CH{=}CHMe)$.[19]

The styrene ligand in complex **4** was found to be labile in solution and can be displaced readily. Over a period of 1 day, the ^1H NMR spectrum of **4** in wet CD_2Cl_2 showed that the signals for **4** dropped gradually and a new species along with free styrene was formed concomitantly. This new species, presumably the cationic aquo complex $[L_{OEt}Ru(PPh_3)(CO)(OH_2)]BF_4$ (**5**), could be obtained as an orange solid on recrystallization of **4** from wet CH_2Cl_2/hexane for 2 days. The presence of an aquo ligand is supported by FAB mass spectroscopy, which shows the molecular ion for $[L_{OEt}Ru(PPh_3)(CO)(OH_2)]^+$. It may be noted that aquo complexes of the $TpRu^{II}$ system are well-documented and some have been structurally characterized recently.[7g] The IR spectrum of **5** displays ν_{CO} at 1954 cm^{-1}, which is lower than that for **4**, indicating that the latter complex is more electron deficient because of the presence of a π-accepting styryl group.

Vinylidene Complex. The vinylidene complex $[L_{OEt}Ru(PPh_3)_2(=C=CHPh)](PF_6)$ (**6**) was prepared by the reaction of **1** with PhCCH in the presence of NH_4PF_6. The formation of the vinylidene most likely involves the initial slippage of an η^2 to an η^1 binding of PhC≡CH,

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(17) Mercer, A.; Trotter, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2480.
(18) Wang, M. H.; Kolle, U. *J. Organomet. Chem.* **1993**, *453*, 127.
(19) Bly, R. S.; Bly, R. K. *J. Chem. Soc., Chem. Commun.* **1986**, 1046.

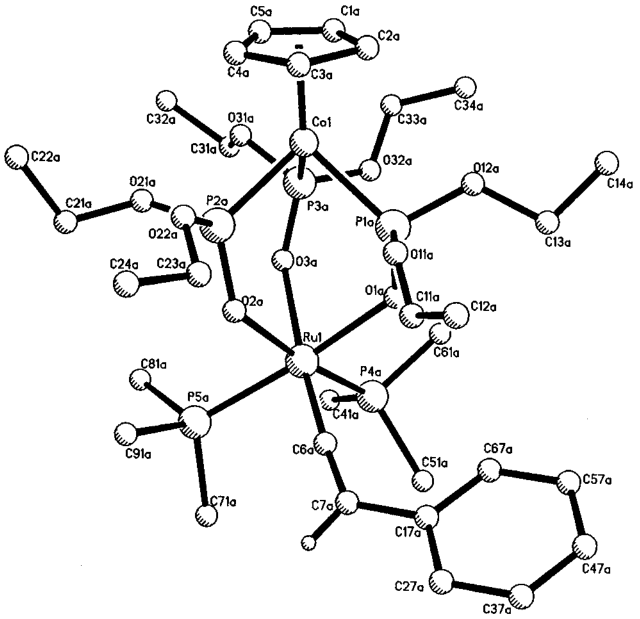

Figure 4. Perspective view of the cation $[L_{OEt}Ru(PPh_3)_2(=C=CHPh)]^+$. The phenyl rings of PPh_3 are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[L_{OEt}Ru(PPh_3)_2(=C=CHPh)]PF_6$ (6)

Ru(1)−P(4A)	2.319(5)	Ru(1)−P(5A)	3.68(4)
Ru(1)−O(1A)	2.156(9)	Ru(1)−O(2A)	2.110(10)
Ru(1)−O(3A)	2.156(9)	Ru(1)−C(6A)	1.80(2)
P(4A)−Ru(1)−P(5A)	98.6(2)	P(4A)−Ru(1)−O(1A)	89.1(3)
P(5A)−Ru(1)−O(1A)	172.3(3)	P(4A)−Ru(1)−O(2A)	172.4(3)
P(5A)−Ru(1)−O(2A)	85.1(3)	O(1A)−Ru(1)−O(2A)	87.3(4)
P(4A)−Ru(1)−O(3A)	88.6(3)	P(5A)−Ru(1)−O(3A)	98.6(2)
O(1A)−Ru(1)−O(3A)	80.8(3)	O(2A)−Ru(1)−O(3A)	84.3(4)
P(4A)−Ru(1)−C(6A)	94.3(5)	P(5A)−Ru(1)−C(6A)	87.0(5)
O(1A)−Ru(1)−C(6A)	93.1(5)	O(2A)−Ru(1)−C(6A)	87.0(5)
O(3A)−Ru(1)−C(6A)	173.3(5)	Ru(1)−C(6A)−C(7A)	173(1)
C(6A)−C(7A)−C(17A)	126(2)		

followed by a 1,2-hydride shift, as suggested by Silvestre and Hoffmann.[20] Figure 4 shows a diagram of the molecule; selected bond lengths and angles are given in Table 4. The mean Ru−O and Ru−P distances are 2.127 and 2.344 Å, respectively. Despite the large standard deviation, the Ru−C(vinylidene) distance in **6** of 1.80(2) Å is within the range expected for ruthenium vinylidene complexes, e.g. 1.845(7) Å for $[CpRu(PMe_3)_2(=C=CHMe)]^+$ [21] and 1.820(5) Å for $[TpRu(TMED)(=C=CHPh)](BPh_4)$ (TMED = *N*,*N*,*N′N′*-tetramethylethylenediamine).[7h] The $Ru-C_\alpha-C_\beta$ linkage is essentially linear (173(1)°). The C_α resonant signal appears as a triplet ($^2J_{PC} = 21$ Hz) at ca. δ 362, which is typical for a Ru(II) vinylidene complex, e.g. δ 350 and 369.9 for $[CpRu(PPh_3)_2(=C=CHPh)]^+$ [21] and $[TpRu(TMED)(=C=CHPh)](PF_6)$,[7h] respectively, indicative of the carbene character of the α carbon. The α-H in **6** was found to be acidic and can be deprotonated by bases such as NaOH. Treatment of **6** with NaOH in THF/MeOH led to isolation of the *σ*-acetylide $L_{OEt}Ru(PPh_3)_2(C{\equiv}CPh)$ (**7**), characterized by NMR and IR spectroscopy. The IR spectrum of **7** shows an intense band at 2066 cm^{-1} assignable to the C≡C stretch.

Cyclic Carbene Complex. In contrast to the $[CpRu(PR_3)_2(=C=CHPh)]^+$ complexes, which react with alcohols to give the alkoxycarbene species,[22] there is no reaction of complex **6** with MeOH even under reflux conditions. Intermolecular nucleophilic attack on the vinylidene carbon was, however, observed. Reaction of complex **1** with 3-butyn-1-ol afforded the 2-oxacyclopentylidene complex $[L_{OEt}Ru(PPh_3)_2\{=C(CH_2)_3O\}](PF_6)$ (**8**), which has been characterized by X-ray crystallography. Figure 5 shows a perspective view of the $[L_{OEt}Ru(PPh_3)_2\{=C(CH_2)_3O\}]^+$ cation; selected bond lengths and angles are given in Table 5. The mean Ru−O and Ru−P distances are comparable to those for **6**. The Ru−C distance of 1.87(1) Å is shorter than that for $[CpRu(PPh_3)_2\{=C(OMe)Et\}]^+$ (1.93 Å)[24] but slightly longer than that in **6**. The ^{13}C NMR spectrum of **8** shows a triplet at δ 305.2 with $^2J_{PC} = 16.5$ Hz, assignable to the carbenic carbon. A similar chemical shift has been reported for the Cp analog $[CpRu(PPh_3)_2\{C(CH_2)_3O\}]^+$ (δ 300.5).[25] The signals for the remaining carbons of the oxacyclopentyl ring can be assigned with reference to the Cp analog.[24]

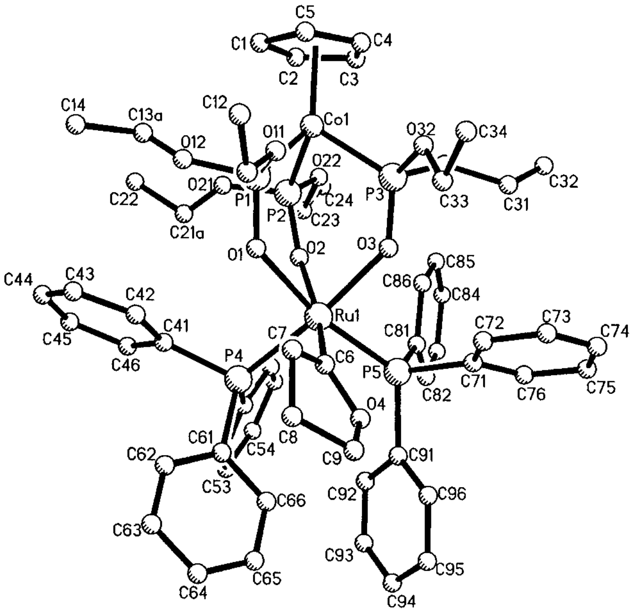

Figure 5. Perspective view of the cation $[L_{OEt}Ru(PPh_3)_2\{=C(CH_2)_3O\}]^+$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[L_{OEt}Ru(PPh_3)_2\{=C(CH_2)_3O\}]PF_6$ (8)

Ru(1)−P(4)	2.337(3)	Ru(1)−P(5)	2.333(4)
Ru(1)−O(1)	2.18(1)	Ru(1)−O(2)	2.205(8)
Ru(1)−O(3)	2.140(7)	Ru(1)−C(6)	1.870(13)
P(4)−Ru(1)−P(5)	98.0(1)	P(4)−Ru(1)−O(1)	93.6(2)
P(5)−Ru(1)−O(1)	168.3(2)	P(4)−Ru(1)−O(2)	89.3(2)
P(5)−Ru(1)−O(2)	97.5(3)	O(1)−Ru(1)−O(2)	81.3(3)
P(4)−Ru(1)−O(3)	172.5	P(5)−Ru(1)−O(3)	85.6(3)
O(1)−Ru(1)−C(6)	88.9(3)	O(2)−Ru(1)−O(3)	83.7(3)
P(4)−Ru(1)−C(6)	88.9(3)	P(5)−Ru(1)−C(6)	91.7(5)
O(1)−Ru(1)−C(6)	89.8(5)	O(2)−Ru(1)−C(6)	170.8(5)
O(3)−Ru(1)−C(6)	97.6(4)		

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[20] Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

[21] Bruce, M. I.; Wallis, R. C. *J. Organomet. Chem.* **1978**, *161*, C1.

[22] Bruce, M. I.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 2203.

[23] Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471.

[24] Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *314*, 213.

[25] Bruce, M. I.; Swincer, A. G.; Thomson, B. J.; Wallis, R. C. *Aust. J. Chem.* **1980**, *33*, 2065.

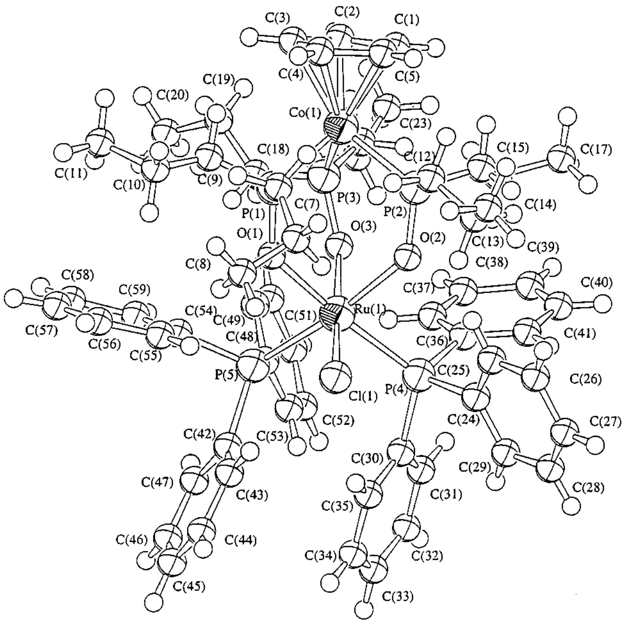

Figure 6. Perspective view of the cation $[L_{OEt}Ru(PPh_3)_2Cl]^+$.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $[L_{OEt}Ru(PPh_3)_2Cl]PF_6$ ($1 \cdot PF_6$)

Ru(1)−Cl(1)	2.300(3)	Ru(1)−P(4)	2.372(3)
Ru(1)−P(5)	2.388(3)	Ru(1)−O(1)	2.128(8)
Ru(1)−O(2)	2.097(7)	Ru(1)−O(3)	2.059(8)
Cl(1)−Ru(1)−P(4)	88.3(1)	Cl(1)−Ru(1)−P(5)	95.2(1)
Cl(1)−Ru(1)−O(1)	88.0(2)	Cl(1)−Ru(1)−O(2)	91.2(2)
Cl(1)−Ru(1)−O(3)	171.5(2)	P(4)−Ru(1)−P(5)	97.6(1)
P(4)−Ru(1)−O(1)	172.6(2)	P(4)−Ru(1)−O(2)	86.2(2)
P(4)−Ru(1)−O(3)	97.1(2)	P(5)−Ru(1)−O(1)	89.1(2)
P(5)−Ru(1)−O(2)	172.6(2)	P(5)−Ru(1)−O(3)	90.5(2)
O(1)−Ru(1)−O(2)	87.5(3)	O(1)−Ru(1)−O(3)	85.6(8)
O(2)−Ru(1)−O(3)	82.7(3)		

Ruthenium(III) Complexes. Interaction of complex **1** with stoichiometric I_2 afforded the cation $[L_{OEt}Ru(PPh_3)_2Cl]^+$ (**1**$^+$) in good yield, isolated as the I_3 salt. Anion metathesis of **1**·I_3 with PF_6 afforded **1**·PF_6, which has been characterized by X-ray crystallography. Figure 6 shows a perspective view of **1**$^+$; selected bond lengths and angles are given in Table 6. The mean Ru−O, Ru−P, and Ru−Cl distances are 2.095, 2.380, and 2.300(3) Å, respectively. As expected, the Ru−O and Ru−Cl distances in **1**$^+$ are shorter than those for the Ru(II) congener **1**. Interestingly, however, the Ru−P distances in **1**$^+$ were found to be longer than that in **1**. This may be rationalized by the fact that Ru(II) forms a stronger π-bond with PPh_3 than the Ru(III) counterpart. This difference is particularly prominent for complexes of L_{OEt}, which is a strong π-donor ligand. Consistent with this bonding picture, the PPh_3 in **1**$^+$ is more substitutionally labile than the Ru(II) congener. **1**·PF_6 was found to undergo substitution reactions with pyridine and 2,2′-bipyridine in THF/MeOH. Reactions of **1**$^+$ with RLi or LiOR, however, led to a reduction of Ru(III) to Ru(II) and formation of complex **1**.

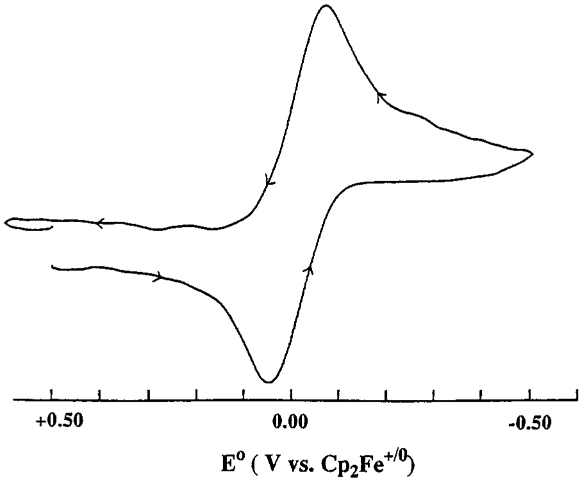

Figure 7. Cyclic voltammogram of $L_{OEt}Ru(PPh_3)_2Cl$ at a glassy-carbon electrode in CH_2Cl_2 with 0.1 M [*n*-$Bu_4N]PF_6$ as supporting electrolyte (scan rate 100 mV s^{-1}).

Electrochemistry. The electrochemistry of the Ru−L_{OEt} complexes in CH_2Cl_2 solutions has been studied by cyclic voltammetry. The cyclic voltammogram (CV) of **1** exhibits a reversible couple at −0.021 V assignable to the metal-centered Ru(III/II) couple (Figure 7). This assignment is confirmed by the fact that oxidation of **1** gives the well-defined Ru(III) cation **1**$^+$, which shows a CV identical with that for **1**. Under the same conditions, the Ru(III/II) potential for $CpRu(PPh_3)_2Cl$ was determined to be 0.451 V vs $Cp_2Fe^{+/0}$. This demonstrates that π-donating L_{OEt} is more capable of stabilizing the Ru(III) state than Cp. The Ru(III/II) couple for **2** (0.386 V) is more anodic than that for **1**, suggesting that DMSO is a stronger π-acid than PPh_3.

Summary. The first ruthenium vinylidene and carbene complexes containing the π-donating oxygen tripod ligand L_{OEt} have been isolated. On the basis of electrochemical, structural, and IR spectroscopic data, it is evident that L_{OEt} is a stronger donor than Cp and, as a result, $L_{OEt}Ru^{III}$ complexes are more easily accessible than the $CpRu^{III}$ analogs. Furthermore, the $L_{OEt}Ru^{II}$ fragment is very electron-rich and tends to form strong bonds with π-acid ligands, suggesting that Ru−L_{OEt} complexes are potentially useful in homogeneous catalysis. The study of the catalytic activities of these complexes is under investigation.

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Supporting Information Available: Listings of calculated atomic coordinates, bond lengths and angles, and thermal parameters for complexes **1**, **2**, **6**, **8**, and **1**·PF_6 (98 pages). Ordering information is given on any masthead page.

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