Synthesis and Electrochemistry of Ruthenium Complexes with an Oxygen Tripod Ligand

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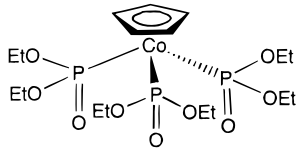
Reaction of $[Ru(COD)Cl_2]_x$ (COD = 1,5-cyclooctadiene) with NaL_{OEt} afforded $L_{OEt}(COD)RuCl$ (**1**). The average Ru−O, average Ru−C and Ru−Cl distances in **1** are 2.129, 2.164, and 2.398(3) Å, respectively. Treatment of **1** with $AgBF_4$ in acetone/H_2O afforded $[L_{OEt}(COD)Ru(OH_2)]BF_4$ (**2**), which reacts with L to give the respective adducts $[L_{OEt}(COD)RuL]BF_4$ (L = *t*-$BuNH_2$ (**3**), *p*-$MeC_6H_4NH_2$ (**4**), NH_3 (**5**), N_2H_4 (**6**), pyridine (**7**), 4,4′-bipyridine (**8**), MeCN (**9**), Et_2S (**10**), and Me_2SO (**11**)). The structures of **3** and **4** have been characterized by X-ray crystallography. The average Ru−O, Ru−C, and Ru−N distances in **3** are 2.115, 2.162, and 2.197(6) Å, respectively. The corresponding bond distances for **4** are 2.113, 2.160 and 2.174(5) Å. Reaction of **8** with **2** afforded the 4,4′-bipyridine-bridged binuclear complex $[\{L_{OEt}(COD)Ru\}_2(\mu\text{-}4,4'\text{-bipy})](PF_6)_2$ (**12**). Deprotonation of complexes **2** and **4** gave the hydroxide $L_{OEt}(COD)RuOH$ (**13**) and the amide $L_{OEt}(COD)Ru(NHC_6H_4Me\text{-}p)$ (**14**), respectively. The structure of $[L_{OEt}(CO)(PPh_3)Ru(OH_2)]BF_4$ (**15**) has been characterized by X-ray crystallography. The average Ru−O(L_{OEt}), Ru−C, Ru−P, and Ru−O(aquo) distances in **15** are 2.118, 1.83(1), 2.285(3), and 2.091(7) Å, respectively. Interaction of **15** with *p*-$MeC_6H_4NH_2$, PPh_3, and NaN_3 gave $[L_{OEt}(CO)(PPh_3)Ru(p\text{-}MeC_6H_4NH_2)]BF_4$ (**16**), $[L_{OEt}(PPh_3)_2Ru(CO)]PF_6$ (**17**), and $L_{OEt}(CO)(PPh_3)RuN_3$ (**18**), respectively. Deprotonation of **15** and **16** afforded the hydroxide $L_{OEt}(CO)(PPh_3)Ru(OH)$ (**19**) and amide $L_{OEt}(CO)(PPh_3)Ru(NHC_6H_4Me\text{-}p)$ (**20**), respectively. Treatment of $Ru(CO)Cl(H)(PPh_3)_3$ with NaL_{OEt} afforded the hydride $L_{OEt}(CO)(PPh_3)RuH$ (**21**), which reacts with tosyl azide to give the Ru(II) tosylamide $L_{OEt}(CO)(PPh_3)Ru(NHSO_2C_6H_4Me\text{-}p)$ (**22**). Reaction of $[L_{OEt}(PPh_3)_2Ru(MeOH)]^+$ with *t*-BuNC, CNpy (4-cyanopyridine), Me_2SO, and SO_2 afforded the respective adducts $[L_{OEt}(PPh_3)_2RuL]^+$ (L = *t*-BuNC (**23**), CNpy (**24**), Me_2SO (**25**), SO_2 (**26**)), isolated as their PF_6 salts. The cyclic voltammograms for the Ru−L_{OEt} complexes show reversible oxidation couples assignable to Ru(III/II) couples. The availability of electrons in the $L_{OEt}Ru$ complexes for back-bonding can be accessed by their ν(C≡O) and Ru(III/II) potentials.

Introduction

Complexes of ruthenium(II) aquo ion have attracted much attention due to their applications to organometallic catalysis, notably ring-opening metathesis polymerization of cycloolefins[1] and isomerization of olefins[2] in aqueous or polar media. The catalytic activities of these complexes are attributed to the electron-releasing aquo ligands that facilitate the Ru-to-ligand back-bonding. Accordingly Ru(II) aquo ion is found to have high affinities for π acid ligands such as olefins and N-heterocycles. Complexes of the type $[Ru(OH_2)_5L]^{2+}$ (L = CO,[3] N_2,[4] olefin[5−7]) have been synthesized and characterized recently. An understanding of the factors affecting the back-bonding in the Ru aquo complexes will shed light into the mechanisms for the $[Ru(OH_2)_6]^{2+}$-catalyzed reactions. The oxygen tripod ligand $[CpCo\{P(OEt)_2{=}O\}_3]^-$ or L_{OEt}^-, an oxygen analogue for cyclopentadienyl ligands, is known to bind to variety of metal ions.[8] We are particularly interested in organometallic complexes of $L_{OEt}Ru$, which may serve as a model for the *fac*-$[Ru(OH_2)_3]^{2+}$ moiety. Organoruthenium complexes with L_{OEt} are expected to be more amenable than those with aquo ligands due to their high solubilities in common organic solvents including hexane and the kinetic stability. Previously we found that with electron-releasing PPh_3 coligands the $L_{OEt}Ru$ fragment is a good π donor and is capable of stabilizing a variety of hydrocarbyl ligands including σ-acetylide, carbene, vinylidene, and allenylidene.[9] As our continuing effort to develop $L_{OEt}Ru$-based catalysts for activation of small molecules and organic transformations, we set out to study the influence of ancillary ligands on the donor/acceptor property of the $L_{OEt}Ru$ fragment. Herein we report the synthesis and electrochemistry of complexes containing the L_{OEt}-(COD)Ru, $L_{OEt}(CO)(PPh_3)Ru$, and $L_{OEt}(PPh_3)_2Ru$ cores.

L_{OEt} ≡ 

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Experimental Section

General Considerations. NMR spectra were recorded on a Bruker ALX 300 spectrometers operating at 300 and 121.5 MHz for ^{1}H and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $Si(CH_3)_4$ (^{1}H) and H_3PO_4 (^{31}P). 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 were glassy carbon and $Ag/AgNO_3$ (0.1 M in acetonitrile), respectively. Potentials were reported with reference to ferrocenium−ferrocene ($Cp_2Fe^{+/0}$). Elemental analyses were performed by Medac Ltd, Surrey, U.K.

Solvents were purified by standard procedures and distilled prior to use. NaL_{OEt},[10] $[Ru(COD)Cl_2]_x$ (COD = 1,5-cyclooctadiene),[11] $[L_{OEt}(CO)(PPh_3)Ru(OH_2)]BF_4$,[9a] $Ru(CO)Cl(H)(PPh_3)_3$,[12] $L_{OEt}(PPh_3)_2RuCl$,[9a] and tosyl azide[13] were prepared according to the literature methods. 4,4′-Bipyridine (4,4′-bipy) and 4-cyanopyridine (CNpy) were purchased from Aldrich.

Syntheses. Preparation of L_{OEt}Ru(COD)Cl (1). To a solution of NaL_{OEt} (0.12 g, 0.22 mmol) in acetone/dimethyl formamide (50 mL, 1:4) was added $[Ru(COD)Cl_2]_x$ (96 mg, 0.34 mmol), and the mixture was heated at reflux overnight. The solvent was pumped off in vacuo, and the residue was extracted with Et_2O/hexane (4 × 20 mL, 3:1). Slow evaporation of the filtrate at room temperature gave orange crystals (yield 0.1 g, 61%). ^{1}H NMR ($CDCl_3$): δ 1.21 (t, 6H, C*H*$_3$), 1.26 (t, 6H, C*H*$_3$), 1.31 (t, 6H, C*H*$_3$), 1.86−1.96 (m, 4H, C*H*$_2$ of COD), 2.27−2.34 (s, 2H, C*H*$_2$ of COD), 2.49−2.63 (m, 2H, C*H*$_2$ of COD), 3.71−4.35 (m, 16H, CH═C and OC*H*$_2$), 5.03 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 111.7−113.2 (m, $PO(OEt)_2$). Anal. Calcd for $CoRuC_{25}H_{47}ClO_9P_3$: C, 38.4; H, 6.0. Found: C, 38.7; H, 6.1.

Preparation of $[L_{OEt}(COD)Ru(OH_2)]BF_4$ (2). To a solution of **1** (0.2 g, 0.26 mmol) in acetone/H_2O (60 mL, 1:1) was added $AgBF_4$ (90 mg, 0.46 mmol). The reaction mixture was stirred at room temperature for 2 h and filtered. Recrystallization from CH_2Cl_2/hexane afforded yellow crystals (yield 0.147 g, 68%). ^{1}H NMR ($CDCl_3$): δ 1.26 (t, 6H, CH_3), 1.31 (t, 6H, CH_3), 1.34 (t, 6H, CH_3), 2.03−2.40 (m, 8H, CH_2 of COD), 3.94−4.28 (m, 16H, OCH_2 and olefinic protons of COD), 5.06 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 152.0 (m, $PO(OEt)_2$).

Preparation of $[L_{OEt}(COD)RuL]BF_4$ (L = *t*-BuNH$_2$, *p*-MeC$_6$H$_4$NH$_2$, NH$_3$, N$_2$H$_4$, MeCN, py, 4,4′-bipy, Et$_2$S, Me$_2$SO). Typically, to a solution of **2** (64 mg, 0.077 mmol) in CH_2Cl_2 (20 mL) was added 2 equiv of L, and the mixture was stirred at room temperature overnight. The solvent was pumped off, and the residue was extracted with CH_2Cl_2. Careful addition of hexane to the filtrate afforded the crude yellow product, which was further recrystallized from CH_2Cl_2/hexane (yield 50−70%).

Characterization data for $[L_{OEt}(COD)Ru(t\text{-}BuNH_2)]BF_4$ (**3**). ^{1}H NMR ($CDCl_3$): δ 1.24 (t, 6H, CH_3), 1.34 (overlapping t, 12H, CH_3), 1.41 (s, 9H, *t*-Bu), 1.92−2.32 (m, 8H, CH_2 of COD), 3.93−4.20 (m, 16H, OCH_2 and olefinic protons of COD), 5.13 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 115.6 (m, $PO(OEt)_2$). MS (FAB): *m*/*z* 817 ($M^+ - BF_4$). IR (cm^{-1}, Nujol): 3294, 3250 ν(N−H). Anal. Calcd for $RuCoBC_{29}H_{58}F_4NO_9P_3$: C, 38.5; H, 6.4, N, 1.6. Found: C, 38.4; H, 6.5; N, 1.6.

Characterization data for $[L_{OEt}(COD)Ru(p\text{-}MeC_6H_4NH_2)]BF_4$ (**4**). ^{1}H NMR ($CDCl_3$): δ 1.29 (t, 6H, CH_3), 1.30 (t, 6H, CH_3), 1.35 (t, 6H, CH_3), 1.45−1.91 (m, 8H, CH_2 of COD), 2.29 (s, 3H, *p*-Me), 3.90−4.15 (m, 16H, OCH_2 and olefinic protons of COD), 5.11 (s, 5H, C_5H_5), 7.08 (d, 2H, H_m), 7.47 (d, 2H, H_o). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 115.7 (m, $PO(OEt)_2$). MS (FAB): *m*/*z* 851 ($M^+ - BF_4$). IR (cm^{-1}, Nujol): 3290, 3244 ν(N−H). Anal. Calcd for $CoRuC_{32}H_{56}BF_4NO_9P_3$: C, 40.9, H, 6.0, N, 1.5. Found: C, 40.7; H, 6.0; N, 1.6.

Characterization data for $[L_{OEt}(COD)Ru(NH_3)]BF_4$ (**5**). ^{1}H NMR ($CDCl_3$): δ 1.27 (t, 6H, CH_3), 1.30 (t, 6H, CH_3), 1.33 (t, 6H, CH_3), 1.88−1.95 (m, 4H, CH_2 of COD), 2.33−2.37 (m, 4H, CH_2 of COD), 3.61−4.19 (m, 16H, OCH_2 and olefinic protons of COD), 5.01 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 116.3 (m, $PO(OEt)_2$). MS (FAB): *m*/*z* 761 ($M^+ - BF_4$). IR (cm^{-1}, Nujol): 3294, 3250 ν(N−H). Anal. Calcd for $CoRuC_{25}H_{50}BNF_4O_9P_3$: C, 35.4; H, 6.0, N, 1.7. Found: C, 35.1; H, 6.0; N, 1.7.

Characterization data for $[L_{OEt}(COD)Ru(N_2H_4)]BF_4$ (**6**). ^{1}H NMR ($CDCl_3$): δ 1.21 (t, 6H, CH_3), 1.31 (t, 6H, CH_3), 1.33 (s, 6H, CH_3), 1.87−1.96 (m, 4H, CH_2 of COD), 2.34−2.41 (m, 4H, CH_2 of COD), 3.71−4.19 (m, 16H, OCH_2 and olefinic protons of COD), 5.03 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 116.0 (m, $PO(OEt)_2$). MS (FAB): *m*/*z* 776 ($M^+ - BF_4$). IR (cm^{-1}, Nujol): 3348, 3266 ν(N−H). Anal. Calcd for $CoRuC_{25}H_{51}BF_4N_2O_9P_3$: C, 34.8; H, 6.0, N, 3.2. Found: C, 34.0; H, 6.0; N, 3.6.

Characterization data for $[L_{OEt}(COD)Ru(py)]BF_4$ (**7**). ^{1}H NMR ($CDCl_3$): δ 0.94 (t, 6H, CH_3), 1.27 (t, 6H, CH_3), 1.36 (t, 6H, CH_3), 1.66−1.98 (m, 8H, CH_2 of COD), 3.29−4.24 (m, 16H, OCH_2 and olefinic protons of COD), 4.96 (s, 5H, C_5H_5), 7.58 (dd, 2H, H_m of py), 8.03 (dd, 1H, H_p of py), 8.86 (d, 2H, H_o of py). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 115.2 (m, $PO(OEt)_2$). MS (FAB): *m*/*z* 823 ($M^+ - BF_4$).

Characterization data for $[L_{OEt}(COD)Ru(4,4'\text{-bipy})]BF_4$ (**8**). ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 6H, CH_3), 1.28 (t, 6H, CH_3), 1.36 (t, 6H, CH_3), 1.71−1.74 (m, 2H, CH_2 of COD), 1.96−1.99 (m, 4H, CH_2 of COD), 2.39−2.44 (m, 2H, CH_2 of COD), 3.40−4.27 (m, 16 H, OCH_2 and olefinic protons of COD), 4.97 (s, 5H, C_5H_5), 7.76 (m, 2H, H_m of 4,4′-bipy), 7.93 (d, 2H, H_o of 4,4′-bipy), 8.80 (m, H_o′ of 4,4′-bipy), 9.03 (d, 2H, H_o of 4,4′-bipy). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 115.2 (m, $PO(OEt)_2$). MS (FAB): *m*/*z* 901 ($M^+ + 1 - BF_4$). Anal. Calcd for $CoRuC_{35}H_{55}BF_4N_2O_9P_3$: C, 42.6; H, 5.6; H, 2.8. Found: C, 42.3; H, 5.7; N, 2.8.

Characterization data for $[L_{OEt}(COD)Ru(MeCN)]BF_4$ (**9**). ^{1}H NMR-($CDCl_3$): δ 1.22 (t, 6H, CH_3), 1.32 (t, 6H, CH_3), 1.33 (t, 6H, CH_3), 1.92−1.98 (m, 4H, CH_2 of COD), 2.36−2.39 (m, 4H, CH_2 of COD), 2.76 (s, 3H, MeCN), 3.86−4.16 (m, 16H, OCH_2 and olefinic protons of COD), 5.04 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 116.1 (m, $PO(OEt)_2$). MS (FAB): *m*/*z* 785 ($M^+ - BF_4$). Anal. Calcd for $CoRuC_{27}H_{50}BF_4NO_9P_3$: C, 37.2; H, 5.7, N, 1.6. Found: C, 37.1; H, 5.9; N, 1.6.

Characterization data for $[L_{OEt}(COD)Ru(SEt_2)]BF_4$ (**10**). ^{1}H NMR-($CDCl_3$): δ 1.22 (t, 6H, CH_3), 1.31 (t, 6H, CH_3), 1.36 (t, 6H, CH_3), 1.47 (t, 6H, CH_3 of Et_2S), 1.77−1.84 (m, 4H, CH_2 of COD), 2.36−2.66 (m, 4H, CH_2 of COD), 2.98 (q, 4H, CH_2 of Et_2S), 3.87−4.20 (m, 16H, OCH_2 and olefinic protons of COD), 5.14 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 114.1 (m, $PO(OEt)_2$). MS (FAB): *m*/*z* 834 ($M^+ - BF_4$). Anal. Calcd for $CoRuC_{29}H_{57}BF_4O_9P_3S$: C, 37.4; H, 6.2. Found: C, 37.8; H, 6.2.

Characterization data for $[L_{OEt}(COD)Ru(Me_2SO)]BF_4$ (**11**). ^{1}H NMR-($CDCl_3$): δ 1.25 (t, 6H, CH_3), 1.32 (t, 6H, CH_3), 1.38 (t, 6H, CH_3), 1.61−1.90 (m, 4H, CH_2 of COD), 2.43−2.63 (m, 4H, CH_2 of COD), 3.41 (s, 6H, Me_2SO), 3.93−4.22 (m, 16H, OCH_2 and olefinic protons of COD), 5.19 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 114.8 (m, $PO(OEt)_2$). MS (FAB): *m*/*z* 822 ($M^+ - BF_4$).

Preparation of $[\{L_{OEt}(COD)Ru\}_2(\mu\text{-}4,4'\text{-bipy})](BF_4)_2$ (12). To a solution of **8** (50 mg, 0.05 mmol) in CH_2Cl_2 (10 mL) was added 1 equiv of **2** (43 mg, 0.05 mmol), and the mixture was stirred at room temperature overnight. Removal of solvent and recrystallization from CH_2Cl_2/hexane gives a yellow solid (yield 60 mg, 70%). ^{1}H NMR ($CDCl_3$): δ 0.90 (t, 12H, CH_3), 1.28 (t, 12H, CH_3), 1.36 (t, 12H, CH_3), 1.73−1.99 (m, 12 H, CH_2 of COD), 2.41 (m, 4H, CH_2 of COD), 3.40−4.27 (m, 32H, OCH_2 and olefinic protons of COD), 4.96 (s, 10H, C_5H_5), 8.38 (d, J = 6.8 Hz, 4H, H_m of 4,4′-bipy), 9.03 (d, J = 6.8 Hz, 4H, H_o of 4,4′-bipy). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 114.5 (m, $PO(OEt)_2$). Anal. Calcd for $Co_2Ru_2C_{60}H_{102}B_2F_8N_2O_{18}P_6$: C, 39.1; H, 5.6; N, 1.8. Found: C, 39.6; H, 5.8; N, 1.5.

Preparation of L_{OEt}(COD)Ru(OH) (13). To a solution of **2** (60 mg, 0.07 mmol) in MeOH/H_2O (25 mL, 1:1) at 0 °C was added NaOH

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(25 mg) and the resulting mixture was stirred at room temperature for 30 min. The solvent was pumped off, and the residue was extracted with hexane. Concentration and cooling at −10 °C afforded yellow crystals (yield 22 mg, 40%). ^{1}H NMR (C_6D_6): δ 1.19 (t, 6H, CH_3), 1.26 (t, 6H, CH_3), 1.37 (t, 6H, CH_3), 2.18−3.02 (m, 8H, CH_2 of COD), 3.95−4.27 (m, 12 H, OCH_2), 4.46−4.57 (m, 4H, olefinic protons of COD), 5.01 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR (C_6D_6): δ 113.0 (m, PO(OEt)$_2$). Anal. Calcd for $CoRuC_{25}H_{48}NO_9P_3 \cdot H_2O$: C, 38.5, H, 6.4. Found: C, 37.7; H, 6.5.

Reaction of 13 with PhOH. To a solution of **13** (8 mg) in C_6D_6 (0.5 mL) was added PhOH (2 mg), and the mixture was left to stand at room temperature for 1 h. A new species, presumably the phenoxide complex L_{OEt}(COD)Ru(OPh), was identified by NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 1.26 (t, 6H, CH_3), 1.29 (t, 6H, CH_3), 1.35 (t, 6H, CH_3), 2.16−2.16 (m, 4H, CH_2 of COD), 2.49−2.51 (m, 2H, CH_2 of COD), 3.03−3.06 (m, 2H, CH_2 of COD), 4.03−4.42 (m, 16H, OCH_2 and olefinic protons of COD), 5.02 (s, 5H, C_5H_5), the phenoxide protons signals were not assigned due to overlap with the PhOH signals. ^{31}P{^{1}H} NMR (C_6D_6): δ 113.8 (m, PO(OEt)$_2$).

Preparation of L_{OEt}(COD)Ru(NHC$_6$H$_4$Me-*p*) (14). To a solution of **5** (70 mg, 0.075 mmol) in THF (30 mL) at 0 °C was added NaH (6 mg). The resulting mixture was stirred at room temperature under nitrogen for 30 min during which the color changed from yellow to red. The solvent was pumped off and the residue was extracted with hexane. Concentration and cooling at −10 °C afforded red crystals (yield 41 mg, 58%). ^{1}H NMR (C_6D_6): δ 1.23 (t, 6H, CH_3), 1.27 (t, 6H, CH_3), 1.29 (t, 6H, CH_3), 1.89−2.66 (m, 8H, CH_2 of COD), 2.41 (s, 3H, *p*-Me), 3.94−4.32 (m, 16H, OCH_2 and olefinic protons of COD), 5.01 (s, 5H, C_5H_5), 7.14 (d, 2H, H_m), 7.31 (d, 2H, H_o). ^{31}P{^{1}H} NMR (C_6D_6): δ 113.1 (m, PO(OEt)$_2$). IR (cm^{-1}, Nujol): 3426 br ν(N−H). Anal. Calcd for $CoRuC_{32}H_{35}NO_9P_3$: C, 45.2; H, 6.5, N, 1.7. Found: C, 44.6; H, 6.6; N, 1.5.

Preparation of [L_{OEt}(CO)(PPh$_3$)Ru(*p*-MeC$_6$H$_4$NH$_2$)]BF$_4$ (16). To a solution of [L_{OEt}(CO)(PPh$_3$)Ru(OH$_2$)]BF$_4$ (65 mg, 0.06 mmol) was added *p*-MeC$_6$H$_4$NH$_2$ (11 mg, 0.1 mmol), and the mixture was stirred overnight. Recrystallization from CH_2Cl_2/hexane afforded red crystals (yield 41 mg, 60%). ^{1}H NMR ($CDCl_3$): δ 0.82 (t, 3H, CH_3), 0.97 (t, 3H, CH_3), 1.27 (t, 3H, CH_3), 1.36 (t, 3H, CH_3), 1.39 (t, 3H, CH_3), 1.41 (t, 3H, CH_3), 2.19 (t, 3H, CH_3), 3.27−3.51 (m, 4H, OCH_2), 3.99−4.63 (m, 8H, OCH_2), 5.00 (s, 5H, C_5H_5), 6.52 (d, 2H, H_m), 6.76 (d, 2H, H_o), 7.37−7.56 (m, 15H, PPh_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 51.1 (s, PPh_3), 111.8 (m, PO(OEt)$_2$). IR (cm^{-1}, Nujol): 3295, 3252 ν(N−H), 1950 ν(C≡O). Anal. Calcd for $CoRuBC_{42}H_{59}F_4NO_9P_4$: C, 45.0, H, 5.3, N, 1.3. Found: C, 45.9; H, 5.4; N, 1.2.

Preparation of [L_{OEt}(PPh$_3$)$_2$Ru(CO)]PF$_6$ (17). To a solution of **2** (65 mg, 0.06 mmol) was added excess PPh_3 (100 mg, 0.38 mmol), and the mixture was stirred at room temperature for 1 day. The solvent was pumped off, and the residue was recrystallized from a saturated solution of $NaPF_6$ in MeOH to give pale yellow crystals (yield 39 mg, 50%). ^{1}H NMR ($CDCl_3$): δ 0.95 (t, 6H, CH_3), 1.25 (t, 6H, CH_3), 1.33 (t, 6H, CH_3), 3.06−3.53 (m, 4H, CH_2), 4.83−4.30 (m, 8H, CH_2), 5.05 (s, 5H, C_5H_5), 7.12 (m, 30H, PPh_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 41.0 (s, PPh_3), 111.5 (m, PO(OEt)$_2$). MS (FAB): *m*/*z* 1954 ($M^+ - PF_6$). IR (cm^{-1}, Nujol): 1954 ν(C≡O). Anal. Calcd for $CoRuC_{54}H_{65}F_6O_{10}P_6$: C, 48.6, H, 4.9. Found: C, 47.6, H, 4.9.

Preparation of L_{OEt}(CO)(PPh$_3$)RuN$_3$ (18). To a solution of [L_{OEt}(CO)(PPh$_3$)Ru(OH$_2$)]BF$_4$ (65 mg, 0.06 mmol) in MeOH (20 mL) was added NaN_3 (100 mg) in water (10 mL), and the reaction mixture was heated at reflux for 1.5 h. The yellow precipitate was collected and washed with MeOH/H_2O (1:1) (yield 31 mg, 54%). ^{1}H NMR ($CDCl_3$): δ 0.85 (t, 3H, CH_3), 0.93 (t, 3H, CH_3), 1.28 (t, 3H, CH_3), 1.30−1.37 (overlapping t, 9H, CH_3), 3.09−3.53 (m, 4H, CH_2), 3.97−4.43 (m, 8H, CH_2), 4.99 (s, 5H, C_5H_5), 7.29−7.58 (m, 15H, PPh_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 53.1 (s, PPh_3), 109.8−111.1 (m, PO(OEt)$_2$). IR (cm^{-1}, Nujol): 2204 ν(N≡N), 1931 ν(C≡O). Anal. Calcd for $CoRuC_{36}H_{45}N_3O_{10}P_4$: C, 44.6, H, 4.7, N, 4.3. Found: C, 45.2; H, 5.2; N, 4.1.

Preparation of L_{OEt}(CO)(PPh$_3$)Ru(OH) (19). To a solution of [L_{OEt}(CO)(PPh$_3$)Ru(OH$_2$)]BF$_4$ (65 mg, 0.06 mmol) in MeOH/H_2O (20 mL, 2:1) was added NaOH (5 mg), and the mixture was stirred at room temperature for 30 min. The solvent was pumped off, and the residue was extracted with hexane. Concentration and cooling at −10 °C afforded yellow crystals (yield 23 mg, 40%). ^{1}H NMR (C_6D_6): δ 0.95 (t, 3H, CH_3), 1.06 (t, 3H, CH_3), 1.34 (overlapping t, 6H, CH_3), 1.39 (t, 3H, CH_3), 1.47 (t, 3H, CH_3), 3.36−3.71 (m, 4H, CH_2), 4.23−4.56 (m, 8H, CH_2), 5.01 (s, 5H, C_5H_5). ^{31}P{^{1}H} NMR (C_6D_6): δ 58.7 (s, PPh_3), 109.6−111.8 (m, PO(OEt)$_2$). MS (FAB): *m*/*z* 944 ($M^+ + 1$). IR (cm^{-1}, Nujol): 3396 br ν(O−H), 1922 ν(C≡O). Anal. Calcd for $CoRuC_{36}H_{51}O_{11}P_4$: C, 45.8, H, 5.4. Found: C, 46.0, H, 5.8.

Preparation of L_{OEt}(CO)(PPh$_3$)Ru(NHC$_6$H$_4$Me-*p*) (20). To a solution **16** (50 g, 0.04 mmol) in THF (20 mL) at 0 °C was added NaH (5 mg), and the mixture was stirred at room temperature under nitrogen for 30 min. The solvent was pumped off, and the residue was extracted with hexane. Concentration and cooling at −10 °C afforded red crystals (yield 26 mg, 57%). ^{1}H NMR (C_6D_6): δ 0.96 (t, 3H, CH_3), 1.10 (t, 3H, CH_3), 1.23 (t, 3H, CH_3), 1.32−1.49 (overlapping t, 9H, CH_3), 2.45 (s, 3H, *p*-Me), 3.40−3.45 (2H, m, CH_2), 3.82−3.88 (m, 2H, CH_2), 4.31−4.63 (m, 8H, CH_2), 5.02 (s, 5H, C_5H_5), 7.08−8.22 (m, 19H, phenyl protons). ^{31}P{^{1}H} NMR (C_6D_6): δ 56.0 (s, PPh_3), 110.2 (m, PO(OEt)$_2$). IR (cm^{-1}, Nujol): 3444 br ν(N−H), 1922 ν(C≡O). Anal. Calcd for $CoRuC_{43}H_{58}NO_{10}P_4$: C, 50.0; H, 5.6; N, 1.4. Found: C, 49.6; H, 6.1; N, 1.2.

Preparation of L_{OEt}(CO)(PPh$_3$)RuH (21). To a slurry of Ru(CO)Cl(H)(PPh$_3$)$_3$ (0.3 g, 0.32 mmol) in toluene (40 mL) was added NaLOEt (0.1 g, 0.179 mmol), and the mixture was heated at reflux overnight. The solvent was pumped off, and the residue was extracted with hexane. Concentration and cooling at −10 °C afforded a yellow solid. The product was found to be contaminated with some cocrystallized PPh_3, which has yet to be separated. ^{1}H NMR ($CDCl_3$): δ −15.63 (d d, J_{PH} = 36 Hz, J_{PH}' = 9 Hz, Ru−H), 1.02 (t, 3H, CH_3), 1.13 (t, 3H, CH_3), 1.33 (t, 3H, CH_3), 1.34 (t, 3H, CH_3), 1.42 (t, 3H, CH_3), 1.46 (t, 3H, CH_3), 3.54−3.59 (m, 2H, CH_2), 3.74−3.59 (m, 2H, CH_2), 4.33−4.67 (m, 8H, CH_2), 5.06 (s, 5H, C_5H_5), 7.02−8.17 (m, 15H, PPh_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 70.2 (s, PPh_3), 110.2 (m, PO(OEt)$_2$). MS (FAB): *m*/*z* 927 (M^+). IR (cm^{-1}, Nujol): 1966 ν(Ru−H), 1908 ν(C≡O).

Reaction of 21 with Tosyl Azide. To a solution of the crude product of **21** (95 mg) was added tosyl azide (40 mg, 0.2 mmol) and the mixture was stirred under nitrogen at room temperature for 2 days. The solvent was pumped off and the residue extracted with Et_2O. Recrystallization from Et_2O/hexane afforded a yellow solid characterized as L_{OEt}(CO)(PPh$_3$)Ru(NHTs) (**22**), which was found to be contaminated with some with TsN═PPh$_3$. ^{1}H NMR ($CDCl_3$): δ 0.83 (t, 3H, CH_3), 0.96 (t, 3H, CH_3), 1.14 (t, 3H, CH_3), 1.28 (t, 3H, CH_3), 1.33 (t, 3H, CH_3), 1.39 (t, 3H, CH_3), 2.31 (s, 3H, *p*-Me), 3.19−3.24 (m, 4H, CH_2), 3.74−3.87 (m, 2H, CH_2), 4.05−4.30 (m, 6H, CH_2), 6.99−7.84 (m, 19H, phenyl protons). ^{31}P{^{1}H} NMR (C_6D_6): δ 54.0 (s, PPh_3), 112.0 (m, PO(OEt)$_2$). IR (cm^{-1}, Nujol): 3307 w ν(N−H), 1266 ν(S═O). MS (FAB): *m*/*z* 1097 ($M^+ + 1$). IR (cm^{-1}, Nujol): 1942 ν(C≡O).

Preparation of [L_{OEt}(PPh$_3$)$_2$RuL]PF$_6$ (L = *t*-BuNC, 4-Cyanopyridine, Me$_2$SO). To a solution of L_{OEt}(PPh$_3$)$_2$RuCl (70 g, 0.06 mmol) and NH_4PF_6 (17 mg) in MeOH/THF (20 mL, 1:1) was added L (0.1 mmol), and the solution was stirred at room temperature under nitrogen overnight. The solvent was pumped off and the residue recrystallized from CH_2Cl_2/hexane to give yellow crystals (yield 60−75%).

Characterization data for [L_{OEt}(PPh$_3$)$_2$Ru(*t*-BuNC)]PF$_6$ (**23**). ^{1}H NMR ($CDCl_3$): δ 0.93 (t, 6H, CH_3), 1.16 (t, 6H, CH_3), 1.36 (t, 6H, CH_3), 1.42 (s, 9H, *t*-Bu), 3.00−3.12 (m, 4 H, OCH_2), 3.67−3.76 (m, 4 H, OCH_2), 4.11−4.15 (m, 4 H, OCH_2), 5.19 (s, 5H, C_5H_5), 7.07−7.68 (m, 30 H, PPh_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 48.7 (s, PPh_3), 108.7 (m, PO(OEt)$_2$). IR (cm^{-1}, Nujol): 2114 ν(C≡N).

Characterization data for [L_{OEt}(PPh$_3$)$_2$Ru(CNpy)]PF$_6$ (**24**). ^{1}H NMR ($CDCl_3$): δ 0.93 (t, 6H, CH_3), 1.27 (overlapping t, 12H, CH_3), 2.95−3.52 (m, 4 H, OCH_2), 3.79−4.13 (m, 8 H, OCH_2), 5.10 (s, 5H, C_5H_5), 6.91−7.83 (m, 34 H, aromatic protons). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 44.3 (s, PPh_3), 108.8 (m, PO(OEt)$_2$). IR (cm^{-1}, Nujol): 2214 ν(C≡N). MS (FAB): *m*/*z* 1264 ($M - PF_6$)$^+$.

Characterization data for [L_{OEt}(PPh$_3$)$_2$Ru(Me$_2$SO)]PF$_6$ (**25**). ^{1}H NMR ($CDCl_3$): δ 1.11 (t, 6 H, CH_3), 1.21−1.29 (overlapping t, 12 H, CH_3), 2.89 (s, 6H, *Me*$_2$SO), 3.63−3.93 (m, 12 H, OCH_2), 5.19 (s, 5H, C_5H_5), 7.07−7.68 (m, 30 H, PPh_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 38.5 (s, PPh_3), 108.7 (m, PO(OEt)$_2$).

Table 1. Crystallographic Data and Experimental Details for L_{OEt}(COD)RuCl (**1**), [L_{OEt}(COD)Ru(*t*-$BuNH_2$)]BF_4 (**3**), [L_{OEt}(COD)Ru(*p*-$MeC_6H_4NH_2$)]BF_4 (**4**), and L_{OEt}(CO)(PPh_3)Ru(OH_2)]BF_4 (**15**)

	1	**3**	**4**	**15**
empirical formula	$CoRuC_{25}H_{47}ClO_9P_3$	$CoRuC_{29}H_{58}BF_4NO_9P_3$	$CoRuC_{32}H_{56}BF_4NO_9P_3$	$CoRuC_{36}H_{54}BF_4O_{12}P_4$
fw	780.02	904.51	938.52	1049.52
color, habit	orange, rod	orange; block	yellow, prism	pale; plate
cryst dimens/mm	0.3 × 0.32 × 0.44	0.20 × 0.23 × 0.26	0.12 × 0.12 × 0.23	0.12 × 0.32 × 0.34
a, Å	12.203(2)	12.950(1)	13.090(2)	13.686(2)
b, Å	19.187(2)	18.688(2)	18.112(3)	14.733(4)
c, Å	14.181(2)	17.141(2)	17.502(1)	12.445(2)
α, deg				109.05(2)
β, deg	91.13(1)	100.20(2)	96.904(9)	90.02(1)
γ, deg				89.39(2)
V, Å^3	3319.8(6)	4082.7(7)	4119.5(8)	2372.0(9)
Z	4	4	4	2
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
D_{calc}, g cm^{-3}	1.560	1.471	1.513	1.469
T, °C	28	25	25	28
scan type	$\omega-2\theta$	ω	$\omega-2\theta$	$\omega-2\theta$
μ, cm^{-1}	12.25	9.58	9.52	8.72
no. of reflns measd	5673	5807	5877	6512
no. of reflns obsd	3892	3206	3525	3153
weighting scheme	$1/[\sigma^2(F_o) + 0.03F_o^2/4]$	$1/[\sigma^2(F_o) + 0.016F_o^2/4]$	$1/[\sigma^2(F_o) + 0.016F_o^2/4]$	$1/[\sigma^2(F_o) + 0.005F_o^2/4]$
R,[a] %	4.3	4.0	4.0	4.8
R_w,[b] %	5.9	4.8	4.6	5.5
F(000)	1608	1872	1936	1076
GoF[c]	3.95	1.80	1.85	2.27

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

Preparation of [$L_{OEt}(PPh_3)_2Ru(SO_2)$]PF_6 (26). SO_2 was bubbled to a solution of $L_{OEt}(PPh_3)_2$RuCl (70 mg, 0.06 mmol) and NH_4PF_6 (17 mg) in THF/MeOH (1:1, 20 mL) for 2 min, during which the color changed from red to orange. The solvent was pumped off, and the residue was recrystallized from CH_2Cl_2/hexane to give yellow crystals (yield 53 mg, 65%). ^{1}H NMR ($CDCl_3$): δ 0.93 (t, 6H, CH_3), 1.84 (t, 6H, CH_3), 1.38 (t, 6H, CH_3), 3.02−3.16 (m, 4 H, OCH_2), 3.47−3.70 (m, 4 H, OCH_2), 4.20−4.27 (m, 4 H, OCH_2), 5.08 (s, 5H, C_5H_5), 7.12−7.67 (m, 30 H, PPh_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 32.7 (s, PPh_3), 111.2 (m, $PO(OEt)_2$). MS (FAB): *m*/*z* 1226 ($M^+ - PF_6 + 2$). IR (cm^{-1}, Nujol): 1292 $\nu(SO_2)_{as}$. Anal. Calcd for $CoRuC_{53}H_{65}F_6O_{11}P_6S$: C, 52.0; H, 4.8. Found: C, 51.6; H, 5.0.

X-ray Crystallography. The details of crystal data collection and refinement parameters for L_{OEt}(COD)RuCl (**1**), [L_{OEt}(COD)Ru(*t*-$BuNH_2$)]BF_4 (**3**), [L_{OEt}(COD)Ru(*p*-$MeC_6H_4NH_2$)]BF_4 (**4**), and [L_{OEt}(CO)(PPh_3)Ru(OH_2)]BF_4 (**15**) are listed in Table 1. Single crystals for these complexes were grown from CH_2Cl_2/hexane at room temperature. Data for **1**, **4**, and **15** were collected on a Rigaku AFC7R diffractometer while data for **3** were collected on a MAR-Research image plate diffractometer. Graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was used for the measurements. All data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods (SIR 92[14]) and subsequently refined by full-matrix least-squares routines. Selected bond lengths and angles for **1**, **3**, **4** and **15** are collected in Tables 2−5, respectively.

Results and Discussion

Complexes of the Type [L_{OEt}(COD)RuL]$^{n+}$ (n = 0, 1). The aquo complex [L_{OEt}(COD)Ru(OH_2)]$^+$ was first isolated by Kölle and co-workers by the reaction of [Ru(COD)(OH_2)$_4$]$^{2+}$ with NaL_{OEt}.[6a] We found that L_{OEt}(COD)RuCl (**1**) can be prepared conveniently from NaL_{OEt} and [Ru(COD)Cl_2]$_x$, isolated as air-stable orange crystals. Treatment of **1** with $AgBF_4$ in acetone/H_2O afforded [L_{OEt}(COD)Ru(OH_2)]BF_4 **2** in good yield. Figure 1 shows a perspective view of **1**; selected bond lengths and angles are given in Table 2. The average Ru−O, average Ru−C, and Ru−Cl distances are 2.129, 2.164, and 2.398(3) Å, respectively. The average Ru−C and Ru−O distances in **1** are similar to those for [L_{OEt}(COD)RuOH_2]$^+$.[6a] Complex **2** has proven to be a good starting material for the [L_{OEt}(COD)RuL]-type complexes, the syntheses of which are summarized in Scheme 1.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for L_{OEt}(COD)RuCl (**1**)

Ru(1)−Cl(1)	2.398(3)	Ru(1)−O(1)	2.127(6)
Ru(1)−O(2)	2.130(6)	Ru(1)−O(3)	2.129(6)
Ru(1)−C(18)	2.178(10)	Ru(1)−C(21)	2.154(10)
Ru(1)−C(22)	2.157(9)	Ru(1)−C(25)	2.167(10)
C(18)−C(25)	1.40(1)	C(21)−C(22)	1.37(1)
Cl(1)−Ru(1)−O(1)	160.6(2)	Cl(1)−Ru(1)−O(2)	84.5(2)
Cl(1)−Ru(1)−O(3)	83.9(2)	Cl(1)−Ru(1)−C(18)	116.8(3)
Cl(1)−Ru(1)−C(21)	116.6(3)	Cl(1)−Ru(1)−C(22)	79.8(3)
Cl(1)−Ru(1)−C(25)	79.7(3)	O(1)−Ru(1)−O(2)	82.8(2)
O(1)−Ru(1)−O(3)	82.4(2)	O(1)−Ru(1)−C(18)	76.8(3)
O(1)−Ru(1)−C(21)	77.9(3)	O(1)−Ru(1)−C(22)	114.4(3)
O(1)−Ru(1)−C(25)	114.5(3)	O(2)−Ru(1)−O(3)	93.9(2)
O(2)−Ru(1)−C(18)	158.6(3)	O(2)−Ru(1)−C(21)	89.3(3)
O(2)−Ru(1)−C(22)	88.6(3)	O(2)−Ru(1)−C(25)	162.2(3)
O(3)−Ru(1)−C(18)	158.6(3)	O(3)−Ru(1)−C(21)	159.5(3)
O(3)−Ru(1)−C(22)	163.2(3)	O(3)−Ru(1)−C(25)	162.2(3)
C(18)−Ru(1)−C(21)	80.0(4)	C(18)−Ru(1)−C(22)	93.7(4)
C(18)−Ru(1)−C(25)	37.7(3)	C(21)−Ru(1)−C(22)	37.0(3)
C(21)−Ru(1)−C(25)	90.3(1)	C(22)−Ru(1)−C(25)	80.5(4)

Thus, treatment of **2** with nitrogen or sulfur donor ligands L afforded the respective adducts [L_{OEt}(COD)RuL]$^+$ (L = *t*-$BuNH_2$ (**3**), *p*-$MeC_6H_4NH_2$ (**4**), NH_3 (**5**), N_2H_4 (**6**), pyridine (**7**), 4,4′-bip0y (**8**), MeCN (**9**), Et_2S (**10**), Me_2SO (**11**)) in good yields. For the amine complexes **3**−**6**, two IR N−H bands were found in the 3200−3300 cm^{-1} region. The N−H resonant signals for these complexes were, however, not observed in the ^{1}H NMR spectra. Interaction of **8** with **2** gave the 4,4′-bipy-bridged binuclear complex [{L_{OEt}(COD)Ru}$_2$(μ-4,4′-bipy)]-(BF_4)$_2$ **12**. The ortho pyridyl protons for **12** are magnetically equivalent and so are the meta pyridyl protons, indicating that the 4,4′-bipy coordinates to the two L_{OEt}(COD)Ru fragments symmetrically.

The structures of the *t*-$BuNH_2$ adduct have been established by X-ray crystallography. Figure 2 shows a perspective view

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[L_{OEt}(COD)Ru(NH_2\text{-}t\text{-}Bu)]BF_4$ (**3**)

Ru(1)−O(1)	2.106(5)	Ru(1)−O(4)	2.123(4)
Ru(1)−O(7)	2.117(4)	Ru(1)−N(1)	2.197(6)
Ru(1)−C(18)	2.141(8)	Ru(1)−C(19)	2.171(7)
Ru(1)−C(22)	2.179(7)	Ru(1)−C(23)	2.155(7)
O(1)−Ru(1)−O(4)	84.4(2)	O(1)−Ru(1)−O(7)	85.2(2)
O(1)−Ru(1)−N(1)	157.0(2)	O(1)−Ru(1)−C(22)	112.1(3)
O(1)−Ru(1)−C(19)	114.6(3)	O(1)−Ru(1)−C(22)	112.1(3)
O(1)−Ru(1)−C(23)	75.7(3)	O(4)−Ru(1)−O(7)	88.6(2)
O(4)−Ru(1)−N(1)	77.2(2)	O(4)−Ru(1)−C(18)	161.6(3)
O(4)−Ru(1)−C(19)	160.4(3)	O(4)−Ru(1)−C(22)	88.9(2)
O(4)−Ru(1)−C(23)	92.1(2)	O(7)−Ru(1)−N(1)	83.4(2)
O(7)−Ru(1)−C(18)	90.4(3)	O(7)−Ru(1)−C(19)	97.9(2)
O(7)−Ru(1)−C(22)	164.9(3)	O(7)−Ru(1)−C(23)	157.9(3)
N(1)−Ru(1)−C(18)	120.9(3)	N(1)−Ru(1)−C(19)	85.2(3)
N(1)−Ru(1)−C(22)	81.5(3)	N(1)−Ru(1)−C(23)	118.3(3)
C(18)−Ru(1)−C(19)	37.5(3)	C(18)−Ru(1)−C(22)	96.6(3)
C(18)−Ru(1)−C(23)	82.1(3)	C(19)−Ru(1)−C(22)	80.1(3)
C(19)−Ru(1)−C(23)	88.8(3)	C(22)−Ru(1)−C(23)	37.1(3)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[L_{OEt}(COD)Ru(NH_2C_6H_4Me\text{-}p)]BF_4$ (**4**)

Ru(1)−O(1)	2.094(4)	Ru(1)−O(4)	2.118(4)
Ru(1)−O(7)	2.128(4)	Ru(1)−N(1)	2.174(5)
Ru(1)−C(18)	2.150(7)	Ru(1)−C(19)	2.166(7)
Ru(1)−C(22)	2.169(7)	Ru(1)−C(23)	2.155(7)
O(1)−Ru(1)−O(4)	85.6(2)	O(1)−Ru(1)−O(7)	82.3(2)
O(1)−Ru(1)−N(1)	155.9(2)	O(1)−Ru(1)−C(18)	78.5(2)
O(1)−Ru(1)−C(19)	115.6(3)	O(1)−Ru(1)−C(22)	113.4(2)
O(1)−Ru(1)−C(23)	76.9(2)	O(4)−Ru(1)−O(7)	91.7(2)
O(4)−Ru(1)−N(1)	76.3(2)	O(4)−Ru(1)−C(18)	163.7(2)
O(4)−Ru(1)−C(19)	158.5(3)	O(4)−Ru(1)−C(22)	87.4(2)
O(4)−Ru(1)−C(23)	91.7(2)	O(7)−Ru(1)−N(1)	82.4(2)
O(7)−Ru(1)−C(18)	89.5(2)	O(7)−Ru(1)−C(19)	94.8(2)
O(7)−Ru(1)−C(22)	164.2(2)	O(7)−Ru(1)−C(23)	158.5(2)
N(1)−Ru(1)−C(18)	119.9(2)	N(1)−Ru(1)−C(19)	84.2(3)
N(1)−Ru(1)−C(22)	82.0(3)	N(1)−Ru(1)−C(23)	119.0(3)
C(18)−Ru(1)−C(19)	37.1(3)	C(18)−Ru(1)−C(22)	95.8(3)
C(18)−Ru(1)−C(23)	81.5(3)	C(19)−Ru(1)−C(22)	80.8(3)
C(19)−Ru(1)−C(23)	89.8(3)	C(22)−Ru(1)−C(23)	37.3(3)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $[L_{OEt}(CO)(PPh_3)Ru(OH_2)]BF_4$ (**15**)

Ru(1)−P(4)	2.285(3)	Ru(1)−O(2)	2.091(7)
Ru(1)−O(3)	2.148(8)	Ru(1)−O(4)	2.074(7)
Ru(1)−O(5)	2.133(7)	Ru(1)−C(1)	1.83(1)
P(4)−Ru(1)−O(2)	90.3(2)	P(4)−Ru(1)−O(3)	174.8(3)
P(4)−Ru(1)−O(4)	95.7(2)	P(4)−Ru(1)−O(5)	94.6(2)
P(4)−Ru(1)−C(1)	89.9(4)	O(2)−Ru(1)−O(3)	84.5(3)
O(2)−Ru(1)−O(4)	172.5(3)	O(2)−Ru(1)−O(5)	89.7(3)
O(2)−Ru(1)−C(1)	92.4(5)	O(3)−Ru(1)−O(4)	89.5(3)
O(3)−Ru(1)−O(5)	85.6(3)	O(3)−Ru(1)−C(1)	90.2(5)
O(4)−Ru(1)−O(5)	85.4(3)	O(4)−Ru(1)−C(1)	92.1(5)
O(5)−Ru(1)−C(1)	175.1(5)	Ru(1)−C(1)−O(1)	176(1)

of **3**; selected bond lengths and angles are given in Table 3. The average Ru−O, average Ru−C, and Ru−N distances in **3** are 2.115, 2.162, and 2.197(6) Å, respectively. The Ru−N distance in **3** is slightly shorter than that found for $[(\eta^5\text{-}C_5H_5)\text{-}Ru\{P(OMe)_3\}_2(t\text{-}BuNH_2)]^+$ (2.216(2) Å).[15] The amine ligand is found to be hydrogen bonded to the BF_4 anion with the N(1)···F(3) separation of 3.04(1) Å. The F(3)···H distance and the N(1)−H···F(3) angle were calculated to be 2.18 Å and 144°, respectively. The structure of *p*-toluidine complex **4** has also

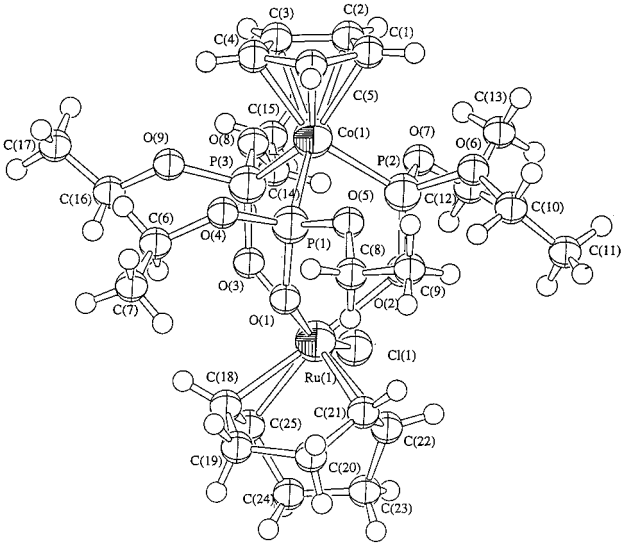

Figure 1. Perspective view of $L_{OEt}(COD)RuCl$ (**1**).

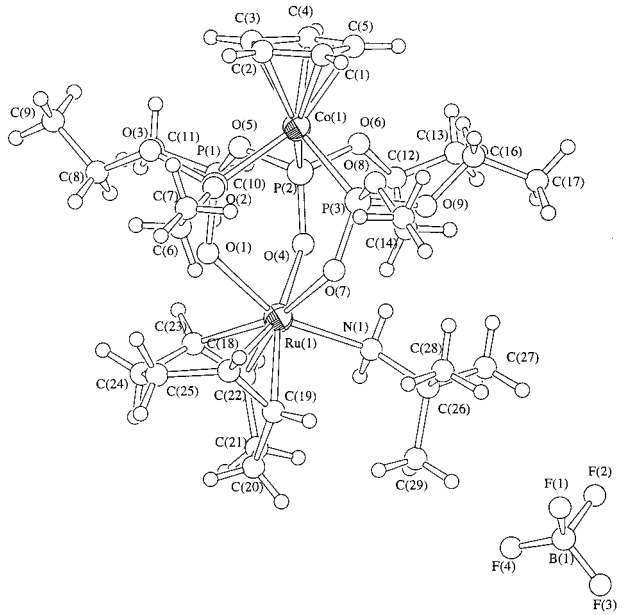

Figure 2. Perspective view of $[L_{OEt}(COD)Ru(t\text{-}BuNH_2)]BF_4$ (**3**).

been determined. Figure 3 shows a perspective view of **4**; selected bond lengths and angles are given in Table 4. The structure of **4** is similar to that for **3** featuring hydrogen bonding between the toluidine ligand and BF_4. The N(1)···F(2) separation is 3.06(9) Å and the F(2)···H distance and N(1)−H···F(2) angle were calculated to be 2.20 Å and 158°, respectively. The average Ru−O, average Ru−C and Ru−N distances in **4** are 2.113, 2.160, and 2.174(5) Å, respectively. The Ru−N distance in **4** is shorter than that in **3** possibly because *p*-tolyl group is less bulky than *tert*-butyl group.

Deprotonation of **2** with NaOH in $MeOH/H_2O$ afforded the hydroxide complex $L_{OEt}(COD)Ru(OH)$ **13**. The formulation of **13** as a neutral hydroxide is in accord with (a) its high solubility in hexane and (b) the absence of the ^{19}F NMR signal for BF_4. It is not clear whether complex **13** is monomeric or dimeric in nature at this point.[16] Complex **13** is stable in the solid state but was found to be moisture sensitive in solutions, in which it is readily protonated to **2**. Reaction of **13** with PhOH in C_6D_6 gave a new species, as evidenced by NMR spectroscopy. The ^1H NMR spectrum of the reaction mixture shows new signals attributable to the phenoxide ligand, which overlap with the

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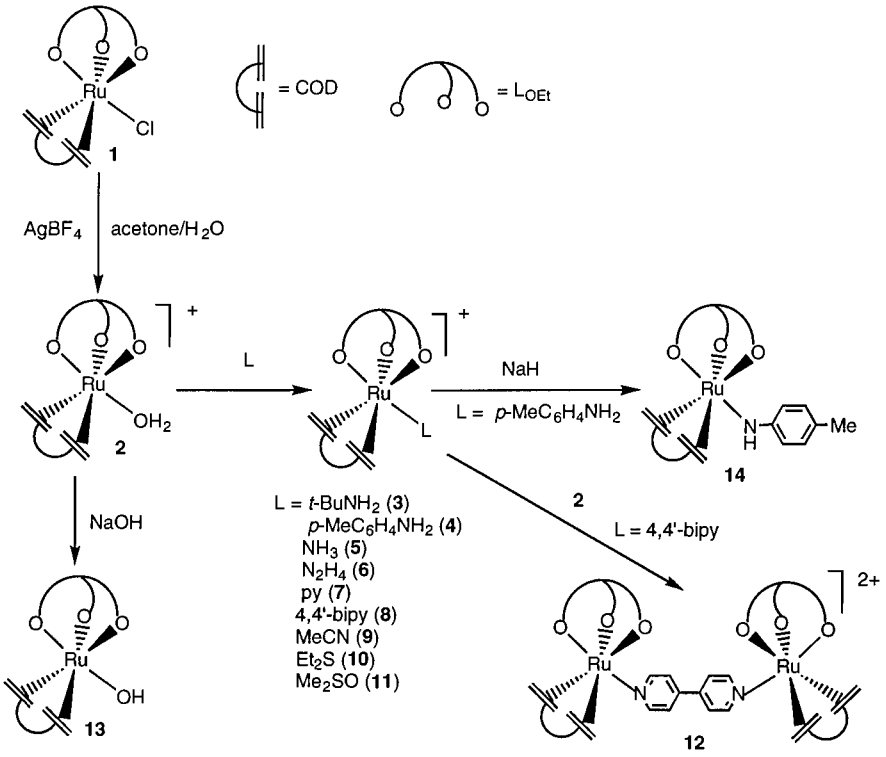
(15) (a) Joslin, F. L.; Johnson, P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 41. (b) Joslin, F. L.; Johnson, P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 2781.

Scheme 1



signals for unreacted phenol, suggestive the formation of the Ru(II) phenoxide L_{OEt}(COD)Ru(OPh). We were, however, unable to exclude the structures based on RuO−H−OPh or RuO−H−OPh.[17] Similarly, treatment of **4** with NaH afforded the *p*-tolyl amide L_{OEt}(COD)Ru(NHC_6H_4Me-*p*) **14**, which is a rare example of mononuclear Ru(II) complex of primary amide.[15,18,19] The IR spectrum of **14** shows one ν(N−H) at 3426 cm^{-1} in contrast to **4**, which exhibits two ν(N−H). Again, the high solubility of **14** in hexane and the absence of BF_4 signal are consistent with the formulation of a neutral amide. Attempts to deprotonate **3** or **5** by NaH were unsuccessful apparently because of the lower acidity of *t*-$BuNH_2$ and NH_3 compared with *p*-$MeC_6H_4NH_2$. Complex **14** reacts with CO_2 to give a brown material, which exhibit an IR band at 1700 cm^{-1}. This may be attributed to the insertion of CO_2 to the Ru-amide bond and the formation of a carbamate.[15] We have yet been able to obtain pure sample of the carbamate for analysis.

Complexes of the Type $[L_{OEt}(CO)(PPh_3)RuL]^{n+}$ (n = 0, 1). Previously we reported the isolation of $[L_{OEt}(CO)(PPh_3)$-$Ru(OH_2)]BF_4$ **15** from the protonation of $L_{OEt}(CO)(PPh_3)$Ru-(CH═CHPh) with HBF_4.[9a] The intermediate η^2-styrene complex could be isolated but was found to be subsitutionally labile presumably because of the competition between the CO and olefin ligands for back-bonding. The structure of **15** has been established by X-ray crystallography and is shown in Figure 4. The Ru−O(aquo), Ru−C, Ru−P, and average Ru−O(L_{OEt}) distances in **15** are 2.091(7), 1.83(1), 2.285(3), and 2.118 Å, respectively. The Ru−O(aquo) distance in **15** is similar to that

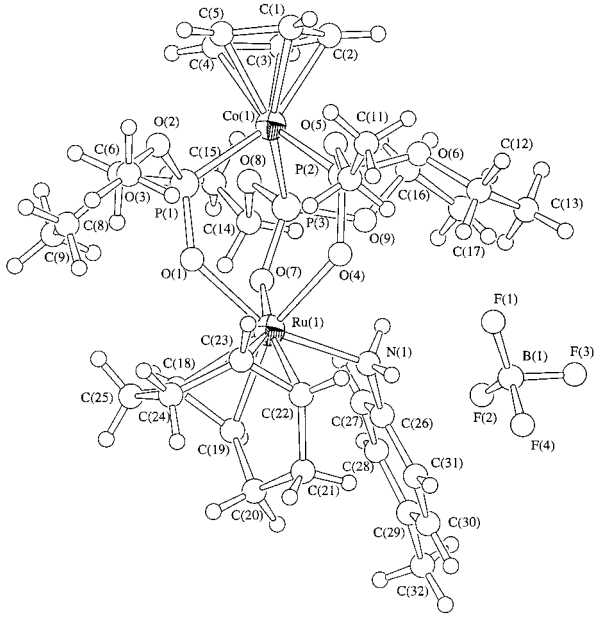


Figure 3. Perspective view of $[L_{OEt}(COD)Ru(p\text{-}MeC_6H_4NH_2)]BF_4$ (**4**).

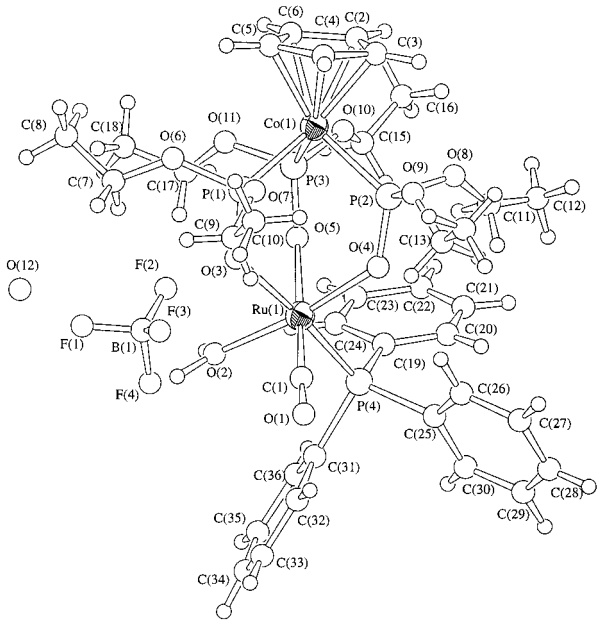


Figure 4. Perspective view of $[L_{OEt}(CO)(PPh_3)Ru(H_2O)]BF_4$ (**15**).

in the COD analogue [LOEt(COD)Ru(H_2O)]$^+$ (2.10(2) Å).[6a] As expected, the aquo ligand binds to Ru(II) in a pyramidal fashion. The Ru−O(3) and Ru−O(5) bonds are considerably longer than the Ru−O(2) bond, which is opposite to the aquo ligand, apparently due to the trans influence of CO and PPh_3, respectively. Hydrogen bonds between the aquo ligand and BF_4 (O(2)···F(3) = 2.66(1) Å) and between the aqua ligand and a water of crystallization (O(2)···O(12) = 2.67(2) Å) were observed. The hydrogen bond distances F(3)···H and O(12)···H were calculated to be 1.69 and 1.96 Å, respectively, while the O(2)−H···F(13) and O(2)−H···O(12) angles are 153 and 128°, respectively. The Ru−P in **15** (2.285(3) Å) is longer than that in $L_{OEt}(PPh_3)_2RuCl$ (average 2.267 Å),[9a] suggesting that the Ru−P in the former is stronger than that in the latter although the latter is more sterically congested. The Ru−P σ bond strength for the two complexes should be comparable given the similar coordination environment around Ru(the phosphines are *trans* to oxygen in both cases). In fact the Ru−P σ bond for **15** is expected to be stronger as the ligands are pulled closer to the metal center due to the positive charge. The fact that the Ru−P bond in the former is longer than that in the latter implies that back-bonding plays a predominant role in the Ru−P bonding in these complexes, consistent with the IR data (see later section). The Ru−P back-bonding in **15** is relatively weak because of the presence of the strong π acid CO.

Like **2**, the aquo ligand in **15** is labile and can be replaced by donor ligands easily. For example, treatment of **15** with *p*-$MeC_6H_4NH_2$, PPh_3, and NaN_3 gave [L_{OEt}(CO)(PPh_3)Ru($NH_2C_6H_4$Me-*p*)]BF_4 (**16**), [$L_{OEt}(PPh_3)_2$Ru(CO)]BF_4 (**17**), L_{OEt}(CO)(PPh_3)RuN_3 (**18**), respectively. Deprotonation of **15** with NaOH afforded the hydroxide L_{OEt}(CO)(PPh_3)Ru(OH) (**19**). The high solubility of **19** in hexane and absence of ^{19}F NMR signal is consistent with its formulation as a neutral Ru(II) hydroxide. In addition, the presence of a strong π-donating OH ligand in **19** is also evidenced by the low value of ν(C≡O) (1922 cm^{-1}) (see later section). Similarly deprotonation of the *p*-toluidine complex **16** with NaH give the amide L_{OEt}(CO)(PPh_3)Ru(NHC_6H_4Me-*p*) **20**, which is soluble in hexane. The ν(C≡O) for **20** of 1922 cm^{-1} is identical to that for **19**, suggestive of the presence of π-donating amide ligand.

Previously we reported that TsN_3 (Ts = tosyl) inserts into the Ru−H of Ru(Et_2dtc)$(PPh_3)_2$(CO)H (Et_2dtc = diethyldithiocarbamate), resulting in the formation of a Ru(II) tosylamide complex.[20] We were therefore interested in the insertion reaction of TsN_3 with the hydride of L_{OEt}Ru. The hydride L_{OEt}(CO)(PPh_3)RuH (**21**) can be prepared by the reaction of Ru(CO)Cl(H)$(PPh_3)_3$ with NaL_{OEt}, isolated as air-stable yellow crystals. The crude product of **21** was found to be contaminated with some PPh_3, which has yet to be separated. The identity of **21** is, however, fully established by NMR, IR and mass spectroscopies. Consistent with the high donor strength of L_{OEt}, the hydride resonant signal for **21** is more upfield (δ −15.63) than that for the cyclopentadienyl analogue (η^5-C_5H_5)(CO)(PPh_3)RuH (δ −11.6).[21] The ν(Ru−H) for **21** of 1966 cm^{-1} is higher than that for (η^5-C_5H_5)(CO)(PPh_3)RuH (1937 cm^{-1})[21] because the hydride in the former is trans to an oxygen while the hydride in the latter is opposite to a carbon ligand, which has a strong trans influence. Upon addition of triflic acid to **21** in $CDCl_3$, the hydride signal vanishes immediately presumably due to protonation of hydride to H_2, which subsequently dissociates from the complex. Attempts to isolate the η^2-dihydrogen intermediate were unsuccessful. Treatment of **21** with TsN_3 afforded the tosylamide complex L_{OEt}(CO)(PPh_3)Ru(NHTs) (**22**), which was characterized by NMR spectroscopy. An analytically pure sample of **22** could not be obtained due to contamination with *N*-tosyl triphenylphosphinimine Ph_3P=NTs, which apparently was formed by the reaction of TsN_3 with the PPh_3 impurity of the starting material. No reactions between **21** and terminal acetylenes such as phenylacetylene were observed.

Table 6. IR CO Stretching Frequencies for [L_{OEt}(CO)(PPh_3)RuL]$^{n+}$

L	*n*	ν(C≡O)/cm^{-1}
H	0	1908
PhCH=CH	0	1918
OH	0	1922
p-MeC_6H_4NH	0	1922
N_3	0	1931
TsNH	0	1942
p-$MeC_6H_4NH_2$	1	1950
H_2O	1	1954
PPh_3	1	1954
$PhCH=CH_2$	1	1978

The ν(C≡O) serves as a good spectroscopic marker to indicate the availability of electrons in [L_{OEt}(CO)(PPh_3)RuX]$^{n+}$ (n = 0, 1). In general, a good donor ligand X will result in strong back-bonding and thus a downshift in ν(CO). The C−O stretching frequencies for the carbonyl complexes are summarized in Table 6. As expected the cationic complexes have lower values of ν(C≡O) than the neutral species. On the basis of ν(C≡O), the donor strength of anionic X decreases in the order H > PhCH=CH > *p*-MeC_6H_4NH ~ OH > TsNH > N_3. The strong σ-donating hydride was found to top the series and is followed by vinyl, hydroxide and amide. Tosyl amide is a weaker donor than *p*-tolylamide due to the presence of the electron-withdrawing tosyl group. For the [LOEt(CO)(PPh_3)RuL]$^+$ series, the ν(CO) increases in the order X = *p*-$MeC_6H_4NH_2$ > H_2O ~ PPh_3 > $PhCH=CH_2$, which roughly parallels the order of π acidity of X. It is surprising that the ν(CO) for [L_{OEt}(CO)(PPh_3)Ru(OH_2)]$^+$ and [$L_{OEt}(PPh_3)_2$Ru(CO)]$^+$ were found to be identical, in light of the higher Lewis basicity of PPh_3. This may be rationalized by the fact that the increase in electron density by P−Ru σ donation is offset by the Ru−P back-bonding. Styrene is such a strong π acid that [L_{OEt}(CO)(PPh_3)Ru(η^2-styrene)]$^+$ is unstable with dissociation in solution.[9a]

Complexes of the Type [$L_{OEt}(PPh_3)_2$RuL]$^+$. Previously we reported that dissolution of $L_{OEt}(PPh_3)_2$RuCl in THF/MeOH (1:1) in the presence of NH_4PF_6 led to chloride dissociation and the resulting cation [$L_{OEt}(PPh_3)_2$Ru(solvent)]$^+$ has a high affinity for unsaturated hydrocarbyl ligands such as carbene, vinylidene, and allenylidene.[9] Although the reaction was carried out under nitrogen, there is no evidence for the formation of the Ru(II) dinitrogen complex. Treatment of [$L_{OEt}(PPh_3)_2$Ru(solvent)]$^+$ with π acid ligands L′ affords the respective adducts [$L_{OEt}(PPh_3)_2$RuL′]$^+$ (L′ = *t*-BuNC (**23**), CNpy (**24**), Me_2SO (**25**), SO_2 (**26**)), isolated as their PF_6 salts. The ν(C≡N) for [$L_{OEt}(PPh_3)_2$Ru(CNpy)]$^+$ (2214 cm^{-1}) is lower than that for free CNpy (2242 cm^{-1}), indicating that Ru coordinates to CNpy via the CN group. Ru binds to the cyano instead of pyridyl nitrogen of CNpy

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Table 7. Formal Potential ($E°$) for $L_{OEt}Ru$ Complexes

complex	$E°$(V vs $Cp_2Fe^{+/0}$) oxidation	reduction
$[L_{OEt}(COD)Ru(t\text{-}BuNH_2)]BF_4$	0.69	
$[L_{OEt}(COD)Ru(NH_3)]BF_4$	0.67	
$[L_{OEt}(COD)Ru(N_2H_4)]BF_4$	0.72[b]	
$[L_{OEt}(COD)Ru(OH_2)]BF_4$	0.73	
$[L_{OEt}(COD)Ru(py)]BF_4$	0.76	
$[L_{OEt}(COD)Ru(MeCN)]BF_4$	0.79	
$[L_{OEt}(COD)Ru(SEt_2)]BF_4$	0.81	
$[L_{OEt}(COD)Ru(p\text{-}MeC_6H_4NH_2)]BF_4$	0.83	
$[L_{OEt}(COD)Ru(Me_2SO)]BF_4$	0.98	
$[L_{OEt}(COD)Ru(4,4'\text{-bipy})Ru(COD)L_{OEt}]^{2+}$	0.76	
$L_{OEt}(COD)Ru(NHC_6H_4Me\text{-}p)$		−0.59
$L_{OEt}(COD)RuCl$	0.31	
$[L_{OEt}(PPh_3)_2Ru(CO)]BF_4$	0.75[b]	
$L_{OEt}(CO)(PPh_3)Ru(OH_2)]BF_4$	0.79	
$[L_{OEt}(CO)(PPh_3)Ru(p\text{-}MeC_6H_4NH_2)]BF_4$	0.99	
$L_{OEt}(CO)(PPh_3)Ru(NHC_6H_4Me\text{-}p)$		−0.76
$L_{OEt}(CO)(PPh_3)Ru(CH{=}CHPh)$		−0.02
$L_{OEt}(CO)(PPh_3)RuN_3$	0.20	
$[L_{OEt}(PPh_3)_2Ru{=}C(OMe)Me]BF_4$	0.58[c]	
$[L_{OEt}(PPh_3)_2Ru{=}C{=}CMePh]BF_4$	0.64[c]	
$[L_{OEt}(PPh_3)_2Ru(CNpy)]^+$	0.66	
$[L_{OEt}(PPh_3)_2Ru(t\text{-}BuNC)]^+$	0.81	
$[L_{OEt}(PPh_3)_2Ru(Me_2SO)]^+$	0.82	

[a] Potential measured in CH_2Cl_2 with 0.1 M $[n\text{-}Bu_4N]PF_6$ as supporting electrolyte; scan rate = 100 mV s^{-1}. [b] Irreversible. [c] Reference 9b.

probably because the former is the stronger π acceptor. Similarly the Me_2SO ligand in **25** is expected to be S-bound, consistent with the electrochemical data (see later section). Sulfur dioxide is known to be a strong π acid that binds to electron-rich metal centers via the sulfur atom.[22] Indeed $[L_{OEt}(PPh_3)_2Ru(solvent)]^+$ reacts with SO_2 almost instantly to give the SO_2 adduct $[L_{OEt}(PPh_3)_2Ru(SO_2)]^+$ (**26**). The $\nu(S{=}O)_{as}$ for **26** was found at 1292 cm^{-1}, in accord with the η^1, S-bound coordination mode of SO_2.[21] Attempts to isolate olefin complexes of $L_{OEt}Ru$ by reacting $[L_{OEt}(PPh_3)_2Ru(solvent)]^+$ with olefins such as styrene were unsuccessful.

Electrochemistry. The formal potentials ($E°$) for the L_{OEt}-Ru complexes in CH_2Cl_2 have been determined by cyclic voltammetry and are collected in Table 7. The cyclic voltammograms for most of the RuL_{OEt} complexes exhibit reversible oxidation couples assignable to the metal-centered Ru(III/II) couples. The Ru(III/II) potential for $L_{OEt}(COD)RuCl$ of 0.31 V vs $Cp_2Fe^{+/0}$ is more positive than that for $L_{OEt}(PPh_3)_2RuCl$ (0.02 V),[9] indicating that in this coordination environment the π acidity for COD is higher than that for two PPh_3. For cationic $[L_{OEt}(COD)RuL]^+$, the Ru(III/II) potential was found to decrease in the order L = t-$BuNH_2 \sim NH_3 > OH_2 >$ py > MeCN > $Et_2S > p$-$MeC_6H_4NH_2 > Me_2SO$. It appears that $E°$[Ru(III/II)] decreases as the Lewis basicity of L increases but increases as the π acidity of L increases. However, a consistent correlation between the $E°$[Ru(III/II)] and ligand donor strength for the series of compounds cannot be made because the $E°$ depends on a lot of factors other than the donor/acceptor strengths of ligand, as noted by Lever and co-workers.[23] The high $E°$ value for the Me_2SO complex suggests that the Me_2SO ligand is S-bound so that the Ru(II) state is stabilized by Ru-to-S back-bonding. Unlike **5**, the oxidation of **6** is irreversible possibly because an irreversible chemical change occurs in the hydrazine ligand upon oxidation.[24] The Ru(III/II) potential for dimeric **12** is almost identical with that for monomeric **8**, suggesting that there is no electronic communication between the two Ru in **12**. The Ru(III/II) couple for the amide **14** occurs at a negative potential (−0.59 V), demonstrating that the Ru(III) state is strongly stabilized by the π-donating amide ligand. Attempts to oxidize **14** in air led to isolation of **4** instead of the Ru(III) amide presumably because the amide ligand is so basic that protonation of **14** is more facile than its redox reaction.

The Ru(III/II) potentials for $[L_{OEt}(CO)(PPh_3)RuL]^+$ are similar to those for the COD analogues, suggesting that the donor/acceptor properties for COD and $(CO)(PPh_3)$ is comparable. For neutral $L_{OEt}(CO)(PPh_3)RuX$, the Ru(III/II) potential decreases in the order X = N_3 > PhCH=CH > p-MeC_6H_4NH. This indicates that the amide is a better donor than the vinyl, which is in contrast to the order obtained on the basis of $\nu(C{\equiv}O)$ (see earlier section). The discrepancy can be accounted for by the fact that the $\nu(C{\equiv}O)$ is solely dependent on the availability of electrons in the complex in the Ru(II) state while the Ru(III/II) potential measures the relative thermodynamic stability of the Ru(II) and Ru(III) states. It appears that the amide ligand is not a good donor for Ru(II) particularly when the amide is cis rather than trans to the carbonyl.[19] On the other hand, Ru(III) is a good acceptor and is strongly stabilized by the amide via $p\pi(N){-}d\pi(Ru)$ interaction.

For the $[L_{OEt}(PPh_3)_2RuL']^+$ complexes, the Ru(III/II) potential decreases in the order: L′ = $Me_2SO > t$-BuNC > CNpy. The Ru(III/II) potentials are high and positive, suggesting that the Ru(II) state for these complexes are strongly stabilized by Ru-to-L′ back-bonding. The Ru(III/II) oxidation for the carbene and allenylidene complexes occurs at similar potentials,[9b] indicating that the carbene and allenylidene should also be good π acceptors. The S-bound SO_2 is such a strong π acid ligand that no oxidation was found for **26** in the observed potential range (−2.00 to 1.2 V).

Summary. We have demonstrated that the $L_{OEt}Ru$ moiety is capable of stabilizing a variety of ligands, depending on the nature of ancillary ligands. The electron-rich $L_{OEt}(PPh_3)_2Ru$ fragment is a good π donor and normally forms stable complexes with π acid ligands. On the other hand, both L_{OEt}-(COD)Ru and $L_{OEt}(CO)(PPh_3)Ru$ fragments are good σ acceptors and have high affinities for N and S donor ligands. Unusual mononuclear amide and hydroxide complexes of Ru(II) can also be stabilized by L_{OEt}. The availability of electrons in the L_{OEt}-Ru complexes for metal-to-ligand back-bonding can be accessed by their IR C≡O stretching frequencies and the Ru(III/II) reduction potentials.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1**, **3**, **4**, and **15** are available on the Internet only. Access information is given on any current masthead page.

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