Ultraviolet spectra were obtained for CH_3CN solutions on a Perkin-Elmer 330 spectrophotometer.

Cyclic voltammograms were recorded with a BAS CV-27 voltammograph and a Houston Instruments Model 100 X-Y recorder. A three-electrode system was employed, consisting of a platinum-button working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. The reference electrode was separated from the bulk of the solution by a cracked-glass bridge filled with 0.1 M TBAP in acetonitrile. Deaeration of all solutions was performed by passing high-purity nitrogen over the solution while measurements were made. Reagent grade acetonitrile was distilled twice from P_2O_5 under nitrogen. The supporting electrolyte, tetra-*n*-butylammonium perchlorate (TBAP), was recrystallized from EtOAc/hexane, dried, and stored in a desiccator. Half-wave potentials were calculated as an average of the cathodic and anodic peak potentials.[20]

The preparation of the ligands has been previously reported.[10] *cis*-$Ru(bpy)_2Cl_2{\cdot}2H_2O$ was prepared according to a procedure described by Meyer and co-workers,[11] and the deuterio analogue, *cis*-$Ru(bpy\text{-}d_8)_2Cl_2{\cdot}2H_2O$, was prepared as described earlier.[14]

Preparation of RuL_3^{2+} Complexes. A mixture of 1 equiv of ruthenium(III) chloride trihydrate (Aldrich) and 4.0 equiv of the appropriate ligand L in ethanol/H_2O (1:1) was refluxed under nitrogen for 15 h. The mixture was cooled and treated with 2.2 equiv of NH_4PF_6 dissolved in a minimum amount of H_2O. The resulting precipitate was collected, dried, and chromatographed on alumina, with CH_3CN or CH_3CN/toluene (3:2) as eluent. The complex crystallized from the eluent upon standing. Yields and elemental analyses are summarized in Table V.

Preparation of $Ru(bpy)_2L^{2+}$ Complexes. The same procedure was followed as outlined above for RuL_3^{2+}, using *cis*-$Ru(bpy)_2Cl_2{\cdot}2H_2O$ or *cis*-$Ru(bpy\text{-}d_8)_2Cl_2{\cdot}2H_2O$ and the ligand L in a molar ratio of 1:1.1. Yields and combustion analyses are summarized in Table V.

Acknowledgment. We are grateful to the Robert A. Welch Foundation and the National Science Foundation (Grant CHE-8607935) for financial support of this work. The NMR spectrometer was partially funded by the NSF (Grant CHE-8616352). V.G. thanks Elf Aquitaine and the French Ministry of Foreign Affaires for a Bourse Lavoiser.

Supplementary Material Available: Table VI, giving ^1H NMR chemical shift assignments for ruthenium(II) complexes (1 page). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Novel (Cyclopentadienyl)nitroruthenium Complexes

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Ruthenium complexes of the type $[Ru(Cp)(L)_2(NO_2)]$ ($Cp = \eta^5\text{-}C_5H_5$; L = PPh_3 (triphenylphosphine), $^1/_2$ dppe (1,2-bis(diphenylphosphino)ethane), $^1/_2$ dppm (bis(diphenylphosphino)methane), $^1/_2$ dmpe (1,2-bis(dimethylphosphino)ethane)) were synthesized in three-step syntheses starting with $RuCl_3{\cdot}3H_2O$. The $[Ru(Cp)(L)_2(NO)](PF_6)_2$ complexes were then synthesized by reaction of $[Ru(Cp)(L)_2(NO_2)]$ with HPF_6. Characterization of these complexes was accomplished through UV-vis, ^1H NMR, and IR spectroscopies, cyclic voltammetry, and elemental analysis. The $[Ru(Cp)(dppe)(NO)](PF_6)_2$ complex displays two reversible one-electron electrochemical reductions in the absence of atmospheric oxygen.

Introduction

The coordination chemistry of (η^5-cyclopentadienyl)ruthenium complexes has been widely studied for the past 20 years.[1-3] While a large number of half-sandwich (cyclopentadienyl)ruthenium complexes have been reported, the majority of these complexes contain carbonyl ligands.[1-5] There has been a limited amount of research reported regarding (cyclopentadienyl)ruthenium complexes that do not contain carbonyl ligands, namely complexes of the type $[Ru(Cp)(L)_2(X)]^n$ (where $Cp = \eta^5\text{-}C_5H_5$, L = phosphine ligand, and X = anionic ligand ($n = 0$) or neutral ligand ($n = 1+$)).[6-11]

There are several examples of (cyclopentadienyl)nitrosylruthenium complexes.[9,12-15] Insertion of nitrosyl ligands into the coordination sphere of (pentamethylcyclopentadienyl)ruthenium has been under investigation by Bergman and co-workers, where they have reported the synthesis of a number of neutral complexes such as $[Ru(\eta^5\text{-}C_5Me_5)(NO)(PMe_3)]$ and $[Ru(\eta^5\text{-}C_5Me_5)(dmpe)(NO)]$.[12,13] In addition, the synthesis of the complex $[Ru(\eta^5\text{-}C_5H_5)(NO)(PMe_3)_2](PF_6)_2$ has been reported separately by Bruce and White[14] and Treichel.[9] Bruce and White attempted the synthesis of $[Ru(\eta^5\text{-}C_5H_5)(NO)(PPh_3)_2](PF_6)_2$ but found it to be unstable in the solid state.[14] With this paper we wish to report that this complex, as well as other (cyclopentadienyl)nitrosylruthenium complexes, is synthetically attainable and is stable in solution as well as in the solid state.

In addition to the synthesis and characterization of the $[Ru(Cp)(L)_2(NO)](PF_6)_2$ complexes, we also wish to report the synthesis and characterization of $[Ru(Cp)(L)_2(NO_2)]$ (L = PPh_3,

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$^1/_2$ dppe, $^1/_2$ dppm, $^1/_2$ dmpe) complexes. While a variety of anionic ligands have been coordinated to (cyclopentadienyl)bis(phosphine)ruthenium complexes,[7,9,11] this is the first time that the synthesis of any (cyclopentadienyl)bis(phosphine)nitroruthenium complex has been reported.

Experimental section

Materials. $RuCl_3\cdot 3H_2O$ was purchased from Johnson Matthey Inc. Dicyclopentadiene and HPF_6 (60% aqueous solution by weight) were purchased from Aldrich Chemical Co. Phosphine ligands were purchased from Aldrich Chemical Co. or Strem Chemicals. $NaNO_2$ was purchased from Fisher Scientific and $Na^{15}NO_2$, 99% pure, was purchased from Cambridge Isotope Laboratories. All of the above compounds, along with solvents and other materials, were of reagent quality and were used without further purification.

Measurements. Elemental analyses were performed by Atlantic Microlabs (Norcross, GA). Infrared spectra were recorded with a Perkin-Elmer 1430 ratio-recording infrared spectrophotometer, using Nujol mulls on NaCl plates, or on a Mattson Cygnus 100 FT-infrared spectrophotometer equipped with a Hewlett Packard HP 7475A plotter, using diffuse-reflectance techniques, with the sample distributed in powdered CsI. UV–visible electronic spectra were obtained on a Bausch and Lomb Spectronic 2000 spectrophotometer equipped with a Houston Instruments Model 200 recorder or on a Milton Roy Spectronic 3000 array spectrophotometer.

Cyclic voltammetric and coulometric measurements were obtained with either an IBM EC/225 voltammetric analyzer, or with a Pine Instrument Co. Model RDE 4 potentiostat, and the current–potential waves were recorded with a Houston Instruments Model 100 recorder. The cyclic voltammetric experiments were performed in a three-electrode, one-compartment cell equipped with a platinum working electrode (Bioanalytical Systems), a platinum auxiliary electrode, and a saturated sodium chloride calomel (SSCE) or a silver-wire reference electrode. Electrochemical measurements in CH_2Cl_2 used 0.1 M tetra-*n*-butylammonium tetrafluoroborate (Bu_4NBF_4) as the supporting electrolyte, while measurements in CH_3CN used 0.1 M tetraethylammonium perchlorate (TEAP) or 0.1 M tetraethylammonium tetrafluoroborate (Et_4NBF_4) as the supporting electrolyte. Coulometric measurements were performed in a two-compartment cell separated by a glass frit, with a platinum-gauze working electrode and either a Ag/Ag^+ (0.01 M $AgNO_3$/0.2 M Et_4NBF_4 in acetonitrile) reference electrode separated from the cell by a Vycor tip or a silver-wire reference electrode in one compartment and a platinum auxiliary electrode in the other. The reduction of $[Ru(Cp)(dppe)(NO)]^{2+}$ to $[Ru(Cp)(dppe)(NO)]^+$ was conducted under an atmosphere of nitrogen and utilized a silver-wire reference electrode, while the reduction of $[Ru(Cp)(dppe)(NO)]^{2+}$ to $[Ru(Cp)(dppe)(NO)]$ was conducted in an inert-atmosphere glovebox and utilized a Ag/Ag^+ reference electrode. Coulometric measurements were conducted in a 0.2 M Et_4NBF_4 solution in acetonitrile, and an Electrosynthesis Co., Inc. digital coulometer, Model No. 630, was used to measure coulombs.

^1H NMR spectra were recorded on either a Varian EM390 NMR spectrometer or a Varian Gemini 300-MHz Fourier transform NMR spectrometer. Chemical shifts are reported in units of parts per million (ppm, δ) downfield from tetramethylsilane, and splitting patterns are abbreviated by using s for singlet, t for triplet, and m for multiplet. Chloroform-*d* ($CDCl_3$) acetonitrile-d_3 (CD_3CN), dichloromethane-d_2 (CD_2Cl_2), and tetramethylsilane were purchased from Aldrich Chemical Co. and used as received.

The [Ru(Cl)(Cp)(dmpe)] and $[Ru(Cp)(dmpe)(NO_2)]$ complexes were found to be air sensitive in solution; therefore, syntheses and cyclic voltammetric measurements involving these complexes were conducted either in an inert-atmosphere glovebox (argon atmosphere) or under nitrogen. The cyclic voltammetric measurements conducted in the glovebox utilized a silver-wire reference electrode, and the peak potentials were adjusted to be the potential vs SSCE. The solutions used to measure the electronic absorption spectra of [Ru(Cl)(Cp)(dmpe)], $[Ru(Cp)(dmpe)(NO_2)]$, and $[Ru(Cp)(dmpe)(NO)](PF_6)_2$ were prepared in the inert-atmosphere glovebox, and the spectra were measured immediately after bringing the cuvettes out of the glovebox.

Syntheses. The complexes $[Ru(Cl)(Cp)(PPh_3)_2]$,[16] [Ru(Cl)(Cp)(dppe)],[11] and [Ru(Cl)(Cp)(dppm)][11] were synthesized by following published procedures.

[Ru(Cl)(Cp)(dmpe)] (Cp = Cyclopentadienyl, dmpe = 1,2-Bis(dimethylphosphino)ethane) (1). In a glovebox, a 0.255-g (0.35-mmol) sample of $[Ru(Cl)(Cp)(PPh_3)_2]$ was combined with 0.107 g (2 equiv) of dmpe in 50 mL of toluene. The solution was heated at reflux for 16.5 h, after which time the solution was allowed to cool to room temperature and then was stirred for an additional 7 h. The cloudy solution was filtered, yielding a small amount of yellow precipitate. The filtrate was reduced to dryness under vacuum, the residue was dissolved in a minimal amount of CH_2Cl_2, and hexanes were then added slowly to induce precipitation. The precipitate was collected by vacuum filtration and combined with the first fraction. Yield: 0.083 g (67%). ^1H NMR ($CDCl_3$): δ 1.6 (m, 16 H), 4.5 (s, 5 H). Anal. Calcd for $C_{11}H_{21}ClP_2Ru$: C, 37.56; H, 6.02. Found: C, 37.72; H, 6.07.

$[Ru(Cp)(^{14}NO_2)(PPh_3)_2]$ (2). A 1.002-g (1.38-mmol) sample of $[Ru(Cl)(Cp)(PPh_3)_2]$ and 0.963 g (10 equiv) of $NaNO_2$ were combined in 500 mL of a 1:1 95% $EtOH/H_2O$ (v/v) solution. The mixture was heated at reflux under N_2 for 4 h, after which time a gold-colored precipitate formed. The precipitate was collected by vacuum filtration, and the isolated solid was purified by column chromatography on a deactivated alumina column (1.0 mL of H_2O/10 mL alumina), eluting with a 30:70 acetonitrile/toluene (v/v) mixture. The yellow band was collected and the solvent removed by rotary evaporation at room temperature. The residue was then dissolved in CH_2Cl_2 and added to hexanes to induce precipitation. The solid was collected by vacuum filtration, washed with hexanes, and air-dried. Yield: 0.648 g (64%). ^1H NMR ($CDCl_3$): δ 4.3 (s, 5 H), 7.2 (m, 30 H). Anal. Calcd for $C_{41}H_{35}NO_2P_2Ru\cdot 0.5H_2O$: C, 66.03; H, 4.86. Found: C, 66.14; H, 4.75.

$[Ru(Cp)(^{15}NO_2)(PPh_3)_2]$ (2a). This complex was synthesized in the same manner as **2**, except that $Na^{15}NO_2$ was used instead of $Na^{14}NO_2$.

$[Ru(Cp)(dppe)(NO_2)]$ (dppe = 1,2-Bis(diphenylphosphino)ethane) (3). A 0.203-g (0.34-mmol) sample of [Ru(Cl)(Cp)(dppe)] was added along with 0.306 g (13 equiv) of $NaNO_2$ to 100 mL of 1:1 95% $EtOH/H_2O$ (v/v) solution. The solution was degassed with N_2 and heated at reflux for 3 h. The precipitate was collected by vacuum filtration and purified by using column chromatography. The sample was passed through a deactivated alumina column (0.5 mL of H_2O/10 mL of alumina), eluting with a 30:70 acetonitrile/toluene (v/v) mixture. The light yellow band was collected, and the eluant was concentrated by using a rotary evaporator, resulting in the precipitation of the product, which was collected by vacuum filtration and air-dried. Yield: 0.131 g (63%). ^1H NMR ($CDCl_3$): δ 2.8 (m, 4 H), 4.5 (s, 5 H), 7.2 and 7.8 (m, 20 H). Anal. Calcd for $C_{31}H_{29}NO_2P_2Ru\cdot 0.75C_6H_5CH_3$: C, 64.05; H, 5.19. Found: C, 63.92; H, 5.12.

$[Ru(Cp)(dppm)(NO_2)]$ (dppm = Bis(diphenylphosphino)methane) (4). A 0.182-g (0.31-mmol) sample of [Ru(Cl)(Cp)(dppm)] was added with 0.224 g (10 equiv) of $NaNO_2$ to 42 mL of a 1:1 95% $EtOH/H_2O$ (v/v) solution. The solution was heated at reflux under N_2 for 40 min and allowed to cool to room temperature. The product, a bright yellow solid, was collected by vacuum filtration. Yield: 0.153 g (83%). ^1H NMR ($CDCl_3$): δ 4.8 (s, 5 H), 5.0 (t, 2 H), 7.3 and 7.7 (m, 20 H). Anal. Calcd for $C_{30}H_{27}NO_2P_2Ru$: C, 60.40; H, 4.56. Found: C, 60.13; H, 4.61.

$[Ru(Cp)(dmpe)(NO_2)]$ (dmpe = 1,2-Bis(dimethylphosphino)ethane) (5). In a glovebox, a 0.243-g (0.34-mmol) sample of $[Ru(Cp)(NO_2)(PPh_3)_2]$ was added with 0.185 g (3.7 equiv) of dmpe to 100 mL of toluene. The solution was heated at reflux for 17.5 h, after which time the solution was allowed to cool and was filtered to remove a small amount of green solid impurity. The solvent was removed from the filtrate under vacuum, and the residue was dissolved in the minimum amount of CH_2Cl_2. The solution was then added to 15 mL of hexanes to precipitate the product. This product was purified by eluting it through an activated alumina column with acetonitrile as the eluant, and the solvent was removed from the eluant under vacuum. The residue was dissolved in a minimal amount of methylene chloride and added to hexanes to precipitate the product. Yield: 0.044 g (37%). ^1H NMR ($CDCl_3$): δ 1.5 and 2.0 (m, 16 H), 4.7 (s, 5 H). Anal. Calcd for $C_{11}H_{21}NO_2P_2Ru$: C, 36.47; H, 5.84. Found: C, 36.57; H, 5.87.

$[Ru(Cp)(NO)(PPh_3)_2](PF_6)_2$ (6). A 0.053-g (0.07-mmol) sample of $[Ru(Cp)(NO_2)(PPh_3)_2]$ was dissolved in 10 mL of MeOH, the solution was filtered, and ~0.5 mL of HPF_6 was added. The solution was then chilled and the product collected by vacuum filtration. Yield: 0.059 g (82%). ^1H NMR (CD_2Cl_2): δ 6.0 (s, 5 H), 7.0 and 7.4 (m, 30 H). Anal. Calcd for $C_{41}H_{35}F_{12}NOP_4Ru$: C, 48.72; H, 3.49. Found: C, 48.43; H, 3.51.

$[Ru(Cp)(dppe)(NO)](PF_6)_2$ (dppe = 1,2-Bis(diphenylphosphino)ethane) (7). A 0.100-g (0.16-mmol) sample of $[Ru(Cp)(dppe)(NO_2)]$ was dissolved in 12 mL of MeOH, the solution was filtered and chilled in an ice bath, and ~2 mL of HPF_6 was added. The product was collected by vacuum filtration and washed with cold MeOH. Yield: 0.134 g (93%). ^1H NMR (CD_3CN): δ 3.5 (m, 4 H), 5.9 (s, 5 H), 7.6 (m, 20 H). Anal. Calcd for $C_{31}H_{29}F_{12}NOP_4Ru\cdot H_2O$: C, 41.25; H, 3.46. Found: C, 41.20; H, 3.37.

$[Ru(Cp)(dppm)(NO)](PF_6)_2$ (dppm = Bis(diphenylphosphino)methane) (8). A 0.062-g (0.10-mmol) sample of $[Ru(Cp)(dppm)(NO_2)]$

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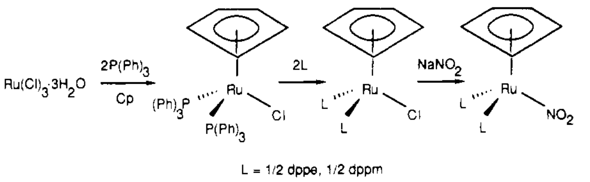
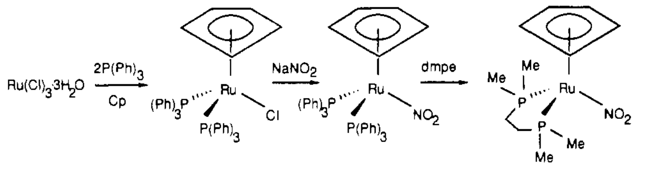
Scheme I



Scheme II



was dissolved in 7 mL of cold MeOH, the solution was filtered, and ~1 mL of HPF_6 was added in stirring, while the solution was chilled with an ice bath. The light yellow precipitate was collected by vacuum filtration and washed with 3 mL of cold MeOH. Yield: 0.075 g (82%). ^1H NMR (CD_3CN): δ 5.7 (t, 2 H), 6.0 (s, 5 H), 7.6 (m, 20 H). Anal. Calcd for $C_{30}H_{27}F_{12}NOP_4Ru$: C, 41.39; H, 3.13. Found: C, 41.49; H, 3.15.

[Ru(Cp)(dmpe)(NO)](PF_6)$_2$ (dmpe = 1,2-Bis(dimethylphosphino)ethane) (9). In the glovebox, a 0.061-g (0.17-mmol) sample of [Ru(Cp)(dmpe)(NO_2)] was dissolved in 15 mL of MeOH. The solution was then brought out of the glovebox and chilled in an ice bath, and ~1 mL of HPF_6 was added. The product, which was light yellow and air stable, was collected by vacuum filtration and washed with cold MeOH. Yield: 0.101 g (94%). ^1H NMR (CD_3CN): δ 2.0 and 2.5 (m, 16 H), 6.1 (s, 5 H). Anal. Calcd for $C_{11}H_{21}F_{12}NOP_4Ru$: C, 20.76; H, 3.33. Found: C, 20.84; H, 3.33.

Results and Discussion

Syntheses. The general reaction scheme for the synthesis of the [Ru(Cp)(L)$_2$(NO_2)] (where L = $^1/_2$ dppe, $^1/_2$ dppm) complexes can be seen in Scheme I. Initially, Ru(Cl)$_3$·3H_2O was reacted with freshly cracked dicyclopentadiene and triphenylphosphine to form [Ru(Cl)(Cp)(PPh_3)$_2$].[16] The [Ru(Cl)(Cp)(L)$_2$] complex was then formed by substituting a bidentate phosphine ligand for the two triphenylphosphine ligands.[11] Finally, the [Ru(Cp)(L)$_2$(NO_2)] complex was synthesized by reacting the corresponding [Ru(Cl)(Cp)(L)$_2$] complex with an excess of $NaNO_2$.

When [Ru(Cl)(Cp)(dmpe)] was reacted with excess $NaNO_2$, the solution turned black and it was necessary to remove all of the solvent to obtain any product. A cyclic voltammogram of this solid revealed that it contained a mixture of products. Therefore, the nitroruthenium complex, [Ru(Cp)(dmpe)(NO_2)] (**5**), had to be prepared by an alternate synthetic route (Scheme II). The first step in this synthesis involved the reaction of Ru(Cl)$_3$·3H_2O with cyclopentadiene and triphenylphosphine to form [Ru(Cl)(Cp)(PPh_3)$_2$]. The second step describes the substitution of the chloride ligand of [Ru(Cl)(Cp)(PPh_3)$_2$] for a nitro ligand, resulting in [Ru(Cp)(NO_2)(PPh_3)$_2$]. In the third step, the [Ru(Cp)(NO_2)(PPh_3)$_2$] complex was reacted with dmpe to produce [Ru(Cp)(dmpe)(NO_2)]. All of the [Ru(Cp)(L)$_2$(NO)](PF_6)$_2$ complexes were synthesized by reacting the [Ru(Cp)(L)$_2$(NO_2)] complex with HPF_6 in methanol.

IR Spectra. Table I lists infrared data concerning the nitro- and nitrosyl(cyclopentadienyl)ruthenium complexes. Infrared spectroscopy was used to determine how the nitro ligand was coordinated to the ruthenium center. Initially, through a comparison of the infrared spectra of [Ru(Cl)(Cp)(PPh_3)$_2$] and [Ru(Cp)($^{14}NO_2$)(PPh_3)$_2$] in the region of 1000–1500 cm^{-1}, we were able to determine which bands were due to the nitro stretches. Then, by an isotopic labeling experiment, a comparison of the infrared spectra of [Ru(Cp)($^{14}NO_2$)(PPh_3)$_2$] and [Ru(Cp)($^{15}NO_2$)(PPh_3)$_2$] was made, whereby we identified the bands due to the asymmetric nitro stretch, $\nu_{as}(NO_2)$, and the symmetric nitro stretch, $\nu_s(NO_2)$ (Figure 1). Upon isotopic labeling, the $\nu_{as}(NO_2)$ band shifted from 1334 to 1304 cm^{-1}, an amount which is 124% of the expected isotopic shift calculated from a Hooke's law approximation. The $\nu_s(NO_2)$ band shifted from 1285 to 1263 cm^{-1}, an amount which is 98% of the expected shift. The magnitude and direction that these bands shifted upon $^{15}NO_2$ labeling are consistent with similar $^{15}NO_2$-labeling experiments.[17,18] The frequencies of the $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ bands of the [Ru(Cp)(NO_2)(PPh_3)$_2$] complex indicate that the nitro ligand is bonded to the ruthenium center through the nitrogen atom.[19,20] The frequencies of the $\nu(NO_2)$ bands for the other (cyclo-

Table I. Infrared Spectroscopic Data (cm^{-1}) for the ν(NO) Bands of the Nitro- and Nitrosyl(cyclopentadienyl)ruthenium Complexes

complex	$\nu_{as}(NO_2)$	$\nu_s(NO_2)$
[Ru(Cp)($^{14}NO_2$)(PPh_3)$_2$] (**2**)	1334	1285
[Ru(Cp)($^{15}NO_2$)(PPh_3)$_2$] (**2a**)	1304	1263
[Ru(Cp)(dppe)(NO_2)] (**3**)	1330	1290
[Ru(Cp)(dppm)(NO_2)] (**4**)	1300	1270
[Ru(Cp)(dmpe)(NO_2)] (**5**)	1300	1260
complex		ν(NO)
[Ru(Cp)(NO)(PPh_3)$_2$](PF_6)$_2$ (**6**)		1860
[Ru(Cp)(dppe)(NO)](PF_6)$_2$ (**7**)		1870
[Ru(Cp)(dppm)(NO)](PF_6)$_2$ (**8**)[a]		1870
[Ru(Cp)(dmpe)(NO)](PF_6)$_2$ (**9**)		1870

[a] Three closely spaced absorbances occur in the region 1850–1900 cm^{-1}; the peak with the highest absorbance is reported.

Table II. $E_{1/2}$ Potentials, ΔE_p, and $i_{p,c}/i_{p,a}$ Values for Chloro- and Nitro(cyclopentadienyl)ruthenium Complexes

complex	$E_{1/2}$, V vs SSCE[a]	ΔE_p, V	$i_{p,c}/i_{p,a}$
[Ru(Cl)(Cp)(dmpe)] (**1**)[b]	+0.25	0.12	1.0
	+1.17[c]		
[Ru(Cp)(NO_2)(PPh_3)$_2$] (**2**)	+1.02[c]		
[Ru(Cp)(dppe)(NO_2)] (**3**)	+0.94[c]		
[Ru(Cp)(dppm)(NO_2)] (**4**)	+0.82[c]		
[Ru(Cp)(dmpe)(NO_2)] (**5**)[b]	+0.70[c]		

[a] Conditions: 0.1 M Bu_4NBF_4 in CH_2Cl_2; Pt working electrode; SSCE reference electrode; scan rate 100 mV/s. [b] Cyclic voltammogram was recorded in the absence of atmospheric oxygen. [c] This wave was irreversible; reported is the E_p for the anodic wave.

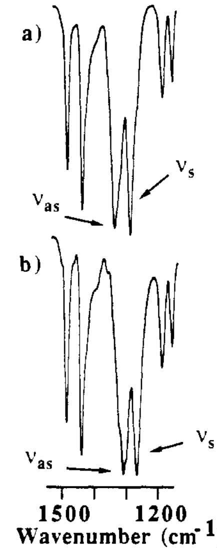


Figure 1. Diffuse-reflectance FT-IR spectra of (a) [Ru(Cp)($^{14}NO_2$)(PPh_3)$_2$] and (b) [Ru(Cp)($^{15}NO_2$)(PPh_3)$_2$]. Arrows indicate the two bands ($\nu_{as}(NO_2)$ and $\nu_s(NO_2)$) that shift upon isotopic labeling.

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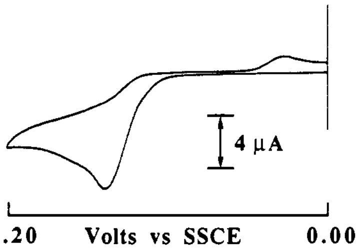

Figure 2. Cyclic voltammogram of [Ru(Cp)(dppm)(NO_2)] recorded under nitrogen in 0.1 M Bu_4NBF_4/CH_2Cl_2 with a platinum working electrode at a scan rate of 100 mV/s vs SSCE.

Table III. $E_{1/2}$ Potentials, ΔE_p, and $i_{p,c}/i_{p,a}$ Values for (Cyclopentadienyl)nitrosylruthenium Complexes

complex	$E_{1/2}$, V vs SSCE	ΔE_p, V	$i_{p,c}/i_{p,a}$
a. In the Absence of Atmospheric Oxygen			
[Ru(Cp)(NO)(PPh_3)$_2$](PF_6)$_2$ (**6**)[a]	+0.24	0.10	1.1
	−0.58[c]		
[Ru(Cp)(dppe)(NO)](PF_6)$_2$ (**7**)[b]	+0.14	0.07	1.0
	−0.58	0.07	1.0
[Ru(Cp)(dppm)(NO)](PF_6)$_2$ (**8**)[b]	+0.14	0.07	1.0
	−0.54	0.07	1.0
[Ru(Cp)(dmpe)(NO)](PF_6)$_2$ (**9**)[b]	−0.08	0.09	1.0
	−0.80	0.08	1.0
b. In the Presence of Atmospheric Oxygen			
[Ru(Cp)(dppe)(NO)](PF_6)$_2$ (**7**)[b]	+0.82[d]		
	+0.14	0.08	1.0
	−0.60[c]		
[Ru(Cp)(dppm)(NO)](PF_6)$_2$ (**8**)[b]	+0.68[d]		
	+0.14	0.07	1.0
	−0.56[c]		
[Ru(Cp)(dmpe)(NO)](PF_6)$_2$ (**9**)[b]	+0.49[d]		
	−0.08	0.09	1.0
	−0.81[c]		

[a] Conditions: 0.1 M Bu_4NBF_4 in CH_2Cl_2; Pt working electrode; SSCE reference electrode; scan rate = 100 mV/s. [b] Conditions: 0.1 M Et_4NBF_4 in CH_3CN; Pt working electrode; SSCE reference electrode; scan rate 100 mV/s. [c] This wave was irreversible; reported is the E_p for the cathodic wave. [d] This wave was irreversible; reported is the E_p for the anodic wave.

pentadienyl)nitroruthenium complexes are consistent with those of the [Ru(Cp)(NO_2)(PPh_3)$_2$] complex, indicating that these complexes also contain a nitro ligand coordinated through the nitrogen atom to the ruthenium center.

The ν(NO) bands for the (cyclopentadienyl)nitrosylruthenium complexes, [Ru(Cp)(L)$_2$(NO)](PF_6)$_2$ (**6**–**9**), are between 1860 and 1870 cm^{-1}, suggesting that a linear nitrosyl ligand is present in these complexes.[20-23]

Cyclic Voltammetry. The cyclic voltammetric data for the [Ru(Cl)(Cp)(dmpe)] complex and the [Ru(Cp)(L)$_2$(NO_2)] complexes are listed in Table II. The cyclic voltammograms for the [Ru(Cp)(L)$_2$(NO_2)] (L = PPh_3, $^1/_2$ dppe, $^1/_2$ dppm) complexes show an anodic peak (oxidation of [Ru(Cp)(L)$_2$(NO_2)]) within the range +0.82 to +1.02 V (listed in Table II) and on the return scan a small cathodic peak within the range +0.14 to +0.22 V (not listed in Table II). Upon continuous scanning, the small cathodic peak defines half of a reversible wave whose $E_{1/2}$ value suggests that [Ru(Cp)(L)$_2$(NO)]$^+$ or [Ru(Cp)(L)$_2$(NO)]$^{2+}$ was formed from the oxidation of [Ru(Cp)(L)$_2$(NO_2)]. Notably, the small reversible wave is not observed if [Ru(Cp)(L)$_2$(NO_2)] is not oxidized. In addition, very small anodic peaks are observed at potential values more positive than the principal anodic peak, probably due to uncharacterized decomposition of [Ru(Cp)(L)$_2$(NO_2)]$^+$. As an example, the cyclic voltammogram of [Ru(Cp)(dppm)(NO_2)] is shown in Figure 2.

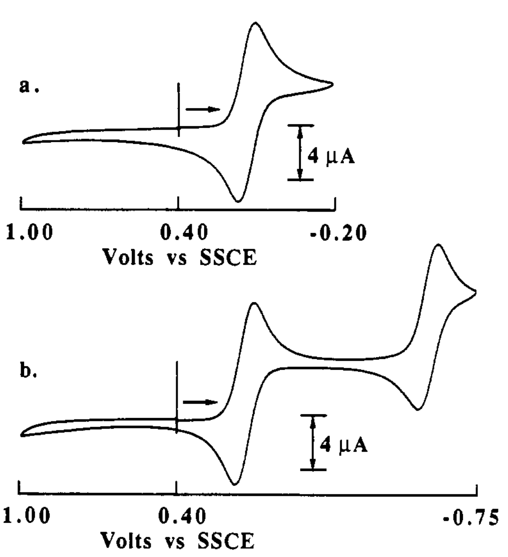

Figure 3. Cyclic voltammograms of [Ru(Cp)(dppe)(NO)](PF_6)$_2$ recorded under nitrogen in a solution of 0.1 M Et_4NBF_4/CH_3CN with a platinum working electrode at a scan rate of 100 mV/s vs SSCE. Scan b was recorded immediately after scan a, and the arrows indicate where the scans were initiated.

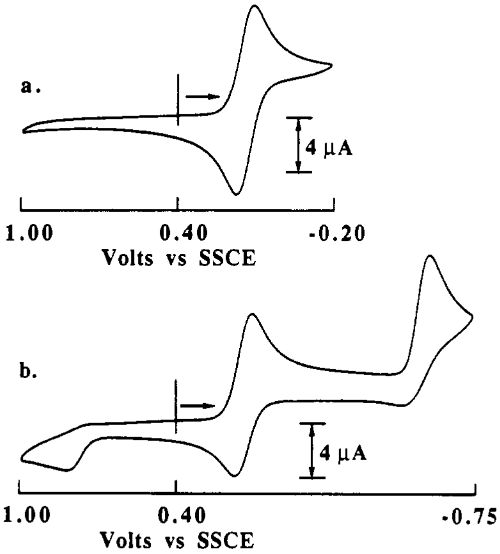

Figure 4. Cyclic voltammograms of [Ru(Cp)(dppe)(NO)](PF_6)$_2$ recorded in the presence of atmospheric oxygen in a solution of 0.1 M Et_4NBF_4/CH_3CN with a platinum working electrode at a scan rate of 100 mV/s vs SSCE. Scan b was recorded immediately after scan a, and the arrows indicate where the scans were initiated.

The cyclic voltammogram of the [Ru(Cp)(dmpe)(NO_2)] complex displays an anodic peak (oxidation of [Ru(Cp)(dmpe)(NO_2)]) at an $E_{p,a}$ of +0.70 V as well as a cathodic peak at an $E_{p,c}$ of −0.68 V. This cathodic peak is not observed if the scan does not access the anodic peak. While the cathodic peak appears to result from the decomposition of the electrochemically generated [Ru(Cp)(dmpe)(NO_2)]$^+$ complex, the products from the decomposition cannot be determined from cyclic voltammetry, for the potential value of the cathodic peak does not suggest the presence of [Ru(Cp)(dmpe)(NO)]$^+$ or [Ru(Cp)(dmpe)(NO)]$^{2+}$. Small anodic peaks at potentials higher than the principal anodic peak also appear in the cyclic voltammogram of the [Ru(Cp)(dmpe)(NO_2)] complex.

The (cyclopentadienyl)nitrosylruthenium complexes, [Ru(Cp)(L)$_2$(NO)](PF_6)$_2$ (L = $^1/_2$ dppe, $^1/_2$ dppm, $^1/_2$ dmpe) (**7**–**9**), display different electrochemistries depending on whether or not the solution was deaerated with an inert gas. The cyclic voltammograms of each of these complexes were recorded in both the absence and the presence of atmospheric oxygen (Table III),

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where the cyclic voltammograms of the [Ru(Cp)(L)$_2$(NO)](PF$_6$)$_2$ (L = $^1/_2$ dppe, $^1/_2$ dppm, $^1/_2$ dmpe) complexes recorded in the absence of atmospheric oxygen display two reversible couples (see Figure 3). Figure 3a is a cyclic voltammogram of [Ru(Cp)(dppe)(NO)]$^{2+}$ where the starting potential is +0.40 V, the first switching potential is −0.20 V, and the second switching potential is +1.00 V. In this cyclic voltammogram, one reversible couple, which corresponds to the reduction of [Ru(Cp)(dppe)(NO)]$^{2+}$ to [Ru(Cp)(dppe)(NO)]$^+$, at an $E_{1/2}$ of +0.14 V was observed. Figure 3b is a cyclic voltammogram of [Ru(Cp)(dppe)(NO)]$^{2+}$ where the starting potential is +0.40 V, the first switching potential is −0.75 V, and the second switching potential is +1.00 V. In this cyclic voltammogram, two reversible couples were observed, one at an $E_{1/2}$ of +0.14 V and the other at an $E_{1/2}$ of −0.58 V. The reversible couple at −0.58 V corresponds to the reduction of [Ru(Cp)(dppe)(NO)]$^+$ to [Ru(Cp)(dppe)(NO)].

In contrast, the cyclic voltammograms of the [Ru(Cp)(L)$_2$(NO)](PF$_6$)$_2$ (L = $^1/_2$ dppe, $^1/_2$ dppm, $^1/_2$ dmpe) complexes recorded in the presence of air display one reversible couple and two irreversible couples (see Figure 4). Figure 4a is a cyclic voltammogram of [Ru(Cp)(dppe)(NO)]$^{2+}$ where the starting potential is +0.40 V, the first switching potential is −0.20 V, and the second switching potential is +1.00 V. This cyclic voltammogram is similar to the cyclic voltammogram in Figure 3a in that one reversible couple at an $E_{1/2}$ of +0.14 V was observed. Figure 4b is a cyclic voltammogram of [Ru(Cp)(dppe)(NO)]$^{2+}$ that was recorded in the same manner as the cyclic voltammogram in Figure 3b; however, in the cyclic voltammogram in Figure 4b we observed a cathodic peak at an $E_{p,c}$ of −0.60 V, a reversible couple at an $E_{1/2}$ of +0.14 V, and an anodic peak at an $E_{p,a}$ of +0.82 V. The reversible couple at +0.14 V corresponds to the reduction of [Ru(Cp)(dppe)(NO)]$^{2+}$ to [Ru(Cp)(dppe)(NO)]$^+$, the cathodic peak at −0.60 V corresponds to the irreversible reduction of [Ru(Cp)(dppe)(NO)]$^+$ to [Ru(Cp)(dppe)(NO)], and the anodic peak at +0.82 V corresponds to the $E_{p,a}$ of the [Ru(Cp)(dppe)(NO$_2$)] complex. This observation suggests that [Ru(Cp)(dppe)(NO)], formed from [Ru(Cp)(dppe)(NO)]$^{2+}$ during the electrochemical experiment, reacts with molecular oxygen to form [Ru(Cp)(dppe)(NO$_2$)], which is reminiscent of the reactivity described by Basolo and Clarkson for [L$_4$Co(NO)] (where L$_4$ = a quadridentate dianion such as *N,N'*-ethylenebis(1-acetonylethylideneaminato)) complexes.[24] Basolo and Clarkson report that the complex [L$_4$Co(NO)] reacts with oxygen in the presence of base or in coordinating solvents to yield [BL$_4$Co(NO$_2$)] (where B = base or coordinating solvent).

The cyclic voltammogram of the [Ru(Cp)(NO)(PPh$_3$)$_2$]$^{2+}$ complex recorded under nitrogen displays a reversible couple at an $E_{1/2}$ of +0.24 V and a second irreversible couple at an $E_{p,c}$ of −0.58 V; see Table IIIa. These data are consistent with Bergman's studies on similar (pentamethylcyclopentadienyl)ruthenium complexes.[12] Bergman has reported that while he was able to isolate the [Ru(η^5-C$_5$Me$_5$)(dmpe)(NO)] complex, he was not able to isolate the [Ru(η^5-C$_5$Me$_5$)(NO)(PMe$_3$)$_2$] complex, which he attributed to an enhanced stability of dmpe complexes relative to bis(trimethylphosphine) complexes.

Coulometry. Coulometric measurements were done to determine the number of electrons passed in the two reductive couples of the [Ru(Cp)(dppe)(NO)](PF$_6$)$_2$ complex. To electrochemically reduce the [Ru(Cp)(dppe)(NO)]$^{2+}$ complex to [Ru(Cp)(dppe)(NO)]$^+$, the cell potential was held at 0.3 V lower than the $E_{1/2}$ value for the first wave. The *n* value of this reduction was 0.9 and the cyclic voltammogram recorded at this point was identical with the original cyclic voltammogram, indicating that no decomposition had occurred. The electrochemical reduction of [Ru(Cp)(dppe)(NO)]$^{2+}$ to [Ru(Cp)(dppe)(NO)] was performed by holding the cell potential at −1.20 V (0.62 V lower than the $E_{1/2}$ value of the second wave), and an *n* value of 1.8 was recorded. The cyclic voltammogram recorded after the [Ru(Cp)(dppe)(NO)]$^{2+}$ complex was reduced to [Ru(Cp)(dppe)(NO)] showed no changes from the original cyclic voltammogram.

Table IV. UV-Visible Spectral Data for (Cyclopentadienyl)ruthenium Complexes

complex	λ_{max}, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})^{a,d}
[Ru(Cl)(Cp)(dmpe)] (**1**)^b	430 sh, 350 (1.4)
[Ru(Cp)(NO$_2$)(PPh$_3$)$_2$] (**2**)^b	350 sh, 290 sh
[Ru(Cp)(dppe)(NO$_2$)] (**3**)^b	309 (3.2)
[Ru(Cp)(dppm)(NO$_2$)] (**4**)^c	380 sh, 314 (3.6)
[Ru(Cp)(dmpe)(NO$_2$)] (**5**)^b	322 (3.2)
[Ru(Cp)(NO)(PPh$_3$)$_2$](PF$_6$)$_2$ (**6**)^c	440 sh, 310 (15)
[Ru(Cp)(dppe)(NO)](PF$_6$)$_2$ (**7**)^c	300 sh, 279 (15)
[Ru(Cp)(dppm)(NO)](PF$_6$)$_2$ (**8**)^b	310 sh, 270 (15)
[Ru(Cp)(dmpe)(NO)](PF$_6$)$_2$ (**9**)^b	380 sh, 265 (6.8)

$^a\lambda_{max}$ and ϵ were determined at a minimum of two concentrations. ^{b}Electronic spectrum recorded in acetonitrile. ^{c}Electronic spectrum recorded in methylene chloride. ^{d}sh = shoulder.

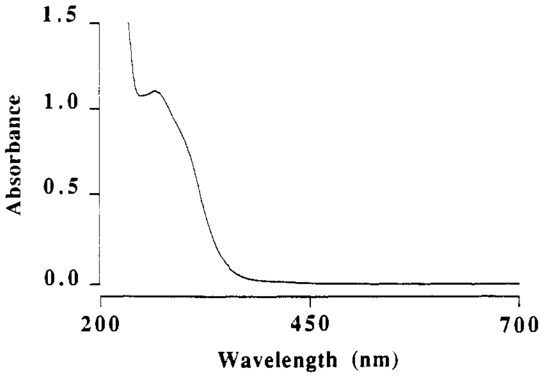

Figure 5. Electronic absorption spectrum of [Ru(Cp)(dppm)(NO)](PF$_6$)$_2$ in CH$_3$CN at a concentration of 7.5 × 10^{-5} M.

These *n* values indicate that the [Ru(Cp)(dppe)(NO)]$^{2+}$ complex can be reduced in two one-electron steps, and to our knowledge, this is the first reported coulometric study where a nitrosylruthenium complex is reduced in two reversible one-electron steps.

Electronic Absorption Spectra. The electronic absorption data for the (cyclopentadienyl)ruthenium complexes can be found in Table IV. The electronic absorption spectra of the nitro- and nitrosylruthenium complexes that utilized phosphine ligands as well as the cyclopentadienyl ligand are significantly different from the electronic absorption spectrum of ruthenocene. Gray reports that ruthenocene, as well as its electrochemical oxidation product at a mercury electrode, contains at least five absorption maxima in the region between 400 and 200 nm.[25] We have found that the electronic absorption spectra of the [Ru(Cp)(L)$_2$(NO$_2$)] complexes display between one and two absorbances in the 700–200-nm region and that no linear relationship between the redox potentials of the metal centers and the frequencies of the absorbance maxima was observed. Each of the [Ru(Cp)(L)$_2$(NO)](PF$_6$)$_2$ complexes displays two absorbances (see Figure 5). Once again, no linear relationship was observed between the frequencies of the absorption maxima and redox potentials of metal centers. Our spectroscopic data represent the only reported spectral values for nitro- and nitrosyl(cyclopentadienyl)ruthenium complexes, since no electronic absorption spectra have been reported by either Bruce and White[14] or Treichel[9] for the [Ru(Cp)(PMe$_3$)$_2$(NO)](PF$_6$)$_2$ complex.

Conclusion

We have developed the synthetic routes necessary to access a variety of (cyclopentadienyl)nitroruthenium complexes and (cyclopentadienyl)nitrosylruthenium complexes. Since the [Ru-

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(Cp)(L)$_2$(NO)] (L = $^1/_2$ dppe, $^1/_2$ dppm, $^1/_2$ dmpe) complexes appear to be stable in solution, we will isolate these complexes and further study their reactivity with molecular oxygen.

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Notes

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X-ray Structure of $\{HB(Me_2pz)_3\}W^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)\{HB(Me_2pz)_3\}$, a Molecule Containing Rare *cis*-$[WO(CO)]^{2+}$ and *syn*-$[W^{VI}W^{IV}O_3(\mu\text{-}O)]^{2+}$ Moieties [$HB(Me_2pz)_3^-$ = Hydrotris(3,5-dimethyl-1-pyrazolyl)borate]

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The study of high-valent organometallic oxo complexes has intensified in recent years, and a timely review by Bottomley and Sutin has appeared.[2] Interest in this area stems from the extensive use of metal oxides as catalysts for organic reactions and the likely involvement of organometallic oxo intermediates in these reactions.[3] The majority of known species are polynuclear cyclopentadienyl and alkyl complexes of oxophilic early transition metals or cluster μ_3-oxo carbonyls of the group 8 and 9[4] metals.[2] In contrast, noncluster oxo carbonyl complexes are extremely rare. In the early 1980s *trans*-$MO_2(CO)_4$ (M = Mo, W),[5,6] and $MO_2(CO)_2$ (M = Cr, Mo, W)[6,7] were identified by matrix isolation techniques and $CrO_2(CO)_3$[8] was obtained in the gas phase. Later that decade the stable oxo carbonyl–W(IV) complex $WOCl_2(CO)(PMePh_2)_2$, formed by reaction of $WOCl_2(PMePh_2)_3$ with CO[9] or oxidative addition of CO_2 to $WCl_2(PMePh_2)_4$,[10] was reported by Mayer and co-workers. In addition to their relevance to catalysis, complexes containing such electronically disparate ligands are of intrinsic interest. Mixed-valence compounds also attract considerable current interest and early-transition-metal compounds of this type have been exhaustively reviewed.[11] Approximately 18 dinuclear mixed-valence complexes of tungsten are known, but only the complexes $L_2W^{IV}(\mu\text{-}S)_2W^{VI}S_2$ (L = $C_5H_5^-$ or $MeC_5H_4^-$)[12] contain the metal in oxidation states of +4 and +6. We report here the synthesis and X-ray structure of the mixed-valence oxocarbonyl complex $\{HB(Me_2pz)_3\}W^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)\{HB(Me_2pz)_3\}$ [**1**; $HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate], formed upon oxidative hydrolysis of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$.

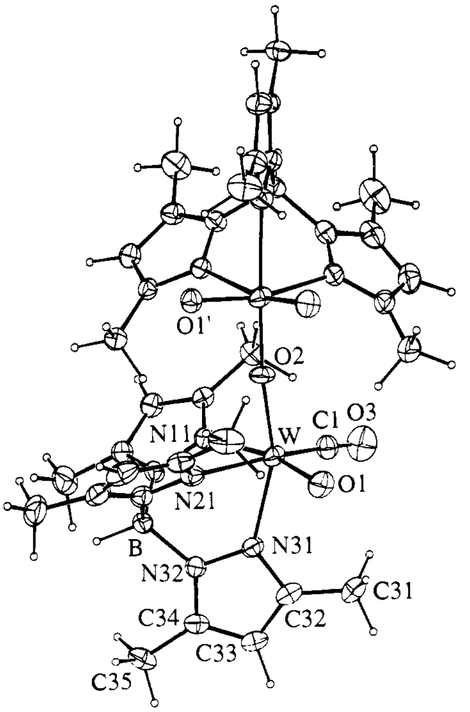

Figure 1. Molecular structure of $\{HB(Me_2pz)_3\}WO_2(\mu\text{-}O)WO(CO)\{HB(Me_2pz)_3\}$ showing the atom-labeling scheme. The carbonyl and O(1′) ligands are disordered and each have an occupancy of 0.5 at the two sites. The numbering of atoms in the pyrazolyl rings containing N(11) and N(21) parallels that shown for the ring containing N(31). Thermal ellipsoids are plotted at the 30% probability level, and hydrogen atoms are represented by small spheres.

Results and Discussion

Recrystallization of $NEt_4[\{HB(Me_2pz)_3\}W(CO)_3]$ from acetonitrile/water, according to the method described by Trofimenko,[13] results in the slow development of a red coloration in the mother liquor upon standing. This coloration is due to the formation of the title compound, which precipitates as red microcrystals. The formation of **1** requires the presence of both water and oxygen, but the mechanism of the reaction involved has not been established. Exhaustive decarbonylation with concomitant oxidation is a useful route to cyclopentadienylmetal oxo compounds and hydrolysis is a common route to organometallic group 4 oxo complexes.[2] The infrared spectrum of the insoluble, diamagnetic complex exhibits bands typical of $HB(Me_2pz)_3^-$ (ν(BH) = 2550 cm^{-1}), a single strong ν(CO) band at 1950 cm^{-1}, three bands of medium to strong intensity assigned to ν(W=O) (955, 940, and 890 cm^{-1}) and a strong band due to ν(WOW) at 820 cm^{-1}. Fast atom bombardment mass spectrometry revealed a strong [M −

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