Organometallics **1993,** *12,* 1029–1037

Articles

Tetraphenylcyclopentadienyl Nitrosyl Complexes of Molybdenum and Tungsten[1]

Peter Legzdins,* Roser Reina, and Michael J. Shaw

Department of Chemistry, The University of British Columbia,
Vancouver, British Columbia, Canada V6T 1Z1

Raymond J. Batchelor and Frederick W. B. Einstein*

Department of Chemistry, Simon Fraser University,
Burnaby, British Columbia, Canada V5A 1S6

Received November 17, 1992

Sequential treatment of $M(CO)_6$ (M = Mo, W) in THF with $Cp^{\phi}Li$ ($Cp^{\phi} = \eta^5\text{-}C_5Ph_4H$) and Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) affords good yields of $Cp^{\phi}M(NO)(CO)_2$ which convert to $Cp^{\phi}M(NO)Cl_2$ upon treatment with PCl_5 in Et_2O. Dialkyl compounds of the type $Cp^{\phi}M(NO)R_2$ ($R = CH_2SiMe_3, CH_2Ph$) are readily preparable from these dichloro precursors by straightforward metathesis reactions. Finally, molybdenum dinitrosyl complexes of the type $Cp^{\phi}Mo(NO)_2X$ (X = Cl, Ph) are obtained when $Cp^{\phi}Mo(NO)(CO)_2$ is reacted with $[NO][PF_6]$ in CH_2Cl_2 and the resulting $[Cp^{\phi}Mo(NO)_2]PF_6$ intermediate salt is treated in situ with a source of X^-. All new complexes have been characterized by conventional means, and an X-ray crystallographic analysis of $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$ has been performed. Crystal data for $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$: triclinic, space group $P\bar{1}$, $a = 10.3870(7)$ Å, $b = 11.6495(7)$ Å, $c = 16.3748(16)$ Å, $\alpha = 81.164(7)°$, $\beta = 84.809(8)°$, $\gamma = 63.925(6)°$, $Z = 2$, $D_c = 1.432$ g cm^{-3}, $R_f = 0.021$ for all 6118 unique reflections. This analysis suggests that the greater air stability and lower reactivity of the Cp^{ϕ} complex may be attributed to the much more hindered approach of incoming reactants toward the tungsten atom than in the analogous Cp complex. Cyclic voltammetry studies of selected compounds also establish that in these complexes the electronic properties of the sterically demanding Cp^{ϕ} ligand more resemble the Cp ($\eta^5\text{-}C_5H_5$) rather than the Cp* ($\eta^5\text{-}C_5Me_5$) ligand.

Introduction

Historically, cyclopentadienyl ligands have played an important role in the evolution and development of transition-metal organometallic chemistry.[2] The $\eta^5\text{-}C_5H_5$ (Cp) ligand typically stabilizes organometallic complexes by occupying three of the metal's coordination sites and by providing the metal center with five valence electrons.[3] The ligand can be made more sterically demanding simply by replacing the ring hydrogens with other groups. Indeed, the number of examples of transition-metal compounds containing substituted cyclopentadienyl ligands has been on the increase in recent years.[4–10] These ligands, by virtue of their greater steric bulk or modified electronic properties relative to $\eta^5\text{-}C_5H_5$, can often stabilize complexes, such as radical species, for which the unsubstituted analogues possess only brief lifetimes under ambient conditions.[4–8] For instance, the η^5-tetraphenylcyclopentadienyl ligand ($Cp^{\phi} = \eta^5\text{-}C_5Ph_4H$) has been employed to prepare relatively air-stable metallocene complexes of Fe, V, Cr, Co, and Ni.[9] Furthermore, this ligand has also been used to stabilize 19-electron, four-legged piano-stool complexes of molybdenum which have been structurally characterized.[11]

Given the apparent ease with which complexes containing the $\eta^5\text{-}C_5Ph_4H$ ligand yield stable crystalline materials, we decided to utilize this ligand during our ongoing investigations[12] of various molybdenum and tungsten nitrosyl systems. Our first objective was to establish how the introduction of the tetraphenylcyclopentadienyl group affects the redox properties of typical organometallic nitrosyl derivatives of these metals. During the present investigation we have thus utilized the Cp^{ϕ} ligand during cyclic voltammetry studies of several nitrosyl

---

(1) Presented in part at the 75th Canadian Chemical Conference, Edmonton, Alberta, June 1992; Abstract 369.

(2) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vols. 3–7.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(4) Gloagen, B.; Astruc, D. *J. Am. Chem. Soc.* **1990,** *112,* 4607.

(5) Vernier, C. G.; Casserly, E. W. *J. Am. Chem. Soc.* **1990,** *112,* 2808.

(6) Briscoe, M. W.; Chambers, R. D.; Mullins, S. J.; Nakamura, T.; Drakesmith, F. G. *J. Chem. Soc., Chem. Commun.* **1990,** 1127.

(7) Brown, K. N.; Field, L. D.; Lay, P. A.; Lindall, C. M.; Masters, A. F. *J. Chem. Soc., Chem. Commun.* **1990,** 408.

(8) Joo, W. C.; Hong, J. H.; Choi, S. B.; Son, H. E.; Kim, C. H. *J. Organomet. Chem.* **1990,** *391,* 27.

(9) (a) Castellani, M. P.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* **1987,** *6,* 1703. (b) Castellani, M. P.; Wright, J. M.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* **1986,** *5,* 1116.

(10) Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991,** *33,* 291.

(11) Mao, F.; Philbin, C. E.; Weakely, T. J. R.; Tyler, D. R. *Organometallics* **1990,** *9,* 1510.

(12) Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.*, in press.

0276-7333/93/2312-1029$04.00/0 © 1993 American Chemical Society

containing compounds of Mo and W whose Cp and Cp* (η^5-C_5Me_5) analogues we have had for some time, but whose electrochemistry we have not examined previously. Specifically, in this paper we describe the synthesis and characterization of the compounds Cp$^{\phi}$M(NO)$(CO)_2$, Cp$^{\phi}$M(NO)Cl_2, Cp$^{\phi}$M(NO)$(CH_2SiMe_3)_2$, Cp$^{\phi}$M(NO)$(CH_2Ph)_2$ (M = Mo, W), Cp$^{\phi}$Mo$(NO)_2$Cl, and Cp$^{\phi}$Mo$(NO)_2$Ph, and we compare the redox properties of the first three types of complexes with their Cp and Cp* analogues.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions in an atmosphere of prepurified dinitrogen.[13,14] General procedures routinely employed in these laboratories have been described in detail previously.[15] Fast atom bombardment (FAB) mass spectra (6-kV ion source, 7–8 kV xenon FAB gun) were recorded with the assistance of Mr. M. Lapawa and Dr. G. Eigendorf on an AEI MS 9 mass spectrometer employing a 3-nitrobenzyl alcohol matrix. Tetraphenylcyclopentadiene[11] and $Mg(CH_2Ph)_2$[16] were synthesized by the published procedures. The hexacarbonyls of molybdenum and tungsten (Pressure Chemical Co.), Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, Aldrich), [NO][PF_6] (Alfa), *n*-BuLi (1.6 M in hexanes, Aldrich), Me_3SiCH_2MgCl (1.0 M in Et_2O, Aldrich), [$(PhCH_2)Et_3N$]Cl (Aldrich), and Na[BPh_4] (Merck) were purchased.

Electrochemical Measurements. The detailed methodology employed for cyclic voltammetry (CV) studies in these laboratories has been outlined elsewhere.[17,18] Ferrocene (Fc) was used as an internal reference in these studies, with the redox couple, Fc/Fc$^+$, occurring at $E^{\circ\prime}$ = 0.54 V versus SCE in THF and $E^{\circ\prime}$ = 0.46 V versus SCE in CH_2Cl_2 over the range of scan rates (ν) used (0.10–1.00 V s^{-1}).

ESR Measurements. Typically, 5×10^{-5} M solutions of the organometallic complexes were prepared in a drybox and were transferred to a capillary tube which was then plugged with silicone grease. The X-band ESR spectra of these samples were recorded on a Varian Associates Model E-3 spectrometer which had been calibrated using a sample of VO$(acac)_2$.

Preparation of Cp$^{\phi}$M(NO)$(CO)_2$ (M = Mo, W). Both complexes were prepared in a similar manner. A hexanes solution of *n*-BuLi (1.6 M, 8.44 mL, 13.5 mmol) was added dropwise to a stirred, off-white slurry of tetraphenylcyclopentadiene (5.00 g, 13.5 mmol) in THF (50 mL). The slurry gradually changed to a clear, orange solution, and stirring was continued for 30 min after the addition of the *n*-BuLi had been completed. $Mo(CO)_6$ (3.56 g, 13.5 mmol) was added to the solution, and the mixture was refluxed overnight. (With $W(CO)_6$, the reflux was continued for 36 h). After cooling to room temperature, solvent was removed from the final solution under reduced pressure. Unreacted $Mo(CO)_6$ (4.5 mmol) was removed from the yellow residue by sublimation in vacuo at 90 °C onto a water-cooled probe. The residual yellow powder was dissolved in THF (50 mL), and the resulting solution was stirred and treated dropwise over 30 min with a solution of Diazald (1.92 g, 9.0 mmol) in THF (20 mL) whereupon it turned red and a gas (presumably CO) was evolved. Stirring was continued for 1 h, and then the solvent was removed under reduced pressure. The remaining residue was extracted with Et_2O (2 × 50 mL), and the extracts were filtered through a column (3 × 10 cm) of basic alumina I supported on a medium-porosity frit. The column was rinsed with Et_2O until the washings were colorless. Hexanes (40 mL) were added to the combined filtrates, and the resulting solution was concentrated in vacuo to incite precipitation. Cooling of this mixture to −30 °C overnight resulted in the deposition of Cp$^{\phi}$Mo(NO)$(CO)_2$ (2.50 g) as a light orange, crystalline solid. An additional 1.10 g of the product complex was obtained by concentration and cooling of the mother liquor. The total yield based on Diazald was 73%.

Anal. Calcd for $C_{31}H_{21}NO_3Mo$: C, 67.52; H, 3.84; N, 2.54. Found: C, 67.48; H, 3.99; N, 2.53. IR (Nujol mull): ν_{CO} 2013, 2000, 1934, 1925 cm^{-1}; ν_{NO} 1684, 1663 cm^{-1}. EI low-resolution mass spectrum (probe temperature 120 °C): *m/z* 553 [P^+], 525 [P^+ − CO], 495 [P^+ − CO − NO], 467 [P^+ − 2CO − NO]. ^1H NMR ($CDCl_3$): δ 7.4–7.0 (m, 20 H, $C_5(C_6H_5)_4H$), 6.05 (s, 1 H, C_5Ph_4H).

Cp$^{\phi}$W(NO)$(CO)_2$ was isolated in 80% yield based on Diazald. Anal. Calcd for $C_{31}H_{21}NO_3W$: C, 58.24; H, 3.31; N, 2.19. Found: C, 58.48; H, 3.34; N, 2.29. IR (KBr): ν_{CO} 2006, 1991, 1923, 1910 cm^{-1}; ν_{NO} 1676, 1657 cm^{-1}. EI low-resolution mass spectrum (probe temperature 120 °C): *m/z* 641 [P^+], 613 [P^+ − CO], 583 [P^+ − CO − NO], 555 [P^+ − 2CO − NO]. ^1H NMR ($CDCl_3$): δ 7.4–7.0 (m, 20 H, $C_5(C_6H_5)_4H$), 6.05 (s, 1 H, C_5Ph_4H).

Preparation of Cp$^{\phi}$M(NO)Cl_2. Both of these complexes were prepared in a similar manner. The synthesis of the molybdenum compound is described as a representative example. A mixture of orange Cp$^{\phi}$Mo(NO)$(CO)_2$ (1.24 g, 2.30 mmol) and yellow PCl_5 (0.47 g, 2.2 mmol) in Et_2O (15 mL) was stirred overnight at room temperature. The solution became green, and a brown solid precipitated. The solid was collected on a frit and washed with hexanes (3 × 10 mL) to obtain 0.91 g (66% yield) of Cp$^{\phi}$Mo(NO)Cl_2.

Anal. Calcd for $C_{29}H_{21}NOCl_2Mo$: C, 61.50; H, 3.71; N, 2.47. Found: C, 60.80; H, 3.84; N, 2.51. IR (Nujol mull): ν_{CO} 1686, 1667 cm^{-1}. EI low-resolution mass spectrum (probe temperature 120 °C): *m/z* 567 [P^+], 537 [P^+ − NO]. ^1H NMR (C_6D_6): δ 7.3–6.8 (m, 20 H, $C_5(C_6H_5)_4H$), 6.55 (s, 1 H, C_5Ph_4H).

Cp$^{\phi}$W(NO)Cl_2 was isolated in 70% yield. Anal. Calcd for $C_{29}H_{21}NOCl_2W$: C, 53.23; H, 3.21; N, 2.14. Found: C, 53.03; H, 3.28; N, 2.13. IR (Nujol mull): ν_{NO} 1670, 1645 cm^{-1}. EI low-resolution mass spectrum (probe temperature 120 °C): *m/z* 655 [P^+], 625 [P^+ − NO], 583 [P^+ − 2Cl]. ^1H NMR (C_6D_6): δ 7.5–6.4 (m, 20 H, $C_5(C_6H_5)_4H$), 6.55 (s, 1 H, C_5Ph_4H).

Preparation of Cp$^{\phi}$M(NO)$(CH_2SiMe_3)_2$. Again, the synthesis of the molybdenum compound is described as a representative example. A stirred solution of Cp$^{\phi}$Mo(NO)Cl_2 (0.57 g, 1.0 mmol) in Et_2O (30 mL) at −78 °C was treated with an Et_2O solution of Me_3SiCH_2MgCl (1.0 M, 2.0 mL), and the mixture was allowed to warm to room temperature over 2 h. The final purple mixture was filtered through Florisil (3 × 10 cm) supported on a medium-porosity frit, and solvent was removed from the filtrate in vacuo. The residue remaining was extracted with Et_2O/pentane (2:1, 15 mL), filtered through Celite, and then cooled overnight at −30 °C to obtain purple microcrystals (0.50 g, 75% yield) of analytically pure Cp$^{\phi}$Mo(NO)$(CH_2SiSiMe_3)_2$.

Anal. Calcd for $C_{37}H_{43}NOSi_2Mo$: C, 66.37; H, 6.43; N, 2.09. Found: C, 66.22; H, 6.60; N, 2.20. IR (Nujol mull): ν_{NO} 1592 cm^{-1}. EI low-resolution mass spectrum (probe temperature 120 °C): *m/z* 581 [P^+ − CH_2SiMe_3]. ^1H NMR (C_6D_6): δ 7.4–7.0 (m, 20 H, $C_5(C_6H_5)_4H$), 6.50 (s, 1 H, C_5Ph_4H), 3.53 (d, 2 H, $CH_aH_xSiMe_3$, $^2J_{HH}$ = 19.8 Hz), 0.24 (d, 2 H, $CH_aH_xSiMe_3$, $^2J_{HH}$ = 19.8 Hz), 0.10 (s, 18 H, $Si(CH_3)_3$).

Cp$^{\phi}$W(NO)$(CH_2SiMe_3)_2$ was isolated in 80% yield. Anal. Calcd for $C_{37}H_{43}NOSi_2W$: C, 58.66; H, 5.68; N, 1.85. Found: C, 58.46; H, 5.64, N. 1.89. IR (Nujol mull): ν_{NO} 1569 cm^{-1}. EI low-resolution mass spectrum (probe temperature 150 °C): *m/z* 757 [P^+], 641 [P^+ − CH_2SiMe_3 − NO]. ^1H NMR (C_6D_6) δ 7.6–6.8 (m, 20 H, $C_5(C_6H_5)_4H$), 6.50 (s, 1 H, C_5Ph_4H), 2.60 (s, 2 H, $CH_aH_xSiMe_3$, $^2J_{HH}$ = 9.8 Hz), 0.25 (s, 18 H, $Si(CH_3)_3$), 0.10 (d, 2 H, $CH_aH_xSiMe_3$, $^2J_{HH}$ = 9.8 Hz).

---

(13) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: Toronto, 1986.

(14) Wayda, A. L.; Darensbourg, M. Y. *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

(15) Dryden, N. H.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2583.

(16) (a) Anderson, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1977**, 809. (b) Anderson, R. A.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 262.

(17) Herring, F. G.; Legzdins, P.; Richter-Addo, G. B. *Organometallics* **1989**, *8*, 1485.

(18) Legzdins, P.; Lundmark, P. J.; Phillips, E. C.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2991.

Preparation of Cp$^{\phi}$M(NO)(CH$_2$Ph)$_2$. In this instance, the synthesis of the tungsten compound is described as a respective example. A mixture of Cp$^{\phi}$W(NO)Cl$_2$ (0.33 g, 0.50 mmol) and Mg(CH$_2$Ph)$_2$ (0.15 g, 0.52 mmol) in Et$_2$O (20 mL) at −78 °C was stirred and allowed to warm slowly to room temperature. Solvent was then removed in vacuo, and the remaining red solid was dissolved in Et$_2$O (10 mL) and was transferred to the top of a Florisil column (2 × 10 cm) made up in Et$_2$O. Elution of the column with Et$_2$O afforded a single red band which was collected. The volume of the red eluate was reduced to 10 mL in vacuo, and hexanes (10 mL) were added. Cooling of this mixture at −30 °C overnight resulted in the deposition of 0.28 g (72% yield) of Cp$^{\phi}$W(NO)(CH$_2$Ph)$_2$ as orange microcrystals which were collected by filtration.

Anal. Calcd for C$_{43}$H$_{35}$NOW: C, 67.46; H, 4.58; N, 1.83. Found: C, 67.70; H, 4.70; N, 1.71. IR (Nujol mull): ν_{NO} 1583, 1573 cm^{-1}. FAB mass spectrum: m/z 765 [P$^+$], 674 [P$^+$ − CH$_2$Ph]. ^{1}H NMR (C$_6$D$_6$): δ 7.4–6.5 (m, 30 H, C$_5$(C$_6$$H_5$)$_4H, CH_2$(C$_6$$H_5$)), 6.10 (s, 1 H, C$_5Ph_4$$H$), 2.90 (d, 2 H, C$H_aH_x$Ph, $^2J_{HH}$ = 8.2 Hz), 1.48 (d, 2 H, CH$_a$$H_x$Ph, $^2J_{HH}$ = 8.2 Hz).

Cp$^{\phi}$Mo(NO)(CH$_2$Ph)$_2$ was isolated in 62% yield. Anal. Calcd for C$_{43}$H$_{35}$NOMo: C, 76.22; H, 5.17; N, 2.07. Found: C, 76.02; H, 5.20; N, 1.91. IR (Nujol mull): ν_{NO} 1613, 1597 cm^{-1}. FAB mass spectrum: m/z 585 [P$^+$ − CH$_2$Ph], 555 [P$^+$ − CH$_2$Ph − NO]. ^{1}H NMR (C$_6$D$_6$): δ 7.35–6.75 (m, 30 H, C$_5$(C$_6$$H_5$)$_4H, CH_2$(C$_6$$H_5$)), 5.90 (s, 1 H, C$_5Ph_4$$H$), 2.97 (d, 2 H, C$H_aH_x$Ph, $^2J_{HH}$ = 6.3 Hz), 1.29 (d, 2 H, CH$_a$$H_x$Ph, $^2J_{HH}$ = 6.3 Hz).

Preparation of Cp$^{\phi}$Mo(NO)$_2$Cl. A mixture of orange Cp$^{\phi}$Mo(NO)(CO)$_2$ (1.28 g, 2.30 mmol) and white [NO][PF$_6$] (0.41 g, 2.2 mmol) in CH$_2$Cl$_2$ (30 mL) was stirred at room temperature for 2 min whereupon the solution became dark green. Stirring was continued for 1 h, and the mixture was then filtered through Celite (2 × 1 cm) supported on a medium-porosity frit. To the filtrate was added [(PhCH$_2$)Et$_3$N]Cl (0.50 g, 2.2 mmol), and the mixture was stirred for 30 min. The final mixture was filtered, hexanes (20 mL) were added to the filtrate, and the resulting solution was cooled to −30 °C overnight to induce the precipitation of dark yellow Cp$^{\phi}$Mo(NO)$_2$Cl (0.87 g, 67% yield).

Anal. Calcd for C$_{29}$H$_{21}$N$_2$O$_2$ClMo: C, 62.11; H, 3.75; N, 4.99. Found: C, 62.31; H, 3.79; N, 5.00. IR (Nujol mull): ν_{NO} 1737, 1665 cm^{-1}. EI low-resolution mass spectrum (probe temperature 120 °C): m/z 562 [P$^+$], 532 [P$^+$ NO], 502 [P$^+$ − 2NO]. ^{1}H NMR (C$_6$D$_6$): δ 7.2–6.7 (m, 20 H, C$_5$(C$_6$$H_5$)$_4$H), 6.14 (s, 1 H, C$_5Ph_4$$H$).

Preparation of Cp$^{\phi}$Mo(NO)$_2$Ph. Cp$^{\phi}$Mo(NO)(CO)$_2$ (1.0 g, 1.8 mmol) was dissolved in CH$_2$Cl$_2$ (30 mL), and 0.33 g (1.8 mmol) of [NO][PF$_6$] was added to the stirred solution. Over a period of 2 min the solution became dark green. Stirring was continued for 1 h, and the mixture was then filtered through Celite (2 × 1 cm) supported on a medium-porosity frit. To the filtrate was added Na[BPh$_4$] (0.74 g, 1.8 mmol). The mixture was stirred at ambient temperatures for 1 h and then filtered through basic alumina I (2 × 10 cm). The column was rinsed with CH$_2$Cl$_2$ until the washings were colorless. The solvent was removed from the combined filtrates under reduced pressure, and the green-brown residue was dissolved in Et$_2$O (50 mL). The resulting brown solution was concentrated in vacuo until incipient precipitation. This mixture was cooled to 8 °C overnight to complete the precipitation of green, crystalline Cp$^{\phi}$Mo(NO)$_2$Ph (0.75 g, 70% yield) which was collected by filtration.

Anal. Calcd for C$_{35}$H$_{26}$N$_2$O$_2$Mo: C, 69.77; H, 4.35; N, 4.65. Found: C, 70.11; H, 4.46; N, 4.33. IR (Nujol mull): ν_{NO} 1736, 1651 cm^{-1}. EI low-resolution mass spectrum (probe temperature 120 °C): m/z 604 [P$^+$], 574 [P$^+$ − NO]. ^{1}H NMR (CDCl$_3$: δ 7.8–6.7 (m, 25 H, C$_5$(C$_6$$H_5$)$_4H, C_6$$H_5$), 6.45 (s, 1 H, C$_5Ph_4$$H$).

Preparation of [Cp$_2$Co][Cp$^{\phi}$Mo(NO)Cl$_2$]. To a stirred green solution of Cp$^{\phi}$Mo(NO)Cl$_2$ (0.56 g, 1.0 mmol) in THF (30 mL) at room temperature was added Cp$_2$Co (0.19 g, 1.0 mmol). A green precipitate formed within 2 min. To the mixture was added Et$_2$O (15 mL), and the precipitate was collected by filtration and washed with Et$_2$O (3 × 10 mL). The isolated green solid was dried in vacuo for 2 h at ambient temperatures to obtain 0.38 g of analytically pure [Cp$_2$Co][Cp$^{\phi}$Mo(NO)Cl$_2$]. A further 0.22 g of crystalline material was isolated from the cooled filtrate (80% total yield).

Table I. Crystallographic Data for the Structure Determination of Cp$^{\phi}$W(NO)(CH$_2$SiMe$_3$)$_2$

formula	WSi$_2$ONC$_{37}$H$_{43}$	cryst syst	triclinic
fw	757.77	space group	$P\bar{1}$
a (Å)^a	10.3870 (7)	ρ_c (g cm^{-3})	1.432
b (Å)	11.6495 (7)	λ (Mo Kα_1) (Å)	0.709 30
c (Å)	16.3748 (16)	μ (Mo Kα) (cm^{-1})	34.5
α (deg)	81.164 (7)	min–max 2θ (deg)	4–50
β (deg)	84.809 (8)	transmission^b	0.514–0.556
γ (deg)	63.925 (6)	crystal dimens (mm)	0.19 × 0.25 × 0.26
V (Å^3)	1758.0	Z	2
R_F^{c}	0.021	R_{wF}^{d}	0.023

^{a} Cell dimensions were determined from 25 reflections (40° ≤ 2θ ≤ 45°). ^{b} The data were corrected analytically for the effects of absorption. ^{c} $R_F = \sum|(|F_o| - |F_c|)|/\sum|F_o|$, for all 6118 unique data (0.017 for 5542 observed). ^{d} $R_{wF} = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o^2)]^{1/2}$ for 6118 data (0.022 for 5542 observed); $w = [\sigma(F_o)^2 + 0.0001F_c^2]^{-1}$.

Anal. Calcd for C$_{39}$H$_{31}$NOCl$_2$MoCo: C, 62.08; H, 4.11; N, 1.86. Found: C, 62.25; H, 4.23; N, 1.80. IR (Nujol mull): ν_{NO} 1561, 1549 cm^{-1}. X-band ESR spectrum: single strong resonance, g = 1.969.

X-ray Crystallographic Analysis of Cp$^{\phi}$W(NO)(CH$_2$SiMe$_3$)$_2$. A dark purple crystal was mounted on a Pyrex filament using epoxy adhesive. Intensity data were collected at ambient temperature with an Enraf-Nonius CAD-4F diffractometer using graphite-monochromatized Mo Kα radiation. The unit cell dimensions were determined from 25 well-centered reflections (40° ≤ 2θ ≤ 45°). Two intensity standards were measured every 1.33 h of exposure time and declined slightly (2%) during the course of data acquisition. The data were corrected analytically for absorption. Data reduction also included corrections for intensity scale variation and for Lorentz and polarization effects.

The structure was solved by standard Patterson/Fourier synthesis methods. After all the non-hydrogen atoms were located and refined, most of the hydrogen atoms were observed in an electron-density difference map but were placed in calculated positions [d(C–H) = 0.95 Å] with initial isotropic thermal parameters assigned dependent on the thermal motion of their respective carbon atoms. The final full-matrix least-squares refinement of 411 parameters, using all 6118 unique reflections, included an extinction parameter,[19] anisotropic thermal parameters for all non-hydrogen atoms, and coordinates for all non-hydrogen atoms except for the methyl carbon atoms which were refined with their hydrogen atoms as rigid groups. All other hydrogen-atom coordinates were linked to those of their respective carbon atoms. Independent parameters representing the mean isotropic thermal motion of each of the following groups of atoms were refined and the shifts applied to the individual isotropic temperature factors: the hydrogen atom on the cyclopentadienyl ring; each pair of methylene hydrogen atoms; the hydrogen atoms of each methyl group; the hydrogen atoms of each phenyl group. An empirical weighting scheme based on counting statistics was applied such that $\langle w(|F_o| - |F_c|)^2\rangle$ was nearly constant as a function of both $|F_o|$ and $[(\sin\theta)/\lambda]^2$. The refinement converged at R_F = 0.021 (R_F = 0.017 for 5542 data having $I_0 \geq 2.5\sigma(I_0)$).

Complex scattering factors for neutral atoms[20] were used in the calculation of structural factors. The programs used for absorption corrections, data reduction, structure solution, initial refinement, and plot generation were from the NRCVAX Crystal Structure System.[21] The program suite CRYSTALS[22] was employed in the final refinement. All computations were carried out on a MicroVAX-II computer. Crystal data are summarized

---

(19) Larson, A. C. In *Crystallographic Computing*: Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1969; p 291.

(20) *International Tables for X-ray Crystallography*; Kynoch Press: Brimingham, England, 1975; Vol. IV, p 99.

(21) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. NRCVAX—An Interactive Program System for Structure Analysis. *J. Appl. Crystallogr.* **1989**, *22*, 384.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^4$) for the Non-Hydrogen Atoms of $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{iso}
W	820.35(9)	1582.83(8)	2140.13(5)	316
Si(1)	2173.0(8)	1752.5(7)	120.8(4)	405
Si(2)	−2857.4(8)	3030.3(8)	1662.4(5)	476
O	−104(3)	4384(2)	2158(1)	576
N	251(2)	3257(2)	2092(1)	398
C(1)	335(3)	155(2)	3196(1)	374
C(2)	1646(3)	−658(2)	2832(1)	363
C(3)	2692(3)	−238(2)	2977(1)	333
C(4)	1985(3)	873(2)	3411(1)	337
C(5)	529(3)	1085(2)	3571(1)	362
C(6)	2533(3)	1346(3)	1260(1)	406
C(7)	1729(5)	549(4)	−262(2)	720
C(8)	717(4)	3394(3)	−122(2)	695
C(9)	3855(3)	1748(3)	−418(2)	586
C(10)	−1006(3)	1703(2)	1575(2)	424
C(11)	−2969(4)	4550(3)	1047(3)	754
C(12)	−3412(4)	3363(5)	2738(3)	916
C(13)	−4208(4)	2626(4)	1253(3)	723
C(21)	1816(3)	−1758(2)	2406(2)	403
C(22)	2627(3)	−2038(3)	1672(2)	555
C(23)	2764(4)	−3086(3)	1303(2)	677
C(24)	2120(4)	−3853(3)	1647(3)	640
C(25)	1328(4)	−3596(3)	2371(3)	597
C(26)	1167(3)	−2549(3)	2752(2)	512
C(31)	4272(3)	−943(2)	2846(1)	375
C(32)	5144(3)	−306(3)	2644(2)	443
C(33)	6621(3)	−998(4)	2569(2)	569
C(34)	7247(3)	−2307(4)	2693(2)	633
C(35)	6408(3)	−2961(3)	2898(2)	588
C(36)	4925(3)	−2277(3)	2980(2)	471
C(41)	2673(3)	1533(2)	3804(1)	371
C(42)	2836(3)	2612(3)	3423(2)	496
C(43)	3395(4)	3222(3)	3837(2)	603
C(44)	3813(3)	2767(3)	4638(2)	583
C(45)	3664(4)	1711(3)	5032(2)	600
C(46)	3102(3)	1081(3)	4616(2)	514
C(51)	−557(3)	1985(2)	4113(1)	395
C(52)	−682(3)	3212(3)	4153(2)	516
C(53)	−1699(4)	3998(3)	4675(2)	631
C(54)	−2608(4)	3574(3)	5156(2)	601
C(55)	−2485(3)	2359(3)	5127(2)	557
C(56)	−1450(3)	1561(3)	4611(2)	481

Table III. Selected Intramolecular Distances (Å) and Angles (deg) for $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$

Distances			
W–N	1.762(2)	W–C(1)	2.389(2)
W–C(2)	2.477(2)	W–C(3)	2.474(2)
W–C(4)	2.350(2)	W–C(5)	2.351(2)
W–Cp[a]	2.082	W–C(6)	2.131(2)
W–C(10)	2.126(2)	Si(1)–C(6)	1.882(2)
Si(1)–C(7)	1.861(3)	Si(1)–C(8)	1.853(3)
Si(1)–C(9)	1.883(3)	Si(2)–C(10)	1.875(3)
Si(2)–C(11)	1.859(4)	Si(2)–C(12)	1.848(4)
Si(2)–C(13)	1.867(3)	O–N	1.218(3)
Angles			
C(6)–W–N	93.7(1)	C(10)–W–N	96.3(1)
C(10)–W–C(6)	111.1(1)	N–W–Cp	126.1
C(6)–W–Cp	113.3	C(10)–W–Cp	113.8
C(7)–Si(1)–C(6)	111.2(2)	C(8)–Si(1)–C(6)	111.5(1)
C(8)–Si(1)–C(7)	110.1(2)	C(9)–Si(1)–C(6)	106.9(1)
C(9)–Si(1)–C(7)	109.9(2)	C(9)–Si(1)–C(8)	107.2(2)
C(11)–Si(2)–C(10)	110.4(1)	C(12)–Si(2)–C(10)	113.0(2)
C(12)–Si(2)–C(11)	107.6(2)	C(13)–Si(2)–C(10)	110.9(1)
C(13)–Si(2)–C(11)	107.4(2)	C(13)–Si(2)–C(12)	107.4(2)
Si(2)–C(10)–W	124.3(1)	Si(1)–C(6)–W	120.4(1)
O–N–W	172.1(2)		

[a] Cp denotes the center of mass of the five C atoms of the Cp ring.

in Table I. The atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table II. Selected bond lengths (Å) and angles (deg) for the complex are presented in Table III. Hydrogen atom parameters, anisotropic thermal parameters, additional bond lengths and angles, torsion angles and least-squares planes are provided as supplementary material. A stereoview of the solid-state molecular structure of $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$ is presented in Figure 1.

Results and Discussion

Synthesis and Characterization of Tetraphenylcyclopentadienyl Mononitrosyl Complexes of Molybdenum and Tungsten. These complexes are prepared by employing synthetic methodology analogous to that used previously[23,24] to synthesize their Cp (η^5-C_5H_5) and Cp* (η^5-C_5Me_5) analogues (eqs 1–3; M = Mo, W). Thus, in the first step of eq 1, tetraphenylcyclopentadiene is deprotonated by *n*-BuLi and the resulting $Cp^{\phi-}$ anion reacts with the metal hexacarbonyl to displace three CO ligands and form the $[Cp^{\phi}M(CO)_3]^-$ anions.[23] These latter anions (which have not been isolated during this work) can be nitrosylated in situ with Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) to obtain the corresponding dicarbonyl nitrosyls (eq 2).

$$Cp^{\phi}H + n\text{-BuLi} + M(CO)_6 \xrightarrow[\text{reflux}]{\text{THF}} Li^+[Cp^{\phi}M(CO)_3]^- + 3CO + n\text{-BuH} \quad (1)$$

$$Li^+[Cp^{\phi}M(CO)_3]^- \xrightarrow[\text{THF},20\,°C]{\text{Diazald}} Cp^{\phi}M(NO)(CO)_2 \quad (2)$$

$$Cp^{\phi}M(NO)(CO)_2 \xrightarrow[Et_2O,\ 20\,°C]{PCl_5} Cp^{\phi}M(NO)Cl_2 \quad (3)$$

The $Cp^{\phi}M(NO)(CO)_2$ (M = Mo, W) complexes are air-stable, orange solids that are readily soluble in common organic solvents. Interestingly, the IR spectra of these complexes as Nujol mulls or KBr pellets display four bands attributable to ν_{CO} and two assignable to ν_{NO} whereas only half of that number is expected for each. Nevertheless, these CO- and NO-stretching frequencies are very similar in energy to those observed for the analogous Cp systems (Table IV), thereby indicating that the amount of electron density available for back-bonding on the metal center in the Cp^{ϕ} complexes more resembles that extant in the Cp systems rather than that in the more electron-rich Cp* systems. This conclusion is supported by their redox properties (vide infra). The electronic similarity of the Cp^{ϕ} and Cp ligands in metallocene complexes of the first-row transition metals has been previously established by other investigators.[8]

The dichloro mononitrosyl species, $Cp^{\phi}M(NO)Cl_2$, are generated by treatment of the dicarbonyl nitrosyl precursors with an equimolar amount of PCl_5 (eq 3). Much longer reaction times than those required to prepare the analogous Cp and Cp* complexes in this manner[24] are necessary to ensure good yields of the desired Cp^{ϕ} products. The $Cp^{\phi}M(NO)Cl_2$ product complexes are air-stable solids

---

[22] Watkin, D. J.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS; Chemical Crystallography Laboratory, University of Oxford: Oxford, England, 1984; Vol. 23, p 2336.

[23] Chin, T. T.; Hoyano, J. K.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1990**, 28, 196.

[24] Dryden, N. H.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 2077.

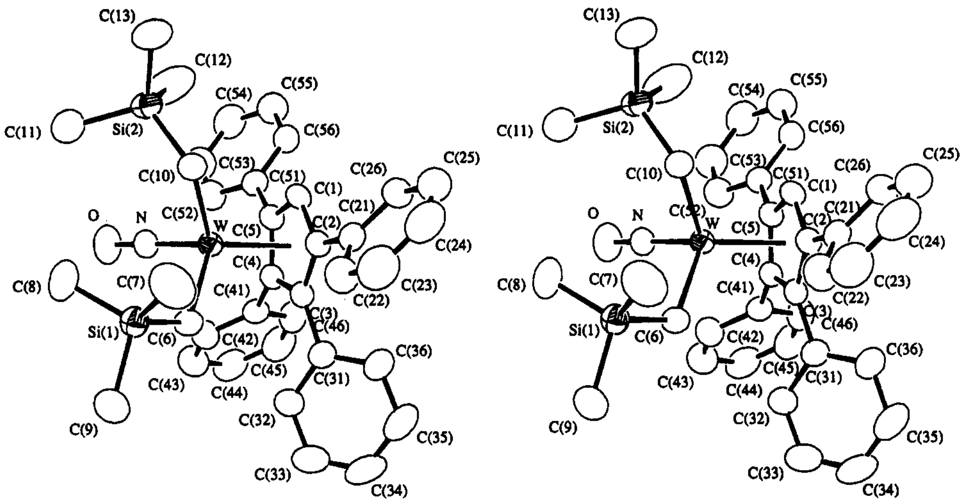


Figure 1. Stereoview of the molecular structure of Cp$^{\phi}$W(NO)(CH_2SiMe_3)$_2$. The hydrogen atoms have been omitted for clarity.

Table IV. Infrared Data (cm^{-1}) for Mononitrosyl Complexes

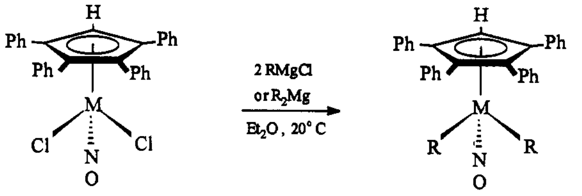
compd	Cp$^{\phi}$		Cp		Cp*	
	ν_{NO}	ν_{CO}	ν_{NO}	ν_{CO}	ν_{NO}	ν_{CO}
Cp′Mo(NO)(CO)$_2$^{a}	1666	2017, 1942	1663	2020, 1937	1639	2004, 1923
Cp′W(NO)(CO)$_2$^{a}	1657	2008, 1930	1665	2010, 1925	1636	1993, 1909
Cp′W(NO)(CO)$_2$^{b}	1676	2006, 1991	1637	2002, 1925	1637	1981, 1903
	1657	1923, 1910		1904		1890
Cp′Mo(NO)Cl_2^{c}	1634		1679		1655	
Cp′W(NO)Cl_2^{c}	1651		1634		1630	
Cp′Mo(NO)(CH_2SiMe_3)$_2$^{d}	1592		1587		1595	
Cp′W(NO)(CH_2SiMe_3)$_2$^{d}	1569		1550		1549	

^{a} CH_2Cl_2. ^{b} KBr. ^{c} THF. ^{d} Nujol.

that are readily soluble in polar organic solvents. The solid molybdenum compound, like all the Cp and Cp* analogues, is orange-brown in color, whereas the tungsten complex is uniquely green. However, solutions of these complexes are all blue-green, a manifestation that they contain the compounds as solvated monomers.[17] Hence, the bulkiest of these complexes, namely Cp$^{\phi}$W(NO)Cl_2, is probably also monomeric in the solid state.[25] This feature does not appear to have an effect on the chemical properties of the tungsten compound relative to its molybdenum congener.

While conversions 1–3 are effective for synthesizing the desired molybdenum and tungsten complexes, they cannot be extended to encompass the corresponding chromium systems. For instance, attempts to obtain pure samples of Cp$^{\phi}$Cr(NO)(CO)$_2$ via reactions of type 2 fail due to the ease with which nitrosylating agents such as Diazald, [NO][PF_6], or alkyl nitrites displace the tetraphenylcyclopentadienyl ring from the metal's coordination sphere in the chromium tricarbonyl anion. Similar problems plague the attempts to generate Cp$^{\phi}$Cr(NO)(CO)$_2$ by treating crude [Cp$^{\phi}$Cr(CO)$_3$]$_2$ with NO gas. The bulky Cp$^{\phi}$ ligands thus appears to be quite substitutionally labile when attached to the smallest member of the group 6 transition metals. Consequently, the chromium analogues of the product complexes in reactions 1–3 have yet to be obtained from such conversions.

Dialkyl compounds of the type Cp$^{\phi}$M(NO)(alkyl)$_2$ are readily preparable from their dichloro precursors by simple metathesis reactions (eq 4). The preparation and isolation of these dialkyl complexes is is generally less complicated than for the Cp and Cp* systems. The syntheses of the latter compounds via reactions of type 4 proceed via isonitrosyl complexes having M–NO→Mg linkages which must be cleaved by water in order to liberate the final Cp′M(NO)(alkyl)$_2$ complexes (Cp′ = Cp, Cp*).[26] In the tetraphenylcyclopentadienyl systems similar magnesium adducts do not persist at room temperature. The net result is that the syntheses of the Cp$^{\phi}$M(NO)(alkyl)$_2$ complexes by reactions 4 are free of any unwanted byproducts.



(4)

R = CH_2SiMe_3 or CH_2Ph

The Cp$^{\phi}$M(NO)(alkyl)$_2$ complexes are orange (CH_2Ph) or purple (CH_2SiMe_3) solids whose spectroscopic properties are consistent with their possessing three-legged piano-stool molecular structures. The Cp$^{\phi}$M(NO)(CH_2SiMe_3)$_2$ complexes are thus formally 16-electron species. The Cp$^{\phi}$M(NO)(CH_2Ph)$_2$ complexes, on the other hand, are 18-electron compounds which are stereochemically nonrigid organometallic molecules possessing

---

(25) The monomeric nature of Cp*W(NO)I_2 has been definitively established; see: Dryden, N. H.; Legzdins, P.; Einstein, F. W. B.; Jones, R. H. *Can. J. Chem.* **1988**, *66*, 2100.

(26) (a) Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411. (b) Hunter, A. D.; Legzdins, P.; Martin, J. T.; Sánchez, L. *Organomet. Synth.* **1986**, *3*, 58.

$Cp^{\phi}M(NO)(\eta^2\text{-}CH_2Ph)(\eta^1\text{-}CH_2Ph)$ instantaneous structures like their Cp and Cp* analogues.[27] The $Cp^{\phi}M(NO)(alkyl)_2$ systems are also more stable with respect to air and moisture than are the analogous Cp′ (Cp′ = Cp, Cp*) complexes. For instance, while the $Cp'W(NO)(CH_2SiMe_3)_2$ compounds readily convert to $Cp'W(O)_2(CH_2SiMe_3)$ complexes upon exposure to air,[28] solutions of $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$ are stable in air at ambient temperatures for at least 1 month. This observation suggests that the incoming O_2 molecules simply cannot access the expected reactive site[12,26] at the tungsten center in the Cp^{ϕ} complex as readily as they can in the Cp′ species. To establish that no unexpected structural features contribute to the unusual stability of $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$, a single-crystal X-ray crystallographic analysis of the complex was performed.

Crystal Structure of $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$. The crystal structure consists of molecules of $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$ separated by typical van der Waals distances. The shortest intermolecular separations are as follows: O(1)–H(25) ($x, 1 + y, z$), 2.59 Å; C(8)–H(82) ($-x, 1 - y, -z$), 2.75 Å; H(82)–H(82) ($-x, 1 - y, -z$) 2.26 Å. A stereoview of the molecule is shown in Figure 1, and selected bond lengths (Å) and angles (deg) for the complex are presented in Table III. The molecule has a typical three-legged piano-stool structure, the Cp^{ϕ} ligand being oriented about the W to Cp^{ϕ} centroid axis such that C(3) approximately eclipses C(6) while C(1) roughly eclipses C(10). The dihedral angle between the best least-squares plane through the phenyl ring C(41–46) and that of the Cp^{ϕ} ring is 94.2(2)°, while the analogous dihedral angles for the other phenyl rings are 41.7(2)° [C(21–26)], 39.7(2)° [C(31–36)], and 37.2(2)° [C(51–56)]. It should be noted, however, that the plane of the latter ring is rotated away from the Cp^{ϕ} plane in the opposite sense from the preceding two.

Analogous bond lengths and angles for $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$ and $CpW(NO)(CH_2SiMe_3)_2$[29] are quite similar. The greater stability and slower reactivity of $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$ may indeed be attributed to the much more hindered approach of incoming reactants toward the tungsten atom. Not only do the phenyl groups block approach from the Cp^{ϕ} side of the molecule but their presence also results in rotation of one of the CH_2SiMe_3 groups about the C(6)–W bond toward the other CH_2SiMe_3 ligand (cf. the bond torsion angles: C(10)–W–C(6)–Si(1) 18.2(1)° and C(6)–W–C(10)–Si(2) –127.5(2)°, thus further blocking access to the metal center's vacant orbital[12,26] in the plane bisecting the $H_2C\text{–}M\text{–}CH_2$ angle on the side of the complex opposite to the Cp^{ϕ} ligand. The second CH_2SiMe_3 ligand takes advantage of the opening left by the unsubstituted position on the Cp^{ϕ} ring (at C(1)) to remain in approximately the same conformation as those in $CpW(NO)(CH_2SiMe_3)_2$.[29] It can be expected that other rotamers of $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$ will similarly display some blocking of reactant approach to the metal center from the side opposite the Cp^{ϕ} group by one or both of the CH_2SiMe_3 groups. Evidently, this blocking is sufficient to prevent the attack of O_2 and the subsequent oxidation of the complex under ambient conditions.

Synthesis and Characterization of Tetraphenylcyclopentadienyl Dinitrosyl Complexes of Molybdenum. The conventional method for synthesizing $Cp'M(NO)_2Cl$ complexes involves treating $Cp'M(NO)(CO)_2$ with an equimolar amount of nitrosyl chloride.[23,30] However, this methodology does not work for the Cp^{ϕ} systems. Thus, treatment of $Cp^{\phi}Mo(NO)(CO)32$ with ClNO in CH_2Cl_2 at 20 °C affords only trace amounts of the desired $Cp^{\phi}Mo(NO)_2Cl$ complex but copious quantities of purple tetraphenylcyclopentadienone, the latter being readily identifiable by mass spectrometry. It thus appears that the Cp^{ϕ} ligand is prone to oxidation and displacement from the metal's coordination sphere by ClNO. This problem can be overcome for the molybdenum complexes by utilizing NO^+ as the nitrosylating agent[31] as shown in the sequential reactions summarized in eq 5. The first step generates a cationic dinitrosyl species which can combine with a source of chloride or phenyl anion to produce the neutral dinitrosyl chloride or phenyl complex, respectively. This behavior is consistent with that previously observed for the other $[Cp'M(NO)_2]^+$ cations.[32] Regrettably, all attempts to prepare the analogous tetraphenylcyclopentadienyl tungsten dinitrosyl complexes by similar methods have failed to date. IR monitoring indicates that reaction of $Cp^{\phi}W(NO)(CO)_2$ with $[NO][PF_6]$ in CH_2Cl_2 at 20 °C does indeed generate the $[Cp^{\phi}W(NO)_2]^+PF_6^-$ salt (cf. eq 5). However, subsequent treatment of the dinitrosyl cation with a variety of nucleophiles does not afford neutral $Cp^{\phi}W(NO)_2$-containing complexes.[33]

$$Cp^{\phi}Mo(NO)(CO)_2 \xrightarrow[CH_2Cl_2,\ 20\ ^{\circ}C]{[NO][PF_6]}$$

$$[Cp^{\phi}Mo(NO)_2]^+ PF_6^- \xrightarrow[CH_2Cl_2,\ 20\ ^{\circ}C]{X^-} Cp^{\phi}Mo(NO)_2X \qquad (5)$$

$$X = Cl, Ph$$

The $Cp^{\phi}Mo(NO)_2X$ complexes (X = Cl, Ph) are air-stable solids whose spectroscopic properties are consistent with their being 18-valence-electron species possessing piano-stool molecular structures. Most notably, the ν_{NO}'s evident in their IR spectra are virtually identical to those exhibited by their Cp analogues. Thus, the ν_{NO} values of $Cp^{\phi}Mo(NO)_2Ph$ and $CpMo(NO)_2Ph$ in CH_2Cl_2 are 1736, 1647 and 1741, 1649 cm^{-1}, respectively, thereby indicating again the electronic similarities of the Cp^{ϕ} and Cp ligands.

Cyclic Voltammetry Studies. The redox properties, particularly the reduction behavior, of the new Cp^{ϕ} complexes synthesized during this work have been established by cyclic voltammetry and have been compared with those of their Cp and Cp* analogues. Much of this latter comparative data has been obtained for the first time during this investigation. Before we consider specific cases, some important features concerning our electrochemical studies must be noted. The cyclic voltammograms of the various complexes in CH_2Cl_2 or THF show only minor variations. Secondly, the designation below of a feature as reversible means that it is similar to that

---

[27] Legzdins, P.; Jones, R. H.; Phillips, E. C.; Yee, V. C.; Trotter, J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 986.

[28] Legzdins, P.; Phillips, E. C.; Sánchez, L. *Organometallics* **1989**, *8*, 940.

[29] Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1988**, *7*, 2394.

[30] Legzdins, P.; Martin, D. T. *Organometallics* **1983**, *2*, 1785.

[31] Stewart, R. P.; Moore, G. T. *Inorg. Chem.* **1975**, *14*, 2699.

[32] Legzdins, P.; Richter-Addo, G. B.; Einstein, F. W. B.; Jones, R. H. *Organometallics* **1990**, *9*, 431.

[33] Treatment of $[CpW(NO)_2L]^+$ with X^- affords radicals rather than the expected $CpW(NO)_2X$; see: Yu, Y. S.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1982**, *21*, 3106.

Table V. Cyclic Voltammetry Data

compd	scan rate (V s^{-1})	$E^{\circ\prime}_1$ (V)	ΔE (mV)	i_{pa}/i_{pc}	ΔE (mV) Fc/Fc$^+$
$Cp^{\phi}Mo(NO)(CO)_2$[a]	0.1	−1.73	180	0.82	96
	0.5	−1.73	240	0.91	138
	1	−1.73	330	0.98	176
$CpMo(NO)(CO)_2$[b,c]		−1.73			
$Cp^*Mo(NO)(CO)_2$[b]	0.1	−1.84	110	0.93	110
	0.5	−1.84	160	0.98	171
	1	−1.84	210	0.99	
$Cp^{\phi}W(NO)(CO)_2$[b]	0.1	−1.66	90	0.95	110
	0.5	−1.66	130	1.00	187
	1	−1.66	190	1.02	233
$CpW(NO)(CO)_2$[b]	0.1	−1.77	130	1.00	111
	0.5	−1.77	190	1.03	170
	1	−1.77	240	1.04	221
$Cp^*W(NO)(CO)_2$[b]	0.1	−1.86	120	1.00	110
	0.5	−1.86	190	1.00	188
	1	−1.86	240	1.00	230
$Cp^{\phi}Mo(NO)Cl_2$[a]	0.1	−0.10	70	1.00	91
	0.5	−0.10	102	1.01	147
	1	−0.10	130	1.00	183
$Cp^{\phi}Mo(NO)Cl_2$[b]	0.1	−0.13	98	1.03	157
	0.5	−0.13	146	1.08	250
	1	−0.13	187	1.09	320
$CpMo(NO)Cl_2$[a,17]		−0.10			
$Cp^*Mo(NO)Cl_2$[a],[17]		−0.35			
$Cp^{\phi}W(NO)Cl_2$[a]	0.1	−0.42	64	0.87	110
	0.5	−0.42	106	0.98	154
	1	−0.42	123	0.98	228
$CpW(NO)Cl_2$[a,d]	0.1	−0.39			
	0.5	−0.39			179
	1	−0.39			224
$Cp^*W(NO)Cl_2$[a,e]	0.1	−0.68			104
	0.5	−0.68			166
	1	−0.68			211
$Cp^{\phi}Mo(NO)(CH_2SiMe_3)_2$[a]	0.1	−1.19	90	1.00	77
	0.5	−1.19	160	1.06	135
	1	−1.19	200	1.05	169
$CpMo(NO)(CH_2SiMe_3)_2$[b]	0.1	−1.23	140	1.05	124
	0.4	−1.23	230	1.05	
	0.5	−1.23	230	1.05	207
$Cp^*Mo(NO)(CH_2SiMe_3)_2$[b,18]		−1.55			
$Cp^{\phi}W(NO)(CH_2SiMe_3)_2$[a]	0.1	−1.43	90	1.00	83
	0.5	−1.43	120	1.03	124
	1	−1.43	140	1.02	150
$CpW(NO)(CH_2SiMe_3)_2$[a,17]		−1.51			
$Cp^*W(NO)(CH_2SiMe_3)_2$[a,17]		−1.66			

[a] CH_2Cl_2. [b] THF. [c] 233 K, see also ref 35a. [d] $E_{p,c}$ (irreversible reduction). [e] A second reduction occurs at −1.18 V.

exhibited by ferrocene and a plot of $i_{p,c}$ vs $\nu^{1/2}$ for that feature is indeed linear. Furthermore, all complexes studied undergo irreversible oxidations[34] whose exact natures we have not investigated further at the present time.

(1) Dicarbonyl Nitrosyl Complexes. The behavior of all the $Cp'M(NO)(CO)_2$ complexes (Cp′ = Cp, Cp*, or Cp^{ϕ}) upon the addition of electrons is quite similar, as evidenced by the electrochemical data for the reductions of the compounds summarized in Table V. All the dicarbonyl nitrosyl compounds in CH_2Cl_2 or THF undergo a facile one-electron chemical reduction that can be represented by eq 6. For $Cp^{\phi}Mo(NO)(CO)_2$ this reduction

$$[Cp'M(NO)(CO)_2] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Cp'M(NO)(CO)_2]^- \quad (6)$$

appears to be a quasi-reversible process, as evidenced by the large peak separations as compared to Cp_2Fe (Table V). This feature is similar to the behavior exhibited by $CpMo(NO)(CO)_2$ at low temperatures.[35a] The quasi-reversibility of these molybdenum systems may be due to the occurrence of some structural rearrangement upon reduction.[35b] In contrast, $Cp^*Mo(NO)(CO)_2$ and the tungsten congeners exhibit fully reversible behavior. A cyclic voltammogram of $Cp^{\phi}W(NO)(CO)_2$ in THF is displayed in Figure 2 from which the reversible nature of the reduction is clearly evident.

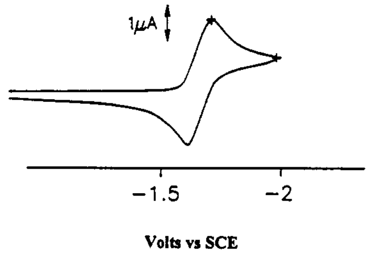


Figure 2. Ambient-temperature cyclic voltammogram of 5 × 10^{-4} M $Cp^{\phi}W(NO)(CO)_2$ in THF containing 0.1 M $[n\text{-}Bu_4N]PF_6$ measured at a platinum-bead electrode at a scan rate of 0.1 V s^{-1}.

From the data presented in Table V it is also clear that the reduction behavior of the Cp^{ϕ} complexes is quite similar to that of their Cp analogues. This behavior of the Cp^{ϕ} compounds encouraged us to attempt the synthesis of one of the radical anions by chemical reduction. Addition of an Et_2O solution of $Cp^{\phi}W(NO)(CO)_2$ to a suspension of Cp^*_2Co in Et_2O results in the precipitation of a very unstable brown solid which exhibits spectroscopic properties consistent with it containing the 19-electron $[Cp^{\phi}W(NO)(CO)_2]^-$ radical anion. Thus, the solid as a Nujol mull displays two IR bands at 1970 and 1854 cm^{-1} attributable to ν_{CO}, as compared to the four bands exhibited by the starting material at 2004, 1988, 1922, and 1910 cm^{-1}. The position of ν_{NO} in the IR spectrum of the final product is 1590 cm^{-1}, which is 72 cm^{-1} lower than the average ν_{NO} for the starting material. These relatively small shifts in the positions of the IR bands indicate that the majority of the extra electron density in the anion is probably delocalized primarily onto the Cp^{ϕ} ring rather than the NO ligand, as has been observed for the analogous Cp system at low temperature.[35]

(2) Dichloro Nitrosyl Complexes. The cyclic voltammetry data for the reduction of the dichloro nitrosyl complexes are summarized in Table V. Like its Cp and Cp* analogues,[17] $Cp^{\phi}Mo(NO)Cl_2$ undergoes a reversible, one-electron reduction. Unlike the molybdenum species which exhibit similar reduction behavior regardless of the nature of the cyclopentadienyl ligand, the $Cp'W(NO)Cl_2$ complexes display somewhat different electrochemical behavior as Cp′ is varied. The cyclic voltammogram of $Cp^{\phi}W(NO)Cl_2$ in CH_2Cl_2 is displayed in Figure 3a. Under the experimental conditions employed throughout this study, the compound exhibits a reversible one-electron reduction of $E^{\circ\prime}$ = −0.42 V versus SCE. These facts are consistent with the stoichiometry of the reduction of the 16-electron $Cp^{\phi}W(NO)Cl_2$ species being as indicated in eq 7. Figure 3b contains the cyclic voltammogram of $CpW(NO)Cl_2$ recorded under identical experimental con-

---

[34] Oxidation potentials vs SCE for the various complexes are: $Cp^{\phi}Mo(NO)(CO)_2$ in CH_2Cl_2, 1.73 V; $Cp^{\phi}W(NO)(CO)_2$ in THF, 0.98 V; $Cp^{\phi}Mo(NO)(CH_2SiMe_3)_2$ in CH_2Cl_2, 1.30 V; $Cp^{\phi}W(NO)(CH_2SiMe_3)_2$ in CH_2Cl_2, 1.23 V.

[35] (a) Geiger, W. E.; Rieger, P. H.; Tulyathan, B.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 7000. (b) Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 275. (c) A reviewer has suggested another possible interpretation of the pertinent electrochemical and IR data, namely that the unstable $[Cp^{\phi}W(NO)(CO)_2]^{\bullet-}$ radical anion may well contain a bent NO ligand. We acknowledge that the available data do not exclude such a possibility.

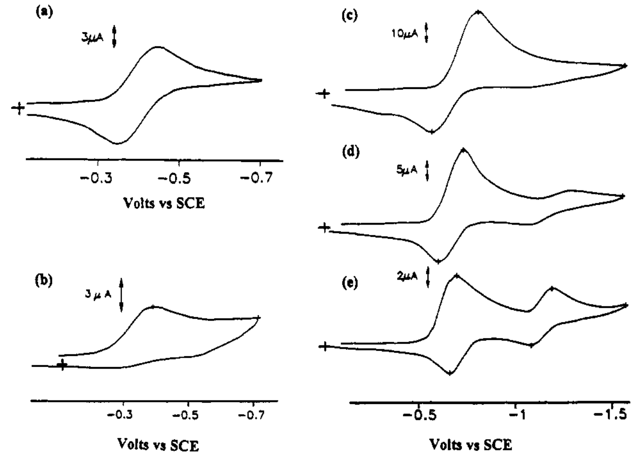


Figure 3. (a) Ambient-temperature cyclic voltammogram of 5 × 10^{-4} M $\mathrm{Cp^{\phi}W(NO)Cl_2}$ in $\mathrm{CH_2Cl_2}$ containing 0.1 M $[n\text{-}\mathrm{Bu_4N}]\mathrm{PF_6}$ measured at a platinum-bead electrode at a scan rate of 0.2 V $\mathrm{s^{-1}}$. (b) Ambient-temperature cyclic voltammogram of 5 × 10^{-4} M $\mathrm{CpW(NO)Cl_2}$ in $\mathrm{CH_2Cl_2}$ containing 0.1 M $[n\text{-}\mathrm{Bu_4N}]\mathrm{PF_6}$ measured at a platinum-bead electrode at a scan rate of 0.5 V $\mathrm{s^{-1}}$. (c) Ambient-temperature cyclic voltammogram of 5 × 10^{-4} M $\mathrm{Cp^{*}W(NO)Cl_2}$ in $\mathrm{CH_2Cl_2}$ containing 0.1 M $[n\text{-}\mathrm{Bu_4N}]\mathrm{PF_6}$ measured at a platinum-bead electrode at 2.75 V $\mathrm{s^{-1}}$. (d) Ambient-temperature cyclic voltammogram of 5 × 10^{-4} M $\mathrm{Cp^{*}W(NO)Cl_2}$ in $\mathrm{CH_2Cl_2}$ containing 0.1 M $[n\text{-}\mathrm{Bu_4N}]\mathrm{PF_6}$ measured at a platinum-bead electrode at 0.8 V $\mathrm{s^{-1}}$. (e) Ambient-temperature cyclic voltammogram of 5 × 10^{-4} M $\mathrm{Cp^{*}W(NO)Cl_2}$ in $\mathrm{CH_2Cl_2}$ containing 0.1 M $[n\text{-}\mathrm{Bu_4N}]\mathrm{PF_6}$ measured at a platinum bead electrode at 0.1 V $\mathrm{s^{-1}}$.

ditions. The experimental trace indicates that the complex undergoes an irreversible reduction at $E_{\mathrm{p,c}} = -0.39$ V. Cyclic voltammograms of the pentamethylcyclopentadienyl analogue, $\mathrm{Cp^{*}W(NO)Cl_2}$, in $\mathrm{CH_2Cl_2}$ at different scan rates

$$[\mathrm{Cp^{\phi}W(NO)Cl_2}] \underset{-\mathrm{e^-}}{\overset{+\mathrm{e^-}}{\rightleftharpoons}} [\mathrm{Cp^{\phi}W(NO)Cl_2}]^{\bullet-} \quad (7)$$

are shown in Figure 3c–e for comparison. In this case, at least two quasi-reversible reductions occur. The first occurs at $E^{\circ\prime} = -0.68$ V, and the intensity of the wave for the second redox couple at $E^{\circ\prime} = -1.18$ V becomes more pronounced at lower scan rates. The latter feature probably corresponds to the formation of $[\mathrm{Cp^{*}W(NO)Cl}]_2$, similar behavior having been observed previously for the related $\mathrm{Cp^{*}W(NO)]_2}$ complex.[17] These observations also indicate that of the three $\mathrm{Cp'W(NO)Cl_2}$ complexes the one containing the $\mathrm{Cp^{\phi}}$ ligand forms the most stable complex upon reduction.

The reduction of $\mathrm{Cp^{\phi}Mo(NO)Cl_2}$ can also be effected on a preparative scale by utilizing cobaltocene, a moderately potent one-electron reductant (eq 8). This reductant was used rather than $\mathrm{Cp^{*}{}_2Co}$ because its $E_{1/2}$

$$\mathrm{Cp^{\phi}Mo(NO)Cl_2} + \mathrm{Cp_2Co} \rightarrow [\mathrm{Cp_2Co}]^{+}[\mathrm{Cp^{\phi}Mo(NO)Cl_2}]^{\bullet-} \quad (8)$$

occurs at a lower potential, but it is still sufficiently potent to effect reduction of the organometallic complex.[36] The product salt of reaction 8 is isolable in high yields as a green crystalline solid. As expected, the nitrosyl-stretching

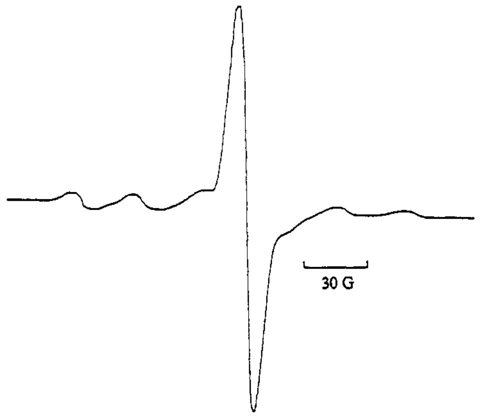


Figure 4. X-Band ESR spectrum of $[\mathrm{Cp_2Co}][\mathrm{Cp^{\phi}Mo(NO)Cl_2}]$ in THF at 20 °C.

frequency evident in the Nujol mull IR spectrum of the radical anion is some 120 $\mathrm{cm^{-1}}$ lower in energy than that displayed by its neutral precursor. The X-band ESR spectrum of $[\mathrm{Cp_2Co}][\mathrm{Cp^{\phi}Mo(NO)Cl_2}]$ in THF (Figure 4) consists of a single strong central resonance ($g = 1.969$) flanked by molybdenum satellite signals due to $^{95}\mathrm{Mo}$ and $^{97}\mathrm{Mo}$ hyperfine coupling ($I = {}^5/_2$, natural abundance 15.9% and 9.6%, respectively). No $^{14}\mathrm{N}$ or $^{1}\mathrm{H}$ hyperfine coupling is evident in this spectrum. Consequently, it appears as though the unpaired electron density in the radical anion is primarily localized at the metal center, the a_{Mo} value of approximately 30 G indicating that about 3% of this electron density is localized in s-type orbitals on the metal center. These features are quite similar to those found previously for the related $[\mathrm{Cp_2Co}][\mathrm{CpMo(NO)Cl_2}]$ salt.[17]

(3) Dialkyl Complexes, $\mathrm{Cp'M(NO)(CH_2SiMe_3)_2}$. Again, the electrochemical data for the reduction of these compounds are summarized in Table V. All of them exhibit chemically reversible one-electron reductions (eq 9). While for the tungsten compounds all reductions are

$$[\mathrm{Cp'M(NO)(CH_2SiMe_3)_2}] \underset{-\mathrm{e^-}}{\overset{+\mathrm{e^-}}{\rightleftharpoons}} [\mathrm{Cp'M(NO)(CH_2SiMe_3)_2}]^{\bullet-} \quad (9)$$

electrochemically reversible, the molybdenum systems show quasi-reversibility.[18] For both $\mathrm{Cp^{\phi}}$ compounds, the electrochemical behavior again more closely resembles that exhibited by their Cp rather than their Cp* analogues. The cathodic shift in the $E^{\circ\prime}$ value as $\mathrm{Cp^{\phi}}$ is replaced by Cp and then by Cp* again reflects the increased electron density at the metal center due to the greater electron-donating ability of the pentamethylcyclopentadienyl ligand. The dialkyl complexes are more difficult to reduce than their dichloro precursors, a manifestation of the fact that alkyl ligands are better electron donors than are chloro ligands.[37]

Epilogue

In addition to establishing the synthesis and characterization of a variety of new tetraphenylcyclopentadienyl nitrosyl complexes of molybdenum and tungsten, this work has also demonstrated that in these complexes involving a second- and a third-row transition metal the bulky $\mathrm{Cp^{\phi}}$ ligand is electronically quite similar to its simpler Cp analogue. Thus, cyclic voltammetry has confirmed that

---

[36] Robbins, J. L.; Edelstein, B.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882.

[37] Kochi, J. K. *Pure Appl. Chem.* **1980**, *52*, 578.

the reduction properties of the various Cp^ϕ-containing complexes are quite similar to those exhibited by their Cp-containing analogues. The greater steric demands of the Cp^ϕ ligand, however, result in diminished reactivity of the $Cp^\phi M(NO)R_2$ (R = CH_2SiMe_3, CH_2Ph) systems with small molecules since requisite access to the reactive site at the metal center is apparently blocked by the ligands. These steric requirements thus result in Cp^ϕ-containing nitrosyl species of molybdenum and tungsten being more kinetically stable with respect to reactions with air and water than are their Cp or Cp* analogues. In future reports we shall present the results of our attempts to employ the Cp^ϕ group in Mo and W chemistry both to trap unstable reaction intermediates and to render reaction products more readily isolable.

One disadvantage of the larger Cp^ϕ group is that it is prone to be displaced from the coordination sphere of the smallest metal in group 6, particularly by oxidizing agents, a feature that has to date precluded the isolation of analytically pure tetraphenylcyclopentadienyl nitrosyl complexes of chromium.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. We also thank the Spanish Ministry of Education for the award of a postdoctoral fellowship to R.R.

Supplementary Material Available: Additional crystallographic data for $Cp^\phi W(NO)(CH_2SiMe_3)_2$ including tables of experimental details, hydrogen atom parameters, anisotropic thermal parameters, bond distances and angles, torsion angles, and least-squares planes (11 pages). Ordering information is given on any current masthead page.

OM9207267