Chloride Metathesis or Nitrosyl N−O Bond Cleavage in $Cp^*W(NO)(CH_2SiMe_3)Cl$ upon Treatment with Alkali-Metal Alkoxides

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The bimetallic compound $[Cp^*W(NO)(CH_2SiMe_3)](\mu_2\text{-}\eta^1{:}\eta^2\text{-}NC\{H\}SiMe_3)[Cp^*W(Cl)(O)]$ (**1**), is produced in low yield by the heterogeneous reaction between $Cp^*W(NO)(CH_2SiMe_3)Cl$ and $KOCMe_3$ in pentane. However, when this reaction is performed in THF or Et_2O, the expected metathesis product, $Cp^*W(NO)(CH_2SiMe_3)(OCMe_3)$, is obtained. When $Cp^*W(NO)(CH_2SiMe_3)Cl$ is treated with KOMe in pentane, a different bimetallic compound, $[Cp^*W(NO)(CH_2SiMe_3)Cl](\mu\text{-}N)[Cp^*W(Cl)(\eta^2\text{-}N\{O\}\{H\}CH_2SiMe_3)]$ (**2**), is produced along with the known dioxo alkyl complex $Cp^*W(O)_2(CH_2SiMe_3)$. Again, the expected alkyl alkoxide product, $Cp^*W(NO)(CH_2SiMe_3)(OMe)$, is produced when the reaction is effected in THF or Et_2O. The roles of $KOCMe_3$ or KOMe during the formation of complexes **1** and **2** are presently unclear. However, when the reactions are performed using the Li or Na alkoxide salts, the expected metathesis products, namely the alkyl alkoxide complexes, are indeed produced. The solid-state molecular structures of bimetallic complexes **1** and **2** have been established by single-crystal X-ray crystallographic analyses.

Introduction

In recent years we have focused our attention primarily on $Cp'M(NO)_x$-containing complexes [$Cp' = Cp$ (η^5-C_5H_5) or Cp^* (η^5-C_5Me_5); M = Cr, Mo, or W; x = 1 or 2]. One of the principal goals of our research has been the development of these complexes as unique synthetic reagents.[1] We have generally found during our studies that the nitrosyl ligands remain intact during various reactions involving these compounds, the utility of the nitrosyl group being its ability to regulate electron density at the metal center due to its strong π-acidity.[2] Recently, however, we have encountered with increasing frequency transformations which involve nitrosyl N−O bond cleavage under a variety of mild conditions.[3] The reaction conditions that prompt these cleavage reactions are variable and differ from metal to metal. For instance, the dissociation of nitrosyl N−O bonds may result from exposing the appropriate group 6 organometallic nitrosyl complexes to thermolysis,[3b] water,[3c] dihydrogen,[3d] zinc,[3e] or dioxygen.[3f] In this paper we report that such N−O bond cleavage can also result from attempts to effect alkoxide-for-halide metathesis reactions by treating $Cp^*W(NO)(CH_2SiMe_3)Cl$ with alkali-metal alkoxides. Interestingly, the cleavage only occurs when the potassium alkoxides $KOCMe_3$ and KOMe are employed in pentane, the analogous lithium and sodium salts affording the expected $Cp^*W(NO)(CH_2SiMe_3)$(alkoxide) products. These reactions are also solvent dependent in that there is no evidence for the occurrence of nitrosyl N−O bond-breaking when solvents such as THF or Et_2O are utilized.

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions using an atmosphere of prepurified dinitrogen. General procedures routinely employed in these laboratories have been described in detail previously.[4] $Cp^*W(NO)Cl_2$,[5] $(Me_3SiCH_2)_2Mg{\bullet}x(\text{dioxane})$,[4] and PMe_3[6] were prepared by the published procedures. KOEt (Aldrich) was used as received, but PPh_3 (Aldrich) was recrystallized from Et_2O.

Generation of $Cp^*W(NO)(CH_2SiMe_3)Cl$. A THF solution (30 mL) of $Cp^*W(NO)(CH_2SiMe_3)Cl$[7] was generated from $Cp^*W(NO)Cl_2$ (0.42 g, 1.0 mmol) and $(Me_3SiCH_2)_2Mg{\cdot}x(\text{dioxane})$ (1.0 mmol of $CH_2SiMe_3^-$) in a Schlenk tube.[8] 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 ($\nu_{NO} = 1616\ cm^{-1}$) was then treated with the appropriate alkoxide salt as described in the following paragraphs.

Reaction of $Cp^*W(NO)(CH_2SiMe_3)Cl$ with KOEt. A pentane solution (20 mL) of $Cp^*W(NO)(CH_2SiMe_3)Cl$ (1.0 mmol) was generated and cooled to −20 °C. This solution was then cannulated into a flask containing KOEt (0.084 g, 1.0 mmol). The mixture was stirred for 2 h, whereupon it became red ($\nu_{NO} = 1582\ cm^{-1}$). The final mixture was filtered through Celite (2 × 5 cm) supported on a sintered glass frit, and the

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filtrate was concentrated and cooled at −30 °C overnight to induce the deposition of $Cp^*W(NO)(CH_2SiMe_3)(OEt)$ as a red oil in ~20% yield.

Anal. Calcd for $C_{16}H_{31}NO_2SiW$: C, 39.92; H, 6.49; N, 2.91. Found: C, 39.71; H, 6.45; N, 2.79. IR (Nujol): $\nu_{NO} = 1566$, $\nu_{Si-C} = 1256, 1244$ cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.93 (q, 2H, OCH_2-CH_3, $^3J_{HH} = 6.9$ Hz), 1.53 (s, 15H, $C_5(CH_3)_5$), 1.17 (t, 3H, OCH_2CH_3, $^3J_{HH} = 6.9$ Hz), 0.76 (d, 2H, CH_2SiMe_3, $^2J_{HH} = 2.4$ Hz), 0.30 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 111.8 ($C_5(CH_3)_5$), 77.9 (OCH_2CH_3), 34.0 (WCH_2, $J_{WC} = 55.0$ Hz), 20.7 (OCH_2CH_3), 9.7 ($C_5(CH_3)_5$), 2.2 ($Si(CH_3)_3$). Low-resolution mass spectrum (probe temperature 120 °C): m/z 481 [P$^+$].

Reaction of $Cp^*W(NO)(CH_2SiMe_3)Cl$ with $KOCMe_3$. A pentane solution (20 mL) of $Cp^*W(NO)(CH_2SiMe_3)Cl$ (1.0 mmol) was generated and cooled to −20 °C. This solution was then cannulated into a flask containing $KOCMe_3$ (0.11 g, 1.0 mmol). The heterogeneous reaction mixture was allowed to warm to room temperature and was stirred overnight. After this time, the reaction mixture consisted of a red-purple solution ($\nu_{NO} = 1624, 1570$ cm^{-1}) and an off-white precipitate. Filtration of the mixture through Celite (2 × 3 cm) afforded a red-purple filtrate. The filtrate was concentrated in vacuo and maintained at −30 °C for several days. Purple needles of $[Cp^*W(NO)(CH_2SiMe_3)](\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}NC\{H\}SiMe_3)[Cp^*W(Cl)(O)]$ (**1**) (0.042 g, 9.3% yield) formed and were separated from the mother liquor by cannulation.

Anal. Calcd for $C_{28}H_{51}N_2O_2Si_2ClW_2$: C, 37.08; H, 5.67; N, 3.09. Found: C, 37.19; H, 5.59; N, 3.07. IR (Nujol): ν_{NO} 1545, ν_{Si-C} 1240, 1154, ν_{W-O} 937 cm^{-1}. ^{1}H NMR (C_6D_6): δ 2.64 (s, 1H, CH), 1.70 (s, 15H, $C_5(CH_3)_5$), 1.68 (CH_AH_B), 1.65 (s, 15H, $C_5(CH_3)_5$), 0.68 (s, 9H, $CHSi(CH_3)_3$), 0.40 (CH_AH_B), 0.40 (s, 9H, $Si(CH_3)_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 117.0 ($C_5(CH_3)_5$), 111.2 (C_5-$(CH_3)_5$), 75.2 (CH), 44.1 (CH_2), 11.1 ($C_5(CH_3)_5$), 10.4 ($C_5(CH_3)_5$), 4.6 ($Si(CH_3)_3$), 1.6 ($Si(CH_3)_3$). Low-resolution mass spectrum (probe temperature 120 °C): m/z 879.

Reaction of $Cp^*W(NO)(CH_2SiMe_3)Cl$ with KOMe. A pentane solution (20 mL) of $Cp^*W(NO)(CH_2SiMe_3)Cl$ (1.0 mmol) was generated and cooled to −20 °C. This solution was then cannulated into a flask containing KOMe (0.070 g, 1.0 mmol). The heterogeneous reaction mixture was stirred and allowed to warm slowly to room temperature. Over the course of 5 h, the reaction mixture changed from blue to orange, and an orange precipitate formed. The final reaction mixture was taken to dryness in vacuo, and the residue was extracted with pentane (2 × 20 mL). The combined extracts were filtered through Celite (2 × 3 cm) supported on a sintered glass frit, and the yellow filtrate was collected and concentrated. Maintaining the concentrated pentane solution at −30 °C overnight resulted in the deposition of crystalline $Cp^*W(O)_2(CH_2SiMe_3)$ (0.11 g, 0.25 mmol, 31% yield based on $Cp^*W(NO)Cl_2$).

The remaining residue was also extracted with Et_2O (2 × 20 mL). The Et_2O extract was filtered through Celite (2 × 3 cm) supported on a sintered glass frit, and the filtrate was collected and concentrated. Maintaining this saturated orange solution at −30 °C overnight resulted in the deposition of $[Cp^*W(NO)(CH_2SiMe_3)Cl](\mu\text{-}N)[Cp^*W(Cl)(\eta^2\text{-}N\{O\}\{H\}CH_2SiMe_3)]$ (**2**) (0.097 g, 0.10 mmol, 13% yield based on $Cp^*W(NO)Cl_2$) as orange needles.

Anal. Calcd for $C_{28}H_{53}N_3O_2Si_2Cl_2W_2$: C, 35.09; H, 5.57; N, 4.38. Found: C, 35.13; H, 5.77; N, 4.22. IR (Nujol): ν_{NO} 1571, ν_{Si-C} 1251, 1233 cm^{-1}. ^{1}H NMR (C_6D_6): δ 9.50 (dd, 1H, NH, $^3J_{HH} = 5.4$ Hz, $^3J_{HH} = 6.6$ Hz), 2.40 (dd, 1H, $N-CH_AH_BSi(CH_3)_3$, $^3J_{HH} = 5.4$ Hz, $^2J_{HH} = 14.6$ Hz), 1.90 (s, 15H, $C_5(CH_3)_5$), 1.76 (s, 15H, $C_5(CH_3)_5$), 1.19 (d, 1H, $W-CH_{A'}H_{B'}Si(CH_3)_3$, $^2J_{HH} = 9.8$ Hz, $^2J_{WH} = 3.9$ Hz), 0.69 (s, 9H, $Si(CH_3)_3$), 0.10 (s, 9H, $Si(CH_3)_3$), −0.45 (d, 1H, $W\text{-}CH_{A'}H_{B'}Si(CH_3)_3$, $^2J_{HH} = 9.8$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 115.1 ($C_5(CH_3)_5$), 105.5 ($C_5(CH_3)_5$), 40.1 (CH_2), 28.2 (CH_2), 6.1 ($C_5(CH_3)_5$), 5.6 ($C_5(CH_3)_5$), 0.3 ($Si(CH_3)_3$), −6.7 ($Si(CH_3)_3$). Low-resolution mass spectrum (probe temperature 100 °C): m/z 820.

This reaction was also performed on an NMR scale to determine the exact ratio of product complexes formed. For example, $Cp^*W(NO)(CH_2SiMe_3)Cl$ (0.02 g, 0.04 mmol) and KOMe (0.003 g, 0.04 mmol) were mixed as solids in a flask. Pentane (5 mL) was added via syringe, and the atmosphere inside the vessel was removed. Overnight, the stirred reaction mixture changed from blue to yellow. The final mixture was taken to dryness in vacuo. The yellow residue was dissolved in C_6D_6 in a glovebox, and the resulting amber-yellow solution was filtered through Celite (6 × 20 mm). The filtrate was collected in an NMR tube, and its ^{1}H NMR spectrum exhibited resonances attributable to only $Cp^*W(O)_2(CH_2SiMe_3)$ and complex **2** in a 5:3 ratio.

Preparation of $Cp^*W(NO)(CH_2SiMe_3)(PMe_3)Cl$. This complex was prepared in 78% isolated yield in a manner analogous to that reported for the synthesis of $Cp^*W(NO)(CH_2CMe_3)(PMe_3)Cl$.[9]

Anal. Calcd for $C_{17}H_{35}NOClSiPW$: C, 37.27; H, 6.44; N, 2.56. Found: C, 37.68; H, 6.53; N, 2.51. IR (Nujol): $\nu_{NO} = 1570, 1549$, $\nu_{Si-C} = 1282, 1236$ cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.53 (s, 15H, $C_5(CH_3)_5$), 1.13 (d, 9H, $P(CH_3)_3$, $^2J_{HP} = 9.6$ Hz), 0.58 (s, 9H, $Si(CH_3)_3$), 0.34 (d, 1H, CH_AH_B, $^2J_{HH} = 10.8$ Hz), −0.33 (dd, 1H, CH_AH_B, $^2J_{HH} = 10.8$ Hz, $^3J_{HP} = 2.4$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 108.6 ($C_5(CH_3)_5$), 26.5 (d, CH_2, $^2J_{CP} = 8.3$ Hz), 12.1 (d, $P(CH_3)_3$, $J_{CP} = 29.7$ Hz), 9.9 ($C_5(CH_3)_5$), 4.4 ($Si(CH_3)_3$). Low-resolution mass spectrum (probe temperature 120 °C): m/z 471 [P$^+$ − PMe_3].

Reaction of $Cp^*W(NO)(CH_2SiMe_3)(PMe_3)Cl$ with $KOCMe_3$. $Cp^*W(NO)(CH_2SiMe_3)(PMe_3)Cl$ (0.27 g, 0.49 mmol) and $KOCMe_3$ (0.055 g, 0.49 mmol) were mixed as solids in a flask, and pentane (20 mL) was added via syringe. The pale yellow reaction mixture became red as it was stirred at ambient temperatures for 2 d. The final reaction mixture was taken to dryness in vacuo, the remaining red-brown oil was redissolved in pentane (15 mL), and the pentane solution was filtered through Celite (2 × 5 cm) supported on a sintered glass frit. Solvent was removed from the filtrate in vacuo to obtain a red oil which was identified as $Cp^*W(NO)(CH_2SiMe_3)(OCMe_3)$ by comparison of its spectroscopic properties with those exhibited by an authentic sample.[10]

X-ray Crystallographic Analyses of $[Cp^*W(NO)(CH_2SiMe_3)](\mu_2\text{-}\eta^1\text{:}\eta^2\text{-}NC\{H\}SiMe_3)[Cp^*W(Cl)(O)]$ (1) and $[Cp^*W(NO)(CH_2SiMe_3)Cl](\mu\text{-}N)[Cp^*W(Cl)(\eta^2\text{-}N\{O\}\{H\}CH_2SiMe_3)]$ (2). Crystallographic data for complexes **1** and **2** appear in Table 1. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with $2\theta = 52.6-65.4°$ for **1** and 10.3−17.1° for **2**. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, decayed linearly by 8.4% for **1** and by 28.2% for **2**. The data were processed, corrected for Lorentz and polarization effects, decay, and absorption (empirical, azimuthal scans for three reflections).[11] It should be noted that both data sets are not up to the usual standards of this laboratory. The data were collected to lower than usual resolution because of crystal decay (particularly for compound **2**) and substantial thermal motion. Crystals of **1** were very small, and it was necessary to use Cu radiation to obtain a usable data set for this weakly diffracting material.

The structures were solved by conventional heavy-atom methods, the coordinates of the heavy atoms being determined from the Patterson functions and those of the remaining atoms from subsequent difference Fourier syntheses. The structure analysis of **1** was initiated in the centrosymmetric space group $P\bar{1}$ on the basis of the E-statistics and the appearance of the Patterson function. This choice was confirmed by subsequent calculations. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms in both **1** and **2** were fixed in idealized positions (methyl group orientations

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[11] *TEXSAN: Crystal Structure Analysis Package (Version 5.1)*; Molecular Structure Corp.: The Woodlands, TX, 1985.

Table 1. Crystallographic Data for Complexes 1 and 2[a]

	compd	
	1	**2**
formula	$C_{28}H_{51}ClN_2O_2Si_2W_2$	$C_{28}H_{53}Cl_2N_3O_2Si_2W_2$
fw	907.05	958.52
color, habit	red-purple, prism	red, prism
cryst size, mm	0.05 × 0.15 × 0.20	0.10 × 0.15 × 0.25
cryst system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	12.140(2)	9.972(3)
b, Å	13.334(2)	20.143(7)
c, Å	11.627(1)	19.020(6)
α, deg	90.54(1)	90
β, deg	107.03(1)	103.30(2)
γ, deg	76.06(1)	90
V, Å^3	1742.8(4)	3718(1)
Z	2	4
ρ_{calc}, g/cm^3	1.728	1.712
F(000)	884	1872
radiation	Cu	Mo
μ, cm^{-1}	137.62	64.25
T, K	294	294
transm factors (relative)	0.22−1.00	0.63−1.00
scan type	$\omega-2\theta$	$\omega-2\theta$
scan range, deg in ω	$0.84 + 0.20 \tan\theta$	$1.10 + 0.35 \tan\theta$
scan rate, deg/min	16	16
data collcd	$+h,\pm k,\pm l$	$+h,+k,\pm l$
$2\theta_{max}$, deg	157	45
cryst decay, %	8.4	28.2
tot. no. of reflcns	7462	5356
no. of unique reflcns	7101	5021
R_{merge}	0.043	0.072
no. of rflns with $I > 3\sigma(I)$	4300	2590
no. of variables	334	353
R	0.042	0.036
R_w	0.041	0.033
gof	2.13	1.64
max Δ/σ (final cycle)	0.01	0.01
resid density e/Å^3	−1.15 to +1.26 (near W)	−0.73 to +0.61 (near W)

[a] Rigaku AFC6S diffractometer, Cu $K\alpha$ radiation ($\lambda = 1.541\ 78$ Å) or Mo $K\alpha$ radiation ($\lambda = 0.710\ 69$ Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1, up to 8 rescans), $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof $= [\sum w(|F_o| - |F_c|)^2/(\text{no. of degrees of freedom})]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$.

based on difference map peak positions, N−H = 0.91 Å, C−H = 0.98 Å, $B_H = 1.2B_{bonded\ atom}$). A secondary extinction correction was applied for **2** (Zachariasen type 2 isotropic), the final value of the extinction coefficient being 1.00(9) × 10^{-7}. Neutral-atom scattering factors and anomalous dispersion corrections were taken from ref 12.

Selected bond lengths and angles for complexes **1** and **2** are given in Tables 2 and 3, respectively. Final atomic coordinates and equivalent isotropic thermal parameters, hydrogen parameters, anisotropic thermal parameters, all bond lengths and angles, torsion angles, least-squares planes, and intermolecular contacts for both complexes are available as Supporting Information.

Results and Discussion

Synthesis of Alkoxo Alkyl Complexes. We have previously reported that alkoxo alkyl complexes, Cp*M(NO)(R)(OR′) (M = Mo, W; R, R′ = hydrocarbyl), are preparable via alkoxide-for-chloride metathesis reactions.[10] As summarized in eq 1, the desired complexes

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses for 1

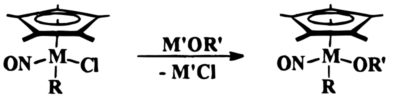
W(1)−N(1)	2.004(7)	W(1)−N(1)−W(2)	143.8(4)
W(1)−C(21)	2.14(1)	W(1)−C(21)−N(1)	64.7(5)
C(21)−N(1)	1.44(1)	N(1)−C(21)−Si(1)	123.2(6)
W(1)−Cl(1)	2.385(3)	N(1)−W(1)−Cl(1)	83.3(2)
W(1)−O(1)	1.697(8)	N(1)−W(1)−O(1)	105.6(3)
W(1)−Cp(1)[a]	2.11	N(1)−W(1)−Cp(1)[a]	132.6
W(2)−N(1)	1.969(7)	N(1)−W(2)−N(2)	96.2(3)
W(2)−N(2)	1.767(8)	W(2)−N(2)−O(2)	166.4(8)
N(2)−O(2)	1.22(1)	N(1)−W(2)−C(25)	107.6(3)
W(2)−C(25)	2.149(9)	C(25)−Si(2)−C(27)	112.0(5)
W(2)−Cp(2)[a]	2.09	N(1)−W(2)−Cp(2)[a]	123.5
C(25)−Si(2)	1.877(9)		

[a] Cp(1) and Cp(2) refer to the unweighted centroids of the C(1−5) and C(11−15) rings, respectively.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses for 2

W(1)−N(1)	1.78(1)	W(1)−N(3)−W(2)	169.8(6)
W(1)−C(11)	2.21(1)	N(3)−W(1)−Cl(1)	75.4(2)
N(1)−O(1)	1.22(1)	N(3)−W(1)−N(1)	90.1(4)
W(1)−Cl(1)	2.557(4)	N(3)−W(1)−C(11)	137.8(5)
W(1)−N(3)	2.11(1)	N(3)−W(1)−Cp(1)[a]	111.8
W(1)−Cp(1)[a]	2.07	W(1)−C(11)−Si(1)	117.6(8)
W(2)−N(3)	1.71(1)	N(3)−W(2)−N(2)	95.8(4)
W(2)−N(2)	2.14(1)	W(2)−N(2)−O(2)	63.9(5)
W(2)−O(2)	2.000(9)	W(2)−O(2)−N(2)	73.7(6)
W(2)−Cl(2)	2.346(4)	W(2)−N(2)−C(25)	133(1)
W(2)−Cp(2)[a]	2.12	N(3)−W(2)−Cp(2)[a]	121.7
N(2)−O(2)	1.50(1)	N(3)−W(2)−Cl(2)	102.4(3)
N(2)−C(25)	1.42(1)	N(2)−C(25)−Si(2)	114(1)
Cl(1)−H(1)	2.33	N(2)−H(1)−Cl(1)	152

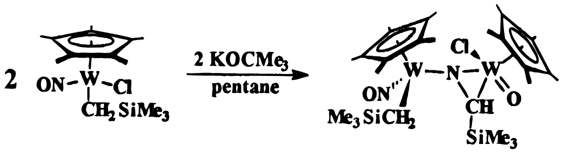
[a] Cp(1) and Cp(2) refer to the unweighted centroids of the C(1−5) and C(15−19) rings, respectively.



(1)

result from treatment of the appropriate alkyl chloro precursor with an alkali-metal alkoxide. Reactions 1 are generally conducted in pentane or Et_2O, and the organometallic products are isolable in yields that range from 20 to 67%, the lower yields being attributable to the high solubility of some of these complexes in pentane. Furthermore, we have found (see ref 10) that a variety of alkali-metal alkoxides such as $LiOCMe_3$, $NaOCMe_3$, NaOPh, NaOMe, and KOEt (this work) may be utilized as the alkoxylating reagents. However, we have now discovered that if the synthesis of either Cp*W(NO)(CH_2SiMe_3)($OCMe_3$) or Cp*W(NO)(CH_2SiMe_3)(OMe) is attempted in pentane with the potassium reagents $KOCMe_3$ or KOMe, the desired alkoxo alkyl complexes do not result. Rather, the novel bimetallic complexes, [Cp*W(NO)(CH_2SiMe_3)](μ_2-η^1:η^2-NC{H}-$SiMe_3$)[Cp*W(Cl)(O)] (**1**) and [Cp*W(NO)(CH_2SiMe_3)Cl](μ-N)[Cp*W(Cl)(η^2-N{O}{H}CH_2SiMe_3)] (**2**), respectively, are produced.

[Cp*W(NO)(CH_2SiMe_3)](μ_2-η^1:η^2-NC{H}$SiMe_3$)-[Cp*W(Cl)(O)] (1). This bimetallic complex is produced by the heterogeneous reaction between Cp*W(NO)(CH_2SiMe_3)Cl and $KOCMe_3$ in pentane, i.e.,



1

(2)

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(12) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99−102 and 149−150.

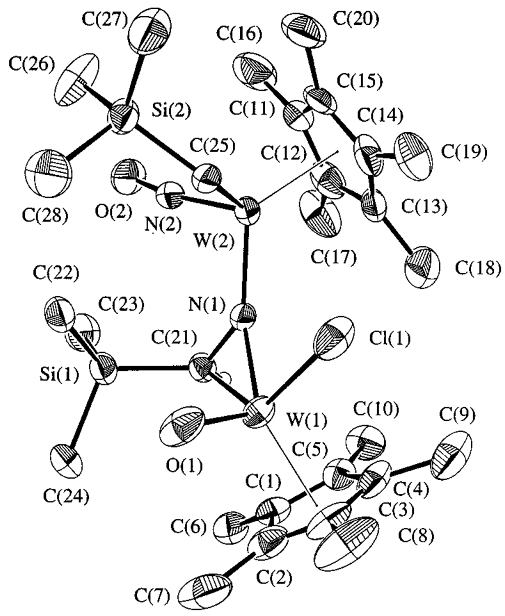
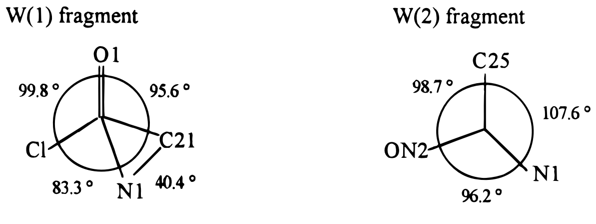


Figure 1. ORTEP diagram of [Cp*W(NO)(CH$_2$SiMe$_3$)](μ_2-η^1:η^2-NC{H}SiMe$_3$)[Cp*W(Cl)(O)] (**1**). Thermal ellipsoids of 33% probability are shown for the non-hydrogen atoms.

Product **1** is isolable as air-sensitive, purple needles in low yields from pentane. ^{1}H NMR spectroscopy confirms that C$_6$D$_6$ solutions of **1** decompose thermally (120 °C) and that **1**, either as a solid or in solutions, reacts rapidly with air to form the known Cp*W(O)$_2$(CH$_2$SiMe$_3$) complex.[3f] Furthermore, the choice of both the solvent and the cation of the alkoxide salt is crucial for the successful synthesis of **1**. Thus, if reaction 2 is performed in THF or Et$_2$O, the expected Cp*W(NO)(CH$_2$SiMe$_3$)(OCMe$_3$) (~30% yield) is produced rather than the bimetallic complex **1**. Similarily, if the alkoxylating reagent is changed to either the sodium or the lithium *tert*-butoxide salt, the alkoxo alkyl complex is also produced.[10]

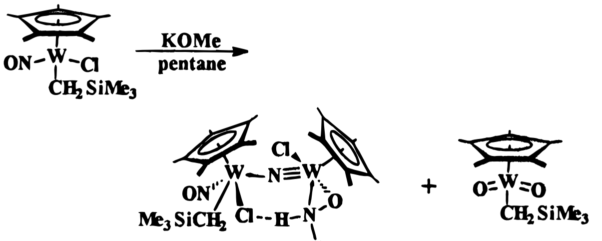
The solid-state molecular structure of **1** has been established by a single-crystal X-ray crystallographic analysis; its ORTEP diagram is shown in Figure 1, and some selected bond lengths and bond angles are collected in Table 2. The bimetallic complex **1** possesses a 14e$^-$ [Cp*W(Cl)(O)] fragment and a 15e$^-$ [Cp*W(NO)(CH$_2$SiMe$_3$)] fragment bridged by a NC{H}SiMe$_3$ group. Both tungsten-containing fragments have three-legged piano-stool type geometries about their metal centers, if the midpoint of the C(21)−N(1) linkage is viewed as occupying one coordination position at W(1). These geometries can be seen most clearly in the Newman projections of the W(1) and the W(2) fragments of complex **1**, each projection looking down the W−Cp* centroid axis:



The W(1)−O(1) bond length in **1** is 1.697(8) Å, well within the range typical for such linkages (1.58−1.78 Å).[13] For comparison, CpW(O)(CH$_2$SiMe$_3$)$_3$ has a W−O bond length of 1.664(8) Å.[14] The essentially linear (166.4(8)°) nitrosyl ligand on W(2) has W(2)−N(2) and N(2)−O(2) bond distances of 1.767(8) and 1.22(1) Å, respectively. The bridging imido ligand, NC{H}SiMe$_3$, is attached in an η^2-fashion to W(1) and η^1 to W(2), thereby formally functioning as a two-electron donor to W(1) and a one-electron donor to W(2). Each metal center thus attains a formal 16-valence-electron configuration. Finally, the geometry about bridging C(21) is approximately tetrahedral, i.e., W(1)−C(21)−Si(1) = 120.0 (5)° and N(1)−C(21)−Si(1) = 123 (2)°. Overall, the structure confirms that during the formation of **1** there is a formal loss of HCl and no incorporation of KOCMe$_3$.

The spectroscopic properties of **1** are consistent with it retaining its solid-state structure in different media. The IR spectrum of **1** as a Nujol mull exhibits a relatively low-energy ν_{NO} at 1545 cm^{-1}, a $\nu_{W=O}$ at 937 cm^{-1}, and a ν_{SiC} at 1240 cm^{-1}. A band at 1154 cm^{-1} is most probably due to a N−C stretch,[15,16] but confirmation of this assignment awaits isotopic labeling of the bridging nitrogen atom. The ^{1}H NMR spectrum of [Cp*W(NO)(CH$_2$SiMe$_3$)](μ_2-η^1:η^2-NC{H}SiMe$_3$)[Cp*W(Cl)(O)] in C$_6$D$_6$ is unremarkable as it generally exhibits the expected signals (see Experimental Section). Although the inequivalent methylene proton resonances are obscured in the normal ^{1}H NMR spectrum, they can be observed in the COSY spectrum of **1** where they appear as doublets at δ 1.68 and 0.40 ppm in the off-diagonal peaks. In addition to the signals due to the two inequivalent Cp* ligands and the two inequivalent SiMe$_3$ groups, the ^{13}C{^{1}H} NMR spectrum of **1** clearly shows the signals attributable to the *C*H of the bridging ligand and the methylene carbon at δ 75.2 and 44.1 ppm, respectively.

[Cp*W(NO)(CH$_2$SiMe$_3$)Cl](μ-N)[Cp*W(Cl)(η^2-N{O}{H}CH$_2$SiMe$_3$)] (2). To determine if reaction 2 is independent of the type of potassium alkoxide employed, we treated Cp*W(NO)(CH$_2$SiMe$_3$)Cl with potassium methoxide in pentane, i.e.



2

(3)

The heterogeneous reaction mixture turns from blue to orange over the course of 5 h, and the bimetallic complex [Cp*W(NO)(CH$_2$SiMe$_3$)Cl](μ-N)[Cp*W(Cl)(η^2-N{O}{H}CH$_2$SiMe$_3$)] **(2)** is isolable as orange crystals from Et$_2$O in 13% yield (based on Cp*W(NO)Cl$_2$). Complex **2** decomposes readily to the known oxo complex, Cp*W-

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[13] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

[14] Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1985**, *4*, 1470.

[15] The N−C vibration of an imido ligand is expected in the range 1300−1100 cm^{-1},[16] whereas W−N stretches usually occur at lower energies (1125−948 cm^{-1}).[13]

[16] Osborn, J. H.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 3098.

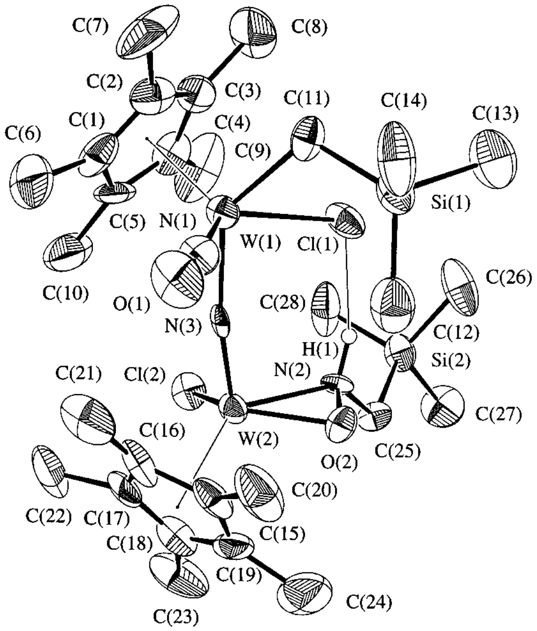

Figure 2. ORTEP diagram of [Cp*W(NO)(CH_2SiMe_3)Cl](μ-N)[Cp*W(Cl)(η^2-N{O}{H}CH_2SiMe_3)] (**2**). Thermal ellipsoids of 33% probability are shown for the non-hydrogen atoms.

$(O)_2(CH_2SiMe_3)$,[3f] in the presence of air. Interestingly, reaction 3 does not occur in solvents other than pentane nor with other methoxide salts. For instance, treatment of Cp*W(NO)(CH_2SiMe_3)Cl with KOMe in THF or with NaOMe in pentane results in the formation of Cp*W(NO)(CH_2SiMe_3)(OMe).[10] Another important feature of reaction 3 is that Cp*W$(O)_2$(CH_2SiMe_3) is also produced (31% isolated yield based on Cp*W(NO)Cl_2), and this product is *not* simply a result of the decomposition of the air-sensitive bimetallic product, **2**. NMR monitoring of the reaction under rigorously oxygen-free conditions indicates that the final reaction mixture contains Cp*W$(O)_2$(CH_2SiMe_3) and **2** in a ratio of 5:3.

An ORTEP diagram of the solid-state molecular structure of [Cp*W(NO)(CH_2SiMe_3)Cl](μ-N)[Cp*W(Cl)(η^2-N{O}{H}CH_2SiMe_3)] (**2**) is shown in Figure 2, and it illustrates the four-legged piano-stool molecular geometry about each electronically saturated tungsten center. Selected bond lengths and angles for this complex are presented in Table 3. The W(1)-containing moiety is essentially a 1:1 adduct of Cp*W(NO)(CH_2SiMe_3)Cl with the nitrido ligand of the W(2)-containing fragment acting as a Lewis base. Surprisingly, the bridging nitrido ligand is situated cis (or lateral) to the nitrosyl ligand and trans (or diagonal) to the alkyl ligand. This is not expected since molecular-orbital calculations and X-ray crystallographic analyses have indicated that the vacant coordination site in 16-electron complexes of the type Cp′M(NO)(Y)(Z) [Y, Z = 1-electron ligand] is located trans (or diagonal) to the NO ligand.[17] For instance, the solid-state molecular structure of Cp*W(NO)(CH_2SiMe_3)Cl exhibits an angle of 109.9° between the alkyl group and the chloride ligand, thereby indicating that this is the most accessible site at the W atom.[7] It has also been demonstrated chemically that Cp*W(NO)(CH_2SiMe_3)Cl and Cp*M(NO)(CH_2CMe_3)Cl (M = Mo, W) form 18-electron, metal-centered phosphine adducts (i.e. Cp′M(NO)(Y)(Z)(PR_3)) in which the phosphine coordinates trans (or diagonal) to the nitrosyl group.[9]

The novel hydroxylamido ligand in **2**, i.e. N{O}{H}CH_2SiMe_3, is bound in an η^2 fashion to W(2) in a manner very similar to that of the η^2-NH_2O ligand in [Cp*W(O)(η^2-NH_2O)(CH_2SiMe_3)]BF_4.[18] Overall, the η^2-N{O}{H}CH_2SiMe_3 ligand functions as a formal three-electron donor to W(2), thereby permitting the metal center to satisfy the 18-valence-electron rule. The linkage containing the bridging nitrido ligand (N(3)) is essentially linear, the W(1)−N(3)−W(2) angle being 169.8(6)°. The distance W(1)−N(3) (2.11(1) Å) indicates the existence of a single bond, whereas the distance W(2)−N(3) (1.71(1) Å) suggests that N(3) is triply bonded to W(2).[19] These distances can be compared to those of W(2)−N(2) (2.14(1) Å) and W(1)-N(1) (1.78(1) Å). The bridging nitride thus functions as a three-electron donor to W(2) and a two-electron donor to W(1), thereby satisfying each metal's electronic requirements. In other words, as noted above, the nitrido ligand behaves as a simple Lewis base to the 16-electron Cp*W(NO)(CH_2SiMe_3)Cl fragment. There are very few examples of this kind of bridging nitrido group, and most of them are found in polymeric species.[13] Thus, comparisons can be made between **2** and $\{W(\mu\text{-}N)(OCMe_3)_3\}_\infty$,[20] a polymer which contains the same type of bridging unit as **2** (i.e., W≡N→W). In this polymer the W≡N bond length is 1.740(15) Å and the dative N→W bond distance is a relatively long 2.661(15) Å.[21] Finally, another interesting feature of the solid-state molecular structure of complex **2** is that it contains an intramolecular hydrogen bond between H(1) located on the N{O}{H}CH_2SiMe_3 ligand of W(2) and the chloride ligand on W(1). The hydrogen−chlorine bond distance of 2.33 Å is in the range expected for hydrogen bonding,[22] and the N−H···Cl angle is 151.5°.

The spectroscopic properties characteristic of **2** (Experimental Section) are fully consistent with its solid-state molecular structure. Thus, the Nujol-mull IR spectrum of **2** exhibits a broad ν_{NO} band at 1571 cm^{-1} and two absorptions due to Si−C stretches at 1252 and 1233 cm^{-1}. However, there are several bands in the 1125−885 cm^{-1} region of the spectrum, and so the ν_{WN} and ν_{WO} stretching frequencies cannot be assigned unambiguously. Furthermore, the ^1H NMR spectrum of [Cp*W(NO)(CH_2SiMe_3)Cl](μ-N)[Cp*W(Cl)(η^2-N{O}{H}CH_2SiMe_3)] in C_6D_6 exhibits two inequivalent Cp* resonances and two inequivalent $SiMe_3$ resonances in addition to the expected signals. The signals due to the diastereotopic methylene protons of the N-bound alkyl group should appear as two doublets of doublets, but only one of these doublet of doublets is observable at δ 2.40 ppm ($^2J_{H_aH_m} = 14.7$ Hz, $^3J_{H_xH_m} = 5.4$ Hz). The other methylene-proton signal is probably obscured in the Cp* resonances.

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[17] Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411.

[18] Legzdins, P.; Rettig, S. J.; Sayers, S. F. *J. Am. Chem. Soc.* **1994**, *116*, 12105.

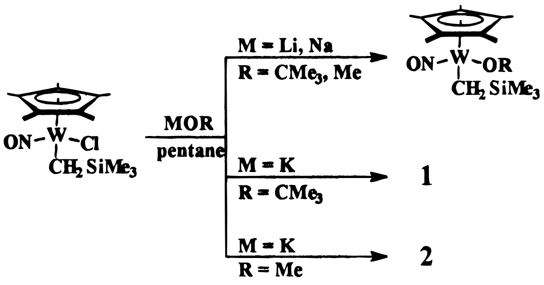
[19] W=N bond distances range from 1.78 to 1.61 Å, and W≡N bond distances range from 1.74 to 1.55 Å.[13]

[20] Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.

[21] For comparison, the W−N(py) bond distance is 2.323(7) Å in $(Me_3CO)_3W(NO)(py)$, see: Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 116.

[22] Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin: New York, 1968; pp 14−16.

Scheme 1



Trapping Attempts with Phosphines. To gain some insight into reactions 2 and 3, selected experiments were performed in an attempt to trap any possible intermediates. Since PPh_3 does not coordinate to the precursor complex, the reaction of Cp*W(NO)(CH_2SiMe_3)Cl with $KOCMe_3$ was performed in the presence of PPh_3. However, the relatively large phosphine did not alter the outcome of the reaction, and complex **1** was isolable in customary yields from the final reaction mixture.

The smaller phosphine, PMe_3, reacts readily with Cp*W(NO)(CH_2SiMe_3)Cl to form the metal-centered adduct, Cp*W(NO)(CH_2SiMe_3)(Cl)(PMe_3).[9] However, this adduct reacts with $KOCMe_3$ in pentane to produce only Cp*W(NO)(CH_2SiMe_3)($OCMe_3$).

Epilogue

The roles of $KOCMe_3$ and KOMe in reactions 2 and 3 are not clear, and to date we have not yet discovered other reagents which effect the same chemical transformations. The potassium cation must play an important function in these reactions since simple metatheses occur if K^+ is replaced by Li^+ or Na^+ (Scheme 1). In addition, it is also evident that the alkoxide anion ($OCMe_3^-$ or OMe^-) influences the outcomes of these reactions. In this connection, it is interesting to note that Schrock and co-workers have also recently found that substitution of the potassium alkoxide, KOCMe(CF_3)$_2$, for its lithium analogue during reactions with group 6 alkylidene chloro complexes leads to markedly different products.[23]

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. We also thank Dr. J. E. Veltheer for assistance and helpful discussions.

Supporting Information Available: Tables of final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, hydrogen parameters, anisotropic thermal parameters, torsion angles, least-squares planes, and intermolecular contacts for complexes **1** and **2** (40 pages). Ordering information is given on any current masthead page.

OM950903E

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[23] Schrock, R. R. *Polyhedron* **1995**, *14*, 3177.