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Synthesis, Characterization, and Reactivity of Alkoxo Complexes Containing Cp*M(NO) Groups (M = Mo, W)[1]

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Stepwise treatment of $Cp^*M(NO)Cl_2$ [$Cp^* = \eta^5\text{-}C_5Me_5$; M = Mo, W] in THF at low temperatures with 2 equiv of alkoxide anion affords first $Cp^*M(NO)(OR)Cl$ complexes and then the bis(alkoxo) compounds $Cp^*M(NO)(OR)_2$ [M = Mo, R = CMe_3; M = W, R = CMe_3, Ph, CH_2Ph], both types of complexes being isolable in reasonable yields. Alkoxo alkyl complexes are preparable from the corresponding alkyl chloro precursors by similar metathesis process. Single-crystal X-ray crystallographic analyses have been performed on $Cp^*W(NO)(OCMe_3)_2$ and $Cp^*W(NO)(OCH_2Ph)_2$ as representative members of the bis(alkoxide) class of compounds. Crystal data for $Cp^*W(NO)(OCMe_3)_2$ (**2**): $a = 23.627(3)$ Å, $b = 15.862(2)$ Å, $c = 11.009(3)$ Å, $V = 4125.7(11)$ Å^3, $Z = 8$, space group *Pbca* (No. 61); $R_F = 0.032$, $R_{wF} = 0.035$ for 2473 reflections with $I \geq 3\sigma(I)$. Crystal data for $Cp^*W(NO)(CH_2Ph)_2$ (**4**): $a = 8.758(2)$ Å, $b = 15.7617(13)$ Å, $c = 16.352(2)$ Å, $V = 2257.3(8)$ Å^3, $Z = 4$, space group *Pnma* (No. 62); $R_F = 0.031$, $R_{wF} = 0.034$ for 1807 reflections with $I \geq 3\sigma(I)$. Complexes **2** and **4** both have normal three-legged piano-stool molecular structures whose intramolecular dimensions are consistent with the existence of some degree of W–O multiple bonding. The IR spectra and electrochemical properties of both types of alkoxide complexes indicate that their metal centers are more electron-rich than those in comparable $Cp'M(NO)R_2$ complexes [R = alkyl, aryl; $Cp' = Cp(\eta^5\text{-}C_5H_5)$, Cp^*; M = Mo, W]. Representative reactions of selected complexes with O_2, H_2O, $CNCMe_3$, and HCl are presented. The outcomes of these reactions establish the relative Lewis acidities of these complexes as well as the polarities of their M–R and M–OR linkages.

Introduction

Previous work in these laboratories has established that the monomeric, 16-valence-electron $Cp'M(NO)R_2$ complexes [$Cp' = Cp(\eta^5\text{-}C_5H_5)$, $Cp^*(\eta^5\text{-}C_5Me_5)$; M = Mo, W; R = alkyl, aryl] have varied and interesting chemistries.[2] A logical extension of this work is the investigation of related compounds containing metal–heteroatom linkages such as metal–alkoxide or metal–amide in place of metal–alkyl or –aryl linkages. These complexes should possess greater metal–ligand bond polarity than their dialkyl or diaryl congeners and thus should exhibit increased reactivity with polar substrates. Furthermore, they should be weaker Lewis acids at the metal centers than the $Cp'M(NO)R_2$ systems since the electronic requirements of the metal centers may be satisfied to some extent by the existence of a degree of M–O or M–N multiple bonding. Consequently, we have decided to effect this extension of our previous research efforts, and in this paper we describe the results of our investigations with the oxygen-containing systems. Specifically, this paper summarizes the synthesis, characterization, and some characteristic chemistry of representative alkoxo and bis(alkoxo) complexes having the compositions $Cp^*M(NO)(OR)Cl$, $Cp^*M(NO)(R')(OR)$, and $Cp^*M(NO)(OR)_2$ (R,R′ = alkyl or aryl). Our related studies with isoelectronic amido complexes have been presented in a separate paper.[3]

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anhydrous conditions in an atmosphere of prepurified dinitrogen. General procedures routinely employed in these laboratories have been outlined elsewhere.[4] The reagents $Cp^*M(NO)Cl_2$,[5] $Cp^*M(NO)(CH_2Ph)Cl$,[6] and $(Me_3SiCH_2)_2Mg\cdot X(\text{dioxane})$[6] were synthesized by published procedures. $[LiOCMe_3]_x$ was prepared by reaction of *n*-BuLi with $HOCMe_3$ in diethyl ether,[7,8] and NaOR [R = Ph, CH_2Ph, Me] reagents were prepared by treating sodium metal in THF with the appropriate alcohol.[8] $CNCMe_3$ (Aldrich) and O_2 (Medigas, 99.5%) were used without any further purification.

The numbering scheme, colors, yields and elemental analysis data for complexes **1**–**13** are collected in Table I. The mass spectral and IR data for these compounds are compiled in Table II, and their ^1H and $^{13}C\{^1H\}$ NMR data are presented in Table III.

Preparation of $Cp^*M(NO)(OR)_2$ Complexes [M = Mo, R = CMe_3 (1); M = W, R = CMe_3 (2), Ph (3), CH_2Ph (4)]. All these complexes were synthesized similarly. The preparation of $Cp^*W(NO)(OCMe_3)_2$ (**2**) is described as a representative example.

A THF solution (20 mL) of $LiOCMe_3$ (0.58 g, 7.2 mmol) was added slowly via an addition funnel to a stirred THF solution

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(2) Legzdins, P.; Veltheer, J. E. *Acc. Chem. Res.* **1993**, *26*, 41; see also references cited therein.

(3) Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* **1993**, *12*, 2103.

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

(5) Dryden, N. H.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1991**, *10*, 2077.

(6) Dryden, N. H.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1991**, *10*, 2857.

(7) Cetinkaya, B.; Gümrükcü, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086.

(8) The compositions of the solids with respect to their active alkoxide equivalents were established by hydrolysis of weighed solid samples and titration of the resulting solutions with 0.100 N HCl using phenolphthalein as the indicator.

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Table I. Numbering Scheme, Colors, Yields, and Elemental Analysis Data for Complexes 1–13

complex	compd. no.	color (yield, %)	anal., % found (calcd) C	H	N
Cp*Mo(NO)(OCMe$_3$)$_2$	**1**	orange (67)	53.31 (53.07)	8.17 (8.16)	3.35 (3.44)
Cp*W(NO)(OCMe$_3$)$_2$	**2**	orange (32)	43.59 (43.65)	6.66 (6.72)	2.84 (2.83)
Cp*W(NO)(OPh)$_2$	**3**	red (20)	49.23 (49.36)	4.80 (4.71)	2.50 (2.62)
Cp*W(NO)(OCH$_2$Ph)$_2$	**4**	red (22)	51.06 (51.17)	5.24 (5.19)	2.45 (2.49)
Cp*Mo(NO)(OCMe$_3$)Cl	**5**	purple (25)	45.09 (45.48)	6.45 (6.54)	3.78 (3.78)
Cp*W(NO)(OCMe$_3$)Cl	**6**	purple-black (37)	36.81 (36.74)	5.40 (5.29)	3.00 (3.06)
Cp*W(NO)(OPh)Cl	**7**	red-black (44)	40.21 (40.23)	4.40 (4.22)	2.70 (2.93)
Cp*Mo(NO)(CH$_2$Ph)(OCMe$_3$)	**8**	red (56)	59.49 (59.29)	7.52 (7.34)	3.31 (3.29)
Cp*Mo(NO)(CH$_2$Ph)(OPh)	**9**	red (39)	62.22 (62.02)	6.03 (6.11)	3.29 (3.14)
Cp*W(NO)(CH$_2$Ph)(OCMe$_3$)	**10**	red (45)	49.05 (49.14)	6.05 (6.09)	2.70 (2.73)
Cp*W(NO)(CH$_2$SiMe$_3$)(OCMe$_3$)	**11**	red oil (≈30)	41.41 (42.44)[a]	6.73 (6.92)	2.87 (2.75)
Cp*W(NO)(CH$_2$SiMe$_3$)(OPh)	**12**	purple (66)	45.58 (45.38)	5.89 (5.90)	2.57 (2.65)
Cp*W(NO)(CH$_2$SiMe$_3$)(OMe)	**13**	red (26)	38.68 (38.55)	6.29 (6.25)	2.90 (3.00)

[a] The elemental analysis of C is expected to be low because of incomplete burning. Addition of V_2O_5 to this oil did not correct this problem.

Table II. Mass Spectral and Infrared Data for Complexes 1–13

compd. no.	MS, m/z[a]	temp,[b] °C	IR: ν_{NO}, cm^{-1} THF	Nujol
1	409 [P$^+$]	80	1589	1601
2	495 [P$^+$]	80	1557	1550
3	535 [P$^+$]	100	1593	1566
4	563 [P$^+$]	80	1556	1557
5	371 [P$^+$]	100	1622	1613
6	457 [P$^+$]	100	1593	1578
7	477 [P$^+$]	80	1595	1589
8	427 [P$^+$]	120	1601, 1593[c,e]	1596, 1586[e]
9	447 [P$^+$]	120	1613, 1588[c,e]	1595, 1578[e]
10	513 [P$^+$]	100	1568	1593, 1557[e]
11	509 [P$^+$]	120	1572[d]	1563
12	529 [P$^+$]	100	1597, 1586[d,e]	1584, 1545[e]
13	467 [P$^+$]	80	1584[d]	1578

[a] m/z values are for the highest intensity peak of the calculated isotopic cluster, i.e. ^{98}Mo and ^{184}W. [b] Probe temperatures. [c] Et$_2$O. [d] pentane. [e] ν_{C-C} are also observed in this region.

(20 mL) of Cp*W(NO)Cl$_2$ (1.5 g, 3.6 mmol), and the progress of the reaction was monitored by IR spectroscopy. The reaction proceeded in a straightforward manner with the initial diminution of the starting nitrosyl absorption band at 1630 cm^{-1} occurring concomitantly with the appearance and growth of a new band at 1593 cm^{-1}. As the addition of LiOCMe$_3$ continued, a second nitrosyl absorption band at 1557 cm^{-1} appeared at the expense of the band at 1593 cm^{-1}. During this time the reaction mixture changed from green to purple to deep orange-red. The solvent was removed from the final reaction mixture in vacuo, and the residue was extracted with hexanes (2 × 50 mL) which were filtered through Celite (3 × 6 cm) supported on a sintered-glass frit. The filtrate was concentrated in vacuo until incipient crystallization, and the mixture was then cooled at −30 °C overnight. The orange crystals of Cp*W(NO)(OCMe$_3$)$_2$ (0.57 g, 32% yield) thus formed were isolated by removal of the supernatant solution by cannulation and drying of the crystals in vacuo.

Preparation of Cp*M(NO)(OR)Cl Complexes [M = Mo, R = CMe$_3$ (5); M = W, R = CMe$_3$ (6), Ph (7)]. Since the synthetic approaches to these complexes are similar, their syntheses are presented in the next paragraph in a generalized manner.

Cp*M(NO)Cl$_2$ (1.00 mmol) and the appropriate alkoxide salt (1.00 mmol) were intimately mixed in a Schlenk tube contained in a glovebox. The tube was removed from the box, and THF (25 mL) was vacuum-transferred onto the solids at −196 °C. The stirred reaction mixture was then allowed to warm slowly to 0 °C, whereupon the color changed from red (M = Mo) or green (M = W) to purple and ν_{NO} diminished by approximately 35 cm^{-1} in the mixture's IR spectrum. The solvent was removed in vacuo, the purple residues were extracted with pentane, and the extracts were filtered through Celite (2 × 5 cm) supported on a sintered-glass frit. The filtrate was concentrated in vacuo until the first signs of crystallization were evident. Additional crystallization occurred upon storing these concentrated solutions at −30 °C overnight. Finally, the desired alkoxo chloro complexes were isolated by removal of the supernatant solution by cannulation and drying of the remaining black to purple needlelike crystals in vacuo.

Preparation of Cp*M(NO)(CH$_2$Ph)(OR) Complexes [M = Mo, R = CMe$_3$ (8), Ph (9); M = W, R = CMe$_3$ (10)]. Again, all of these complexes were prepared similarly. The synthesis of Cp*W(NO)(CH$_2$Ph)(OCMe$_3$) (**10**) is described in detail as a representative example.

In a Schlenk tube contained in a glovebox, Cp*W(NO)(CH$_2$Ph)Cl (0.31 g, 0.65 mmol) and LiOCMe$_3$ (0.050 g, 0.65 mmol) were intimately mixed. The tube was removed from the glovebox, and Et$_2$O (20 mL) was transferred to the tube via syringe. The orange-red reaction mixture was stirred overnight with no apparent color change occurring. The solvent was then removed in vacuo, the remaining red residue was extracted with hexanes (2 × 20 mL), and the extracts were filtered through Celite (2 × 5 cm) supported on a medium-porosity glass frit. The filtered solution was concentrated and cooled at −30 °C overnight to induce the precipitation of Cp*W(NO)(CH$_2$Ph)(OCMe$_3$) (0.33 g, 45% yield) as red needles, which were collected by filtration.

Preparation of Cp*W(NO)(CH$_2$SiMe$_3$)(OR) Complexes [R = CMe$_3$ (11), Ph (12), Me (13)]. A THF solution (30 mL) of Cp*W(NO)(CH$_2$SiMe$_3$)Cl[9] was generated from Cp*W(NO)Cl$_2$ (1.3 g, 3.0 mmol) and (Me$_3$SiCH$_2$)$_2$Mg·X(dioxane) (3.0 mmol CH$_2$SiMe$_3^-$) in a Schlenk tube.[10] The THF was removed from the blue reaction mixture in vacuo, and the blue residue was extracted with pentane (2 × 30 mL). The extracts were filtered through Celite (2 × 5 cm) supported on a sintered-glass frit. The filtrate was divided equally into three Schlenk tubes.

To each of the blue pentane solutions (ν_{NO} = 1616 cm^{-1}) was added the appropriate alkoxide salt (LiOCMe$_3$, NaOPh, or NaOMe; 1.0 mmol each, slight excess). The mixtures were stirred for 2 h and became red for R = CMe$_3$ (ν_{NO} = 1572 cm^{-1}) and Me (ν_{NO} = 1584 cm^{-1}) and purple for R = Ph (ν_{NO} = 1597, 1586 cm^{-1}). The final mixtures were filtered through Celite (2 × 5 cm) supported on sintered-glass frits. The filtered solutions were then concentrated and cooled at −30 °C overnight to induce the deposition of the desired organometallic product complexes. Cp*W(NO)(CH$_2$SiMe$_3$)(OCMe$_3$) (≈30% yield) was thus isolated as a red oil, whereas Cp*W(NO)(CH$_2$SiMe$_3$)(OPh) (0.35 g, 66% yield) and Cp*W(NO)(CH$_2$SiMe$_3$)(OMe) (0.12 g, 26% yield) were obtained as purple and red crystals, respectively.

Reactions of Cp*W(NO)(OCMe$_3$)$_2$ (2), Cp*W(NO)(OCMe$_3$)Cl (6), Cp*W(NO)(CH$_2$Ph)(OCMe$_3$) (10), and Cp*W(NO)(CH$_2$SiMe$_3$)(OPh) (12) with HCl. Et$_2$O solutions of complexes **2**, **6**, **10**, and **12** were treated with 1 equiv of HCl (1.4 M in Et$_2$O). The workup of the final reaction mixtures involved

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(9) Debad, J. D.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1992**, *11*, 6.

(10) Debad, J. D.; Legzdins, P.; Batchelor, R. J.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 2094.

Table III. ^{1}H and ^{13}C{^{1}H} NMR Data for Complexes 1–13 in C_6D_6

compd no.	^{1}H NMR: δ, ppm	^{13}C{^{1}H} NMR: δ, ppm
1	1.73 (s, 15H, $C_5(CH_3)_5$)	116.3 ($C_5(CH_3)_5$)
	1.40 (s, 18H, $OC(CH_3)_3$)	81.3 ($OC(CH_3)_3$)
		33.5 ($OC(CH_3)_3$)
		10.0 ($C_5(CH_3)_5$)
2	1.80 (s, 15H, $C_5(CH_3)_5$)	114.6 ($C_5(CH_3)_5$)
	1.40 (s, 18H, $OC(CH_3)_3$)	81.3 ($OC(CH_3)_3$)
		33.4 ($OC(CH_3)_3$)
		10.0 ($C_5(CH_3)_5$)
3	7.30–6.85 (m, 10H, OC_6H_5)	
	1.60 (s, 15H, $C_5(CH_3)_5$)	
4	7.00–7.60 (m, 10H, $OCH_2C_6H_5$)	142.7, 129.1, 128.6, 127.5 ($OCH_2C_6H_5$)
	5.95 (s, 4H, $OCH_2C_6H_5$)	
	1.60 (s, 15H, $C_5(CH_3)_5$)	114.7 ($C_5(CH_3)_5$)
		84.2 ($OCH_2C_6H_5$)
		9.4 ($C_5(CH_3)_5$)
5	1.67 (s, 15H, $C_5(CH_3)_5$)	118.4 ($C_5(CH_3)_5$)
	1.47 (s, 9H, $OC(CH_3)_3$)	32.8 ($OC(CH_3)_3$)^a
		10.1 ($C_5(CH_3)_5$)
6	1.71 (s, 15H, $C_5(CH_3)_5$)	116.0 ($C_5(CH_3)_5$)
	1.42 (s, 9H, $OC(CH_3)_3$)	86.0 ($OC(CH_3)_3$)
		32.7 ($OC(CH_3)_3$)
		9.9 ($C_5(CH_3)_5$)
7	7.22–6.85 (m, 5H, OC_6H_5)	129.6, 123.7, 122.5, 118.9 (OC_6H_5)
	1.65 (s, 15H, $C_5(CH_3)_5$)	116.7 ($C_5(CH_3)_5$)
		9.7 ($C_5(CH_3)_5$)
8	7.42 (d, 2H, *o-H*, $^2J_{HH}$ = 8.4 Hz)	147.3, 129.8, 128.4, 124.2 ($CH_2C_6H_5$)
	7.15 (t, 2H, *m-H*, $^2J_{HH}$ = 12.0 Hz)	
	6.98 (t, 1H, *p-H*, $^2J_{HH}$ = 10.2 Hz)	112.8 ($C_5(CH_3)_5$)
	2.86 (d, 1H, CH_aCH_b, $^2J_{HH}$ = 8.4 Hz)	83.0 ($OC(CH_3)_3$)
	2.77 (d, 1H, CH_aCH_b, $^2J_{HH}$ = 8.4 Hz)	50.0 ($CH_2C_6H_5$)
	1.59 (s, 15H, $C_5(CH_3)_5$)	32.0 ($OC(CH_3)_3$)
	1.10 (s, 9H, $OC(CH_3)_3$)	9.7 ($C_5(CH_3)_5$)
9	7.3–6.8 (m, 10H, Ar *H*)	167.6, 134.1, 130.2, 128.9, 128.8, 119.9, 118.6 (Ar *C*)
	3.42 (d, CH_aCH_b, $^2J_{HH}$ = 6.0 Hz)	
	2.59 (d, 1H, CH_aCH_b, $^2J_{HH}$ = 6.0 Hz)	
	1.58 (s, 15H, $C_5(CH_3)_5$)	112.3 ($C_5(CH_3)_5$)
		53.9 ($CH_2C_6H_5$)
		9.8 ($C_5(CH_3)_5$)
10	7.47 (d, 2H, *o-H*, $^2J_{HH}$ = 8.7 Hz)	147.4, 129.6, 128.0, 124.0 ($CH_2C_6H_5$)
	7.20 (t, 2H, *m-H*, $^2J_{HH}$ = 7.5 Hz)	
	6.98 (t, 1H, *p-H*, $^2J_{HH}$ = 7.2 Hz)	111.8 ($C_5(CH_3)_5$)
	2.76 (d, 1H, CH_aCH_b, $^2J_{HH}$ = 11.2 Hz)	83.7 ($OC(CH_3)_3$)
	2.64 (d, 1H, CH_aCH_b, $^2J_{HH}$ = 11.2 Hz)	46.0 ($CH_2C_6H_5$)
	1.62 (s, 15H, $C_5(CH_3)_5$)	31.8 ($OC(CH_3)_3$)
	1.08 (s, 9H, $OC(CH_3)_3$)	9.6 ($C_5(CH_3)_5$)
11	1.65 (s, 15H, $C_5(CH_3)_5$)	112.5 ($C_5(CH_3)_5$)
	1.40 (s, 9H, $OC(CH_3)_3$)	83.2 ($OC(CH_3)_3$)
	0.81 (d, 1H, CH_aCH_b, $^2J_{HH}$ = 12.9 Hz)	33.0 ($OC(CH_3)_3$)
	0.49 (s, 9H, $Si(CH_3)_3$)	27.4 (CH_2)
	−0.24 (d, 1H, CH_aCH_b, $^2J_{HH}$ = 12.9 Hz)	9.9 ($C_5(CH_3)_5$)
		3.1 ($Si(CH_3)_3$)
12	7.28 (d, 2H, *o-H*, $^2J_{HH}$ = 7.5 Hz)	129.5, 123.0, 118.2, 100.3 (OC_6H_5)
	7.18 (t, 2H, *m-H*, $^2J_{HH}$ = 8.4 Hz)	
	6.84 (t, 1H, *p-H*, $^2J_{HH}$ = 6.9 Hz)	111.9 ($C_5(CH_3)_5$)
	1.60 (s, 15H, $C_5(CH_3)_5$)	44.4 (CH_2)
	1.56 (d, 2H, CH_aH_b, $^2J_{HH}$ = 11.4 Hz)	9.9 ($C_5(CH_3)_5$)
	1.39 (d, 2H, CH_aH_b, $^2J_{HH}$ = 11.4 Hz)	2.0 ($Si(CH_3)_3$)
	0.25 (s, 9H, $Si(CH_3)_3$)	
13	4.70 (s, 3H, OCH_3)	111.7 ($C_5(CH_3)_5$)
	1.59 (s, 15H, $C_5(CH_3)_5$)	70.4 (OCH_3)
	0.92 (d, 1H, CH_aCH_b, $^2J_{HH}$ = 12.0 Hz)	35.5 (CH_2)
	0.84 (d, 1H, CH_aCH_b, $^2J_{HH}$ = 12.0 Hz)	9.5 ($C_5(CH_3)_5$)
	0.35 (s, 9H, $Si(CH_3)_3$)	2.2 ($Si(CH_3)_3$)

^{a} The resonance attributable to $OC(CH_3)_3$ was not observed.

removing the solvent in vacuo, extracting the residues with Et_2O, pentane, or CH_2Cl_2, and cooling the combined extracts at −30 °C to obtain crystalline precipitates (80–90% yields) of the product complexes. Comparisons with authentic spectral data confirmed that the organometallic products of these reactions were Cp*W(NO)(OCMe$_3$)Cl, Cp*W(NO)Cl$_2$,[5] Cp*W(NO)(CH$_2$Ph)Cl,[6] and Cp*W(NO)(CH$_2$SiMe$_3$)Cl,[9] respectively.

Reaction of Cp*Mo(NO)(CH$_2$Ph)(OCMe$_3$) (8) with O$_2$. Treatment of complex 8 in Et_2O (10 mL) with O_2 (1 atm) resulted in a color change from purple to yellow over the course of several hours at room temperature. The solvent was removed in vacuo, the residue was extracted with Et_2O (4 × 20 mL), and the extracts were filtered through Celite (2 × 5 cm). The filtrate was concentrated in vacuo and cooled at −30 °C overnight to induce the precipitation of small amounts of [Cp*Mo(O)$_2$]$_2$(μ-O).[11]

Reactions of Cp*W(NO)(CH$_2$Ph)(OCMe$_3$) (10) and Cp*W(NO)(CH$_2$SiMe$_3$)(OPh) (12) with O$_2$ or H$_2$O. Stirred Et_2O solutions (10 mL) of complexes **10** and **12** (1 mmol each) were exposed to O_2 (1 atm) or H_2O (50 μL). The colors of the reaction mixtures immediately turned from red (**10**) or purple (**12**) to yellow. The final reaction mixtures were taken to dryness in vacuo, the residues were extracted with Et_2O (2 × 10 mL), and the extracts were filtered through Celite (2 × 5 cm). The filtrates were concentrated in vacuo and cooled at −30 °C to induce the deposition of colorless crystals of the dioxo alkyl complexes Cp*W(O)$_2$(CH$_2$Ph) and Cp*W(O)$_2$(CH$_2$SiMe$_3$),[12] respectively, in virtually quantitative yields.

Reaction of Cp*Mo(NO)(OCMe$_3$)Cl (5) with H$_2$O. A solution of **5** (0.33 g, 1.0 mmol) in Et_2O (20 mL) was treated with an excess of deaerated H_2O (50 μL). The stirred reaction mixture turned red-black immediately and was stirred for a further 2.5 h at room temperature. After this time, the mixture was taken to dryness in vacuo, and the residue was redissolved in Et_2O (20 mL). The black Et_2O solution was filtered through Celite (2 × 5 cm) supported on a medium-porosity frit. Concentration of this filtrate and cooling at −30 °C afforded black crystals (0.11 g, 35% yield) of a complex formulated as [Cp*Mo(NO)(OH)Cl]$_2$.

Anal. Calcd for $C_{10}H_{16}NO_2ClMo$: C, 38.30; H, 5.14; N, 4.47. Found: C, 38.57; H, 5.13; N, 4.50. IR (Nujol mull): ν_{OH} 3642, 3631; ν_{NO} 1613 br cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.75 (s, 15H, $C_5(CH_3)_5$), 1.63 (s, 1H, O*H*). ^{13}C{^{1}H} NMR (C_6D_6): δ 119.0 ($C_5(CH_3)_5$), 10.2 ($C_5(CH_3)_5$). Low-resolution mass spectrum (probe temperature 80 °C): *m/z* 608 [P$^+$ − H_2O].

Reaction of Cp*W(NO)(OCMe$_3$)Cl (6) with H$_2$O. A stirred Et_2O solution (15 mL) of **6** (0.23 g, 0.50 mmol) was treated with an excess of deaerated H_2O (50 μL). The reaction mixture turned brown immediately. The brown mixture was taken to dryness in vacuo, and Et_2O (20 mL) was added to the brown residue. The resulting mixture was filtered through Celite (2 × 5 cm) supported on a glass frit. The filtrate was concentrated under reduced pressure to incipient crystallization and was cooled to −30 °C overnight to obtain brown crystals (0.070 g, 35% yield) of a solid formulated as [Cp*W(NO)(OH)Cl]$_2$, which were isolated by filtration.

Anal. Calcd for $C_{10}H_{16}NO_2ClW$: C, 29.91; H, 4.02; N, 3.49. Found: C, 29.72; H, 4.20; N, 3.30. IR (Nujol mull): ν_{OH} 3641, 3626; ν_{NO} 1588 br cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.94 (s, 15H, $C_5(CH_3)_5$), 1.75 (s, 15H, $C_5(CH_3)_5$), 1.44 (s, 2H, O*H*). Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 768 [P$^+$ − Cl].

Reaction of Cp*W(NO)(CH$_2$SiMe$_3$)(OPh) (12) with CNCMe$_3$. Complex **12** (0.10 g, 0.19 mmol) was dissolved in CNCMe$_3$ (0.20 mL, excess). The purple solid turned yellow as it dissolved. The excess CNCMe$_3$ was then removed in vacuo to afford a yellow oil. This oil was dissolved in pentane (20 mL), and the resulting yellow solution was filtered through Celite (2 × 5 cm). The yellow filtrates were collected and concentrated in vacuo. Maintaining the concentrated solution at −30 °C resulted in the deposition of 0.092 g (80% yield) of Cp*W(NO)(η^2-C{NCMe$_3$}CH$_2$SiMe$_3$)(OPh) as yellow nuggets.

Anal. Calcd for $C_{25}H_{40}N_2O_2SiW_2$: C, 49.02; H, 6.58; N, 4.57. Found: C, 49.19; H, 6.59; N, 4.49. IR (Nujol mull): ν_{CN} 1670, ν_{NO} 1585 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7.32–7.24 (m, 4H, Ar *H*), 6.87–6.74 (m, 1H, Ar *H*), 2.94 (d, 2H, J_{HH} = 11 Hz, CH_AH_B), 2.45 (d, 2H,

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(11) (a) Faller, J. W.; Ma, Y. *J. Organomet. Chem.* **1988**, *340*, 59. (b) Legzdins, P.; Lundmark, P. J.; Phillips, E. C.; Rettig, S. J.; Veltheer, J. E. *Organometallics* **1992**, *11*, 2991.

(12) Legzdins, P.; Phillips, E. C.; Sánchez, L. *Organometallics* **1989**, *8*, 940.

Table IV. Crystallographic and Experimental Data[a] for the Complexes Cp*W(NO)(OCMe$_3$)$_2$ (2) and Cp*W(NO)(OCH$_2$Ph)$_2$ (4)

complex	2	4
color	orange	orange
formula	$C_{18}H_{33}NO_3W$	$C_{24}H_{29}NO_3W$
fw	495.31	563.35
crystal system	orthorhombic	orthorhombic
space group	*Pbca* (No. 61)	*Pnma* (No. 62)
a, Å	23.627(3)	8.758(2)
b, Å	15.862(2)	15.7617(13)
c, Å	11.009(3)	16.352(2)
V, Å^3	4125.7(11)	2257.3(8)
Z	8	4
d_{calcd}, Mg/m^{-3}	1.595	1.658
$F(000)$	1968	1112
μ(Mo Kα), cm^{-1}	57.31	52.48
T, K	293	293
cryst dimens, mm^3	0.250 × 0.300 × 0.500	0.200 × 0.300 × 0.350
transm factors	0.74–1.00	0.87–1.00
scan type	ω–2θ	ω–2θ
scan range, deg	0.94 + 0.35 tan θ	1.00 + 0.35 tan θ
scan speed, deg/min	16.0	16.0
2θ limits, deg	$0 \le 2\theta \le 55.0$	$0 \le 2\theta \le 60.0$
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of unique reflns	5292	3717
no. of reflns with $I > 3\sigma(I)$	2473	1807
no. of variables	208	140
R_F[b]	0.032	0.031
R_{wF}[c,d]	0.035	0.034
goodness of fit[e]	1.29	1.21
max Δ/σ (final cycle)	0.03	0.01
residual density, e/Å^3	−1.04 to +2.51	−0.89 to +1.00

[a] Rigaku AFCF6 diffractometer, Mo Kα radiation, graphite monochromator. [b] $R_F = \sum||F_o| - |F_c|| / \sum|F_o|$. [c] $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum F_o^2]^{1/2}$. [d] $w = 4F_o^2/\sigma^2(F_o^2)$. [e] GOF $= [\sum w(|F_o| - |F_c|)^2/(\text{no. of degrees of freedom})]^{1/2}$.

Table V. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for Complex 2

atom	x	y	z	B_{eq}[a]
W(1)	0.368044(12)	0.45572(2)	0.31072(3)	2.28(1)
O(1)	0.3888(2)	0.5539(3)	0.2241(5)	3.0(2)
O(2)	0.4128(2)	0.4465(3)	0.4538(5)	3.2(3)
O(3)	0.2506(3)	0.4902(5)	0.3942(6)	5.8(4)
N(1)	0.3010(3)	0.4829(4)	0.3681(6)	3.4(3)
C(1)	0.3451(4)	0.3145(5)	0.2761(8)	3.0(4)
C(2)	0.3272(3)	0.3619(5)	0.1715(7)	2.6(3)
C(3)	0.3764(4)	0.3911(5)	0.1128(7)	3.0(4)
C(4)	0.4245(3)	0.3629(6)	0.1772(8)	3.3(4)
C(5)	0.4036(4)	0.3142(5)	0.2793(8)	3.3(4)
C(6)	0.3052(4)	0.2683(6)	0.3617(9)	4.4(5)
C(7)	0.2667(4)	0.3722(6)	0.1322(8)	3.8(4)
C(8)	0.3776(4)	0.4412(5)	−0.0053(7)	4.0(5)
C(9)	0.4850(4)	0.3787(7)	0.1442(9)	5.2(5)
C(10)	0.4411(4)	0.2715(6)	0.3700(10)	5.4(6)
C(11)	0.3648(4)	0.6381(6)	0.2055(9)	4.3(4)
C(12)	0.3618(6)	0.6842(6)	0.3278(11)	8.6(8)
C(13)	0.4032(6)	0.6808(7)	0.1146(13)	8.9(9)
C(14)	0.3063(5)	0.6303(7)	0.1518(12)	6.9(7)
C(15)	0.4037(4)	0.4608(7)	0.5832(7)	3.9(4)
C(16)	0.4587(5)	0.4331(7)	0.6451(9)	5.5(6)
C(17)	0.3925(5)	0.5531(7)	0.6052(9)	6.3(6)
C(18)	0.3555(5)	0.4057(9)	0.6260(10)	6.8(7)

[a] $B_{eq} = (8/3)\pi^2 \sum\sum U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses for 2[a]

W(1)–O(1)	1.890(5)	O(1)–W(1)–O(2)	109.7(2)
W(1)–O(2)	1.903(5)	O(1)–W(1)–N(1)	102.3(3)
W(1)–N(1)	1.758(7)	O(1)–W(1)–Cp	111.4(2)
W(1)–C(1)	2.337(8)	O(2)–W(1)–N(1)	102.8(3)
W(1)–C(2)	2.345(7)	O(2)–W(1)–Cp	111.3(2)
W(1)–C(3)	2.416(7)	N(1)–W(1)–Cp	118.7(2)
W(1)–C(4)	2.471(8)	W(1)–O(1)–C(11)	136.2(5)
W(1)–C(5)	2.422(8)	W(1)–O(2)–C(15)	135.6(5)
W(1)–Cp	2.073(4)	W(1)–N(1)–O(3)	168.1(7)
O(1)–C(11)	1.465(10)	O(2)–C(15)–C(16)	105.3(7)
O(2)–C(15)	1.458(9)	O(2)–C(15)–C(17)	109.5(8)
O(3)–N(1)	1.232(8)	O(2)–C(15)–C(18)	109.1(8)

[a] Here and elsewhere Cp refers to the centroid of the pentamethylcyclopentadienyl ring.

J_{HH} = 11 Hz, CH$_A$$H_B$), 1.73 (s, 15H, $C_5(CH_3)_5$), 1.18 (s, 9H, NC(CH_3)$_3$), 0.21 (s, 9H, Si(CH_3)$_3$). $^{13}\{^1H\}$ NMR (C_6D_6): δ 216.9 (CNCMe$_3$), 168.3, 129.5, 120.7, 117.1 (Ar *C*), 110.9 (*C*$_5$(CH$_3$)$_5$), 29.8 (C(*C*H$_3$)$_3$), 27.4 (*C*H$_2$), 9.8 (C$_5$(*C*H$_3$)$_5$), 0.5 (Si(*C*H$_3$)$_3$). Low-resolution mass spectrum (probe temperature 200 °C): m/z 612 [P$^+$].

X-ray Crystallographic Analyses of Cp*W(NO)(OCMe$_3$)$_2$ (2) and Cp*W(NO)(OCH$_2$Ph)$_2$ (4). Crystallographic data for 2 and 4 appear in Table IV. The final unit-cell parameters were obtained by least-squares procedures using the setting angles for 25 reflections with 2θ = 25.8–35.4° for 2 and 24.0–30.2° for 4. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for 2 and decreased uniformly by 3.5% for 4. The data were processed[13] and corrected for Lorentz and polarization effects, linear decay (for 4), and absorption (empirical, based on azimuthal scans for three reflections).

Both structures were solved by heavy-atom methods, the coordinates of the tungsten atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. Molecules of 4 are situated on a crystallographic mirror plane that passes through the metal atom, the NO ligand, and atoms C(2) and C(4) of the Cp* ligand. All non-hydrogen atoms of both complexes were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions [C–H = 0.98 Å, B(H) = 1.2B(bonded atom), methyl group orientations based on difference map positions]. A correction for secondary extinction was applied for 4, the final value of the extinction coefficient being 2.6(1) × 10^{-7}. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 14. Final atomic coordinates and equivalent isotropic thermal parameters for complexes 2 and 4 are given in Tables V and VII, respectively. Selected bond lengths and angles for the two compounds appear in Tables VI and VIII. Views of the solid-state molecular structures of 2 and 4 are shown in Figure 1. Hydrogen atom parameters, anisotropic thermal parameters, complete bond lengths and bond angles, torsion angles, intermolecular contacts, and least-squares planes are included as supplementary material.

Results and Discussion

Synthesis and Characteristic Properties of the Bis(alkoxo) Complexes Cp*M(NO)(OR)$_2$. Bis(alkoxo) nitrosyl complexes of the type Cp*M(NO)(OR)$_2$ [R = alkyl, aryl] are preparable by treating Cp*M(NO)Cl$_2$ with 2 equiv of alkoxide salts such as LiOCMe$_3$ or NaOR [R = Ph, CH$_2$Ph], i.e. eq 1. The four Cp*M(NO)(OR)$_2$ complexes synthesized during this work (1–4) are isolable as red to orange crystalline solids in 20–67% yields. They are very soluble in common organic solvents. As solids, the bis-

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(13) TEXSAN/TEXRAY structure analysis package which includes versions of the following: MITHRIL, integrated direct methods, by C. J. Gilmore; DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least-squares, and ORFFE, functions and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

Table VII. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for Complex 4

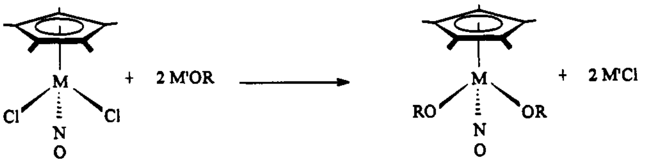
atom	*x*	*y*	*z*	B_{eq}[a]
W(1)	0.22295(4)	$^1/_4$	0.07576(2)	2.82(1)
O(1)	0.3078(8)	$^1/_4$	0.2513(4)	5.3(3)
O(2)	0.0958(5)	0.3478(2)	0.0650(3)	4.0(2)
N(1)	0.2590(8)	$^1/_4$	0.1816(4)	3.7(3)
C(1)	0.3189(10)	$^1/_4$	−0.0640(5)	3.5(4)
C(2)	0.3786(6)	0.3226(4)	−0.0240(4)	3.4(3)
C(3)	0.4689(6)	0.2960(3)	0.0436(4)	3.1(2)
C(4)	0.2210(13)	$^1/_4$	−0.1399(6)	5.7(5)
C(5)	0.3500(8)	0.4137(4)	−0.0475(4)	4.7(3)
C(6)	0.5623(8)	0.3505(4)	0.0992(5)	5.1(4)
C(8)	0.0313(8)	0.3998(4)	0.1290(4)	4.8(3)
C(9)	0.1244(7)	0.4773(4)	0.1424(4)	3.9(3)
C(10)	0.1000(9)	0.5495(5)	0.0967(4)	5.0(4)
C(11)	0.1886(10)	0.6212(5)	0.1067(5)	6.1(4)
C(12)	0.3044(10)	0.6211(5)	0.1643(6)	6.3(5)
C(13)	0.3265(10)	0.5500(6)	0.2093(5)	6.4(5)
C(14)	0.2383(9)	0.4784(5)	0.1992(4)	5.0(4)

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Table VIII. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses for 4[a]

W(1)–O(2)	1.910(4)	O(2)–W(1)–O(2)′	107.6(3)
W(1)–N(1)	1.759(7)	O(2)–W(1)–N(1)	101.3(2)
W(1)–C(1)	2.435(8)	O(2)–W(1)–Cp	112.8(2)
W(1)–C(2)	2.414(5)	N(1)–W(1)–Cp	119.6(2)
W(1)–C(3)	2.333(5)	W(1)–O(2)–C(8)	128.3(4)
W(1)–Cp	2.055(3)	W(1)–N(1)–O(1)	169.8(7)
O(1)–N(1)	1.218(9)	O(2)–C(8)–C(9)	111.1(5)
O(2)–C(8)	1.444(7)		

[a] The primed atom is related to the unprimed atom by the symmetry operation *x*, $^1/_2 - y$, *z*.



(1)

(alkoxo) complexes are indefinitely stable in air. The bis(alkoxo) complexes are also thermally stable in solution, as evidenced by the fact that 2 persists unchanged in C_6D_6 after 16 h at 120 °C. The spectroscopic properties of 1–4, collected in Tables II and III, are consistent with their possessing monomeric, three-legged piano-stool molecular structures.

The progress of reactions 1 can be monitored by observing the changes in the nitrosyl-stretching frequency evident in the IR spectra of the reaction mixtures. For instance, the reaction of Cp*W(NO)Cl_2 (ν_{NO} = 1630 cm^{-1}) with 2 equiv of LiOCMe$_3$ in THF exhibits first an intermediate nitrosyl-stretching band at 1593 cm^{-1} (vide infra), which appears at the expense of the band due to the starting material. As the transformation continues, this absorption feature decreases as the 1557-cm^{-1} band characteristic of the product complex appears and intensifies. In other words, ν_{NO} is shifted to lower energy as the chloro ligands are replaced by the more electron-donating alkoxide groups. In general, the nitrosyl-stretching frequencies[15] of the Cp*M(NO)(OR)$_2$ class of complexes (Table II) indicate that the metal is receiving increased donation of π-electron density from the alkoxide ligands. For comparison, it may be noted that a THF solution of Cp*W(NO)(CH$_2$CMe$_3$)$_2$ exhibits a ν_{NO} at 1568 cm^{-1}, whereas Cp*W(NO)(OCMe$_3$)$_2$ has the same feature at 1557 cm^{-1}.

Consistent with their having more electron-rich metal centers, the Cp*M(NO)(OR)$_2$ complexes are relatively inert chemically. As noted above, these bis(alkoxo) complexes are extremely air-stable. Furthermore, Cp*W(NO)(OCMe$_3$)$_2$ (2) does not react with O_2 (1 atm) in Et_2O or with an excess of H_2O in THF. The stability of 2 toward O_2 suggests that complexes of this type are not easily oxidized. In addition, a cyclic voltammogram of Cp*W(NO)(OCMe$_3$)$_2$ in THF shows no oxidation features up to the solvent limit of 0.85 V.[16] The hydrolytic stability is somewhat surprising since the polar W–O bonds in complex 2 would be expected to be susceptible to nucleophilic attack. Complex 2 also does not react with typical Lewis bases such as CO and PMe$_3$. Consequently, we believe that the chemical inertness of the Cp*M(NO)(OR)$_2$ complexes reflects their inability to form Lewis base adducts at their evidently electron-sufficient metal centers. This behavior is in marked contrast to the 16-electron dialkyl and diaryl species Cp′M(NO)R$_2$, which readily form 1:1 metal-centered adducts with a variety of Lewis bases.[2]

X-ray Crystallographic Analyses of Complexes 2 and 4. X-ray crystallographic analyses of 2 and 4 demonstrate that these representative examples of Cp*W(NO)(OR)$_2$ complexes are best viewed as 18-valence-electron species, the ability of the alkoxide ligands to donate π-electron density effectively satisfying the electronic requirements of the metal centers. Both Cp*W(NO)(OCMe$_3$)$_2$ (2) and Cp*W(NO)(OCH$_2$Ph)$_2$ (4) are monomeric, and their intramolecular geometrical parameters are collected in Table VI. Their chemically most interesting features are the dimensions about the alkoxide ligands. Since OCMe$_3$ and OCH$_2$Ph ligands have very different steric requirements, we believe that the large W–O–C angles (averaging 135.9° for 2 and 128.3° for 4) and short W–O bond lengths (averaging 1.90 Å for 2 and 1.91 Å for 4) are a result of electronic rather than steric effects. The increased W–O bond order likely results from the donation of electron density from filled p orbitals on oxygen to the empty d orbitals on the metal center.[17] The tungsten centers in 2 and 4 are thus relatively more electron-rich (a fact also indicated by their IR and chemical properties, vide supra) than those in their dialkyl or diaryl analogues.[2] Consistently, no evidence for the existence of agostic interactions between the metal and the β-hydrogens of the alkoxide ligands was revealed by the crystallographic analysis of 4.

A bis(alkoxo)chromium complex related to the compounds synthesized during this work was recently described by Hubbard and McVicar.[18] They prepared Cp*Cr(NO)(O-*i*-Pr)$_2$ by treatment of Cp*Cr(NO)$_2$(CH$_2$Cl) with excess Na(O-*i*-Pr) in 2-propanol, a process which results in the formal replacement of NO and CH$_2$Cl ligands by 2-propoxide groups. Such chromium complexes cannot be synthesized via a route analogous to that portrayed in eq 1 since the Cp*Cr(NO)Cl_2 precursor remains unknown.

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(15) For a discussion of the dependence of ν_{NO} on electron density at the metal center, see: Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: New York, 1992; pp 61–68.

(16) The electrochemical experimental details generally employed in our laboratories are summarized in ref 4. The cyclic voltammogram of 2 was recorded using a Pt-bead electrode in THF using 0.1 M [Bu$_4$N]PF$_6$ as the support electrolyte and SCE as the reference electrode. Scan rates ranged from 0.2 to 1.0 V s^{-1}.

(17) (a) Lunder, D. M.; Lobkovsky, E. B.; Streib, W. E.; Caulton, K. G. *J. Am. Chem. Soc.* **1991**, *113*, 1837. (b) McCleverty, J. A.; Seddon, D.; Bailey, N. A.; Walker, N. W. J. *J. Chem. Soc., Dalton Trans.* **1976**, 898.

(18) Hubbard, J. L.; McVicar, W. K. *Inorg. Chem.* **1992**, *31*, 910.

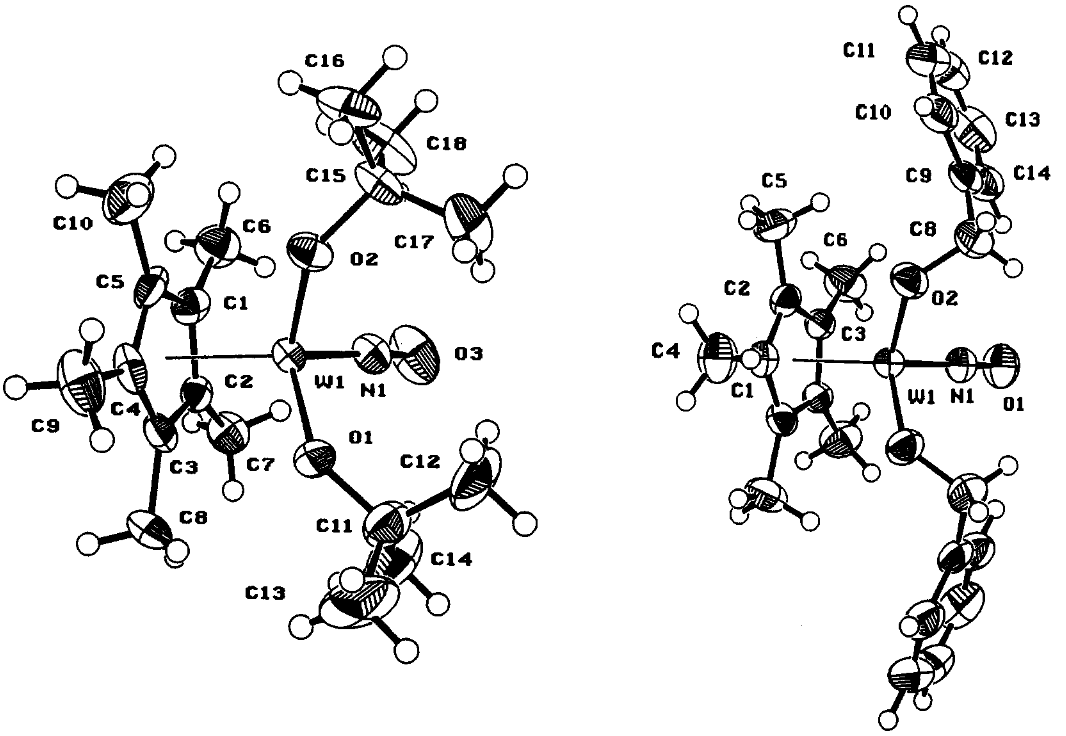
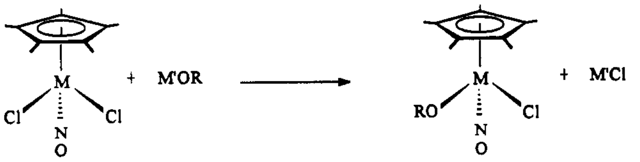


Figure 1. ORTEP diagram of the solid-state molecular structures of $Cp^*W(NO)(OCMe_3)_2$ (**2**) on the left and $Cp^*W(NO)(OCH_2Ph)_2$ (**4**) on the right. Probability ellipsoids at the 50% level are shown for the non-hydrogen atoms.

In other work, McCleverty and co-workers have prepared an extensive series of isoelectronic pyrazolylborate alkoxide compounds, $\{HB(Me_2pz)_3\}M(NO)(OR)_2$ [M = Mo, W], which result from alcoholysis of $\{HB(Me_2pz)_3\}M(NO)X_2$ [X = Cl, I].[19] Interestingly, we find that similar treatment of $Cp^*M(NO)Cl_2$ [M = Mo, W] with alcohols does not produce the bis(alkoxo) complexes synthesized during this work, but rather affords intractable materials. Both McCleverty and Hubbard have attributed the stability of their group 6 bis(alkoxo) complexes to the electron-donating ability of the alkoxo ligands.

Synthesis and Characteristic Properties of the Alkoxo Chloro Complexes $Cp^*M(NO)(OR)Cl$. In order to explore the reactivity of more electron-deficient group 6 alkoxo complexes, we decided to isolate the alkoxo chloro complexes, $Cp^*M(NO)(OR)Cl$, which are the intermediate organometallic species formed during conversions 1. The $Cp^*M(NO)(OR)Cl$ compounds are best obtained via metathesis reactions utilizing 1 equiv of an alkoxide salt at low temperatures, i.e.



(2)

The three such product complexes prepared during this work (**5**–**7**) are isolable as black to purple analytically pure needles in moderate yields (25–44%). The alkoxo chloro complexes, like the bis(alkoxo) compounds, are very soluble in all common organic solvents. In contrast to complexes **1**–**4**, however, the monoalkoxo species are very thermally, oxidatively, and hydrolytically sensitive both as solids and in solutions.

The spectroscopic properties (Tables II and III) of complexes **5**–**7** are consistent with their possessing monomeric, three-legged piano-stool molecular structures. The ν_{NO} bands evident in their IR spectra are higher in energy than those exhibited by the corresponding bis(alkoxo) complexes but lower in energy than those characteristic of the dichloro starting materials. For example, the nitrosyl-stretching frequencies decrease in the order $Cp^*W(NO)Cl_2$ (1630 cm^{-1}) > $Cp^*W(NO)(OCMe_3)Cl$ (1593 cm^{-1}) > $Cp^*W(NO)(OCMe_3)_2$ (1557 cm^{-1}) for THF solutions of the various compounds. Such spectroscopic data indicate that the metal centers in the $Cp^*M(NO)(OR)Cl$ complexes are relatively more electron-deficient than in the analogous $Cp^*M(NO)(OR)_2$ compounds.

Consistent with the greater electron deficiency at the metal centers of complexes **5**–**7**, the $Cp^*M(NO)(OR)Cl$ complexes decompose rapidly both in solution and in the solid state when exposed to the atmosphere. Upon treatment with dry O_2 (1 atm), compounds **5**–**7** decompose to intractable tan solids. Exposure to water results in compounds **5** and **6** being converted to $[Cp^*M(NO)(OH)Cl]_2$ species.[20] Indeed, our attempts to perform reactivity studies of the alkoxo chloro complexes have been hampered by their extreme sensitivity to air and moisture. Nevertheless, we have ascertained to date that the monoalkoxide complexes do react with PMe_3 presumably to form adducts of the type $Cp^*M(NO)(OR)(Cl)(PMe_3)$, but these adducts are only stable at low temperatures.

Synthesis and Characteristic Properties of the Alkoxo Alkyl Complexes $Cp^*M(NO)(R)(OR')$. To enable us to investigate the relative reactivity of alkyl vs alkoxide ligands at the same metal center, we decided to prepare a third class of alkoxide complexes, namely the alkoxo alkyl species, $Cp^*M(NO)(R)(OR')$. We quickly discovered that the limiting factor in the preparation of these compounds by metathesis reactions is the availibility

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[19] McCleverty, J. A.; Wlodarczyk, A. *Polyhedron* **1988**, *7*, 449 and references cited therein.

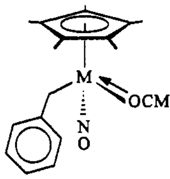
[20] Hunt, M. M.; Kita, W. C.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1978**, 474.

of the requisite alkyl chloro precursors. Until very recently,[21] only the benzyl chloro[6] and (trimethylsilyl)methyl chloro[9,10] complexes Cp*M(NO)(R)Cl [M = Mo, R = CH_2Ph; M = W; R = CH_2Ph, CH_2SiMe_3] were available. The six alkoxo alkyl complexes prepared during this work (**8**–**13**) have been made from these starting materials in the manner summarized in eq 3. The desired

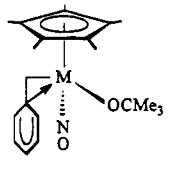
$$Cp^*M(NO)(R)Cl + M'(OR') \rightarrow Cp^*M(NO)(R)(OR') + M'Cl \quad (3)$$

organometallic products are isolable from reactions 3 in yields that range from 25 to 67% even in the presence of excess M′(OR) reagent. The low isolated yields of complexes **11** and **13** may be attributed to their high solubility in pentane. Of the complexes **8**–**13**, Cp*W(NO)(CH_2SiMe_3)($OCMe_3$) (**11**) is an oil and Cp*W(NO)(CH_2SiMe_3)(OMe) (**13**) is thermally sensitive as a solid.

The spectroscopic properties of **8**–**13** are collected in Tables II and III. As expected, the ν_{NO} bands in the IR spectra of the alkoxo alkyl complexes are lower in energy than those exhibited by the symmetric dialkyl compounds but are higher in energy than those characteristic of the bis(alkoxo) compounds (vide supra). To attain electron sufficiency at their metal centers, the following possibilities exist:



OR



The ^1H and $^{13}C\{^1H\}$ NMR spectral data for these compounds clearly distinguish between these two structural possibilities. For instance, the ipso carbon chemical shift at 147 ppm in the $^{13}C\{^1H\}$ NMR spectrum of **10** in C_6D_6 is diagnostic of an η^1-benzyl ligand.[22] Furthermore, the ^1H NMR spectrum of Cp*W(NO)(CH_2Ph)($OCMe_3$) (**10**) in C_6D_6 exhibits an AB pattern due to the diastereotopic methylene protons, for which the low-field chemical shifts (δ 2.76 and 2.64 ppm) and the large $^2J_{HH}$ coupling constant (11.2 Hz) are typical of those displayed by η^1-benzyl ligands.[22] It thus appears that the benzyl ligand is functioning as a one-electron donor in complexes **8**–**10**, the π donation from the alkoxide ligand again providing the extra electron density to the metal centers.

It has been established previously that the bis(benzyl) complexes Cp′M(NO)($CH_2Ph)_2$ react with HCl to produce Cp′M(NO)(CH_2Ph)Cl.[6] We have found that similar treatment of Cp*W(NO)($OCMe_3)_2$ with HCl provides first the monoalkoxo complex Cp*W(NO)($OCMe_3$)Cl and then the dichloro compound Cp*W(NO)Cl_2. The reactions of Cp*M(NO)(R)(OR′) with HCl provide insight into the relative reactivities in M–C versus M–O bonds in these systems. Interestingly, the alkoxo alkyl complexes **10** and **12** react with HCl to produce exclusively the corresponding alkyl chloro species (eq 4). Thus, the preferred site of reactivity of the Cp*M(NO)(R)(OR′) complexes with the polar reagent HCl is indeed the more polar M–O bond rather than the M–C linkage.

$$Cp^*M(NO)(R)(OR') + HCl \rightarrow Cp^*M(NO)(R)Cl + R'OH \quad (4)$$

Both in solution and in the solid state, all six Cp*M(NO)(R)(OR′) complexes decompose rapidly when exposed to the atmosphere. In the case of M = W, O_2 effects the transformations depicted in eq 5. This reactivity parallels that documented for the related dialkyl

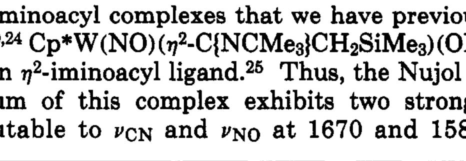
$$Cp^*W(NO)(R)(OR') + O_2 \rightarrow Cp^*W(O)_2R \quad (5)$$

and diaryl complexes of tungsten Cp*W(NO)R_2,[11b,12] the known dioxo alkyl products Cp*W(O)$_2$R[12,23] being the thermodynamically most stable entities formed upon exposure of the various complexes to molecular oxygen. In contrast, the congeneric molybdenum alkoxide species Cp*Mo(NO)(CH_2Ph)($OCMe_3$) (**8**) and Cp*Mo(NO)(CH_2Ph)(OPh) (**9**) react with O_2 to form the known [Cp*Mo(O)$_2$]$_2$(μ-O) complex.[11]

We have previously shown that Cp*W(NO)R_2 compounds are inert with respect to hydrolysis when R = alkyl but react with H_2O to form Cp*W(O)$_2$R when R = aryl.[11b] The alkoxo alkyl compounds **10** and **12** more resemble the diaryl systems in that they both react with H_2O to produce the known Cp*W(O)$_2$(CH_2Ph) and Cp*W(O)$_2$(CH_2SiMe_3) complexes, respectively.

Cp*W(NO)(CH_2SiMe_3)(OPh) (**12**) is a sufficiently potent Lewis acid to form an adduct with PMe_3 at low temperatures, as evidenced by variable-temperature ^1H NMR spectroscopy from +24 to −60 °C. At 24 °C, the purple CD_2Cl_2 solution of **12** and excess PMe_3 exhibits signals due to only **12** and free PMe_3. At −60 °C the solution is yellow, and all signals in the ^1H NMR spectrum are broad. Nevertheless, new resonances consistent with the adduct complex are evident at this temperature, most notably a doublet at δ 1.42 ($^2J_{PH}$ = 6 Hz) attributable to coordinated PMe_3. When the sample is warmed to room temperature, however, its color reverts to purple and its ^1H NMR spectrum is identical to the original spectrum, thereby indicating that this adduct formation is a reversible process.

The Lewis acidic nature of Cp*W(NO)(CH_2SiMe_3)(OPh) (**12**) is also demonstrated in its reaction with $CNCMe_3$. *tert*-Butyl isocyanide reacts with **12** to provide the yellow iminoacyl complex Cp*W(NO)(η^2-C{$NCMe_3$}CH_2SiMe_3)(OPh) in high yield (eq 6). Consistent with other iminoacyl complexes that we have previously isolated,[10,24] Cp*W(NO)(η^2-C{$NCMe_3$}CH_2SiMe_3)(OPh) contains an η^2-iminoacyl ligand.[25] Thus, the Nujol mull IR spectrum of this complex exhibits two strong bands attributable to ν_{CN} and ν_{NO} at 1670 and 1585 cm^{-1},



(6)

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[21] A series of Cp′M(NO)(R)(Cl) complexes has been prepared in our laboratories. For M = W, see ref. 10b. For M = Mo; see: Debad, J. D.; Legzdins, P.; Rettig, S. J.; Veltheer, J. E. *Organometallics*, in press.

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

[23] Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559.

[24] Dryden, N. H.; Legzdins, P.; Lundmark, P. J.; Riesen, A.; Einstein, F. W. B. *Organometallics* **1993**, *12*, 2085.

[25] Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059.

respectively. Like other iminoacyl complexes,[26] Cp*W(NO)(η^2-C{NCMe$_3$}CH$_2$SiMe$_3$)(OPh) is also unstable to water, undergoing hydrolysis to form Cp*W(NO)(η^2-C{NCMe$_3$}Me)(OPh), as evidenced by ^{1}H NMR monitoring.[27]

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Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, complete bond lengths and bond angles, bond lengths and bond angles involving hydrogen atoms, torsion angles, intermolecular distances, and least-squares planes for complexes 2 and 4 (22 pages). Ordering information is given on any current masthead page.

OM9300944

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

[27] ^{1}H NMR data for Cp*W(NO)(C{NCMe$_3$}Me)(OPh) in C$_6$D$_6$: δ 7.42–7.32 (m, 4H, Ar *H*), 6.87–6.80 (m, 1H, Ar *H*), 2.08 (s, 3H, C*H*$_3$), 1.71 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.05 (s, 9H, NC(C*H*$_3$)$_3$).