Structure and Reactivity of (η-C_5R_5)Mo$(NO)_2$−Halide, −Halomethyl, and −Alkyl Complexes: Consecutive Aerobic Methylene and Nitrosyl Ligand Oxidation

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Cp′Mo$(NO)_2(CH_2X)$ complexes are isolated in 80−90% yield after the treatment of the Cp′Mo$(NO)_2$X complexes in CH_2Cl_2 with ethereal diazomethane in the presence of Cu powder (Cp′ = η-C_5H_5 (Cp), η-$C_5(CH_3)_5$ (Cp*); X = Cl, Br). The Cp′Mo$(NO)_2(CH_2I)$ derivatives are obtained in over 90% yield by treating the Cp′Mo$(NO)_2(CH_2Cl)$ derivatives with NaI in THF. Four new halomethyl complexes have been characterized by X-ray crystallography and are compared to the related CpMo$(NO)_2$Br, Cp*Mo$(NO)_2$Cl, and Cp*Mo$(NO)_2(CH_3)$ derivatives. The structural data and IR data indicate the donor properties of the halomethyl ligands to be intermediate between halide and alkyl ligands. The Cp′Mo$(NO)_2(CH_2X)$ complexes react initially with O_2 to give CH_2O and the regeneration of the parent Cp′Mo$(NO)_2$X complexes. The Cp′Mo$(NO)_2$Cl complexes react with O_2 after an induction period to give the well-known Cp′MoO_2Cl complexes, NO_2, NOCl, and N_2O. Exposure of CpCr$(NO)_2(CH(CH_3)Br)$ to $^{18}O_2$ gives $^{18}O{=}CH(CH_3)$ and ^{16}O-labeled CpCr$(NO)_2$Br. The Cp′Mo$(NO)_2$−alkyl complexes react with O_2 to give the corresponding Cp′MoO_2−alkyl derivatives in 40−70% yield (alkyl = CH_3, CH_2CH_3). Electrochemical data show the Mo complexes to oxidize at 0.2−0.3 V lower than the Cr congeners.

Introduction

During the past two decades, the study of fundamental metal−carbon interactions has greatly benefited from the availability of α-halomethyl complexes as precursors for the generation of hydroxymethyl, alkoxymethyl, and methylene complexes.[1] The study of metal−methylene stabilization and methylene transfer to organic substrates is an area of considerable importance.[2] We have reported on a variety of new α-halomethyl complexes, focusing primarily on the study of intramolecular methylene insertion processes to give C−C bond formation.[3−9]

During a similar period, activity in the study of homogeneous organometallic oxo complexes has also dramatically increased. Organometallic-oxo complexes like CH_3ReO_3 are important new members in the area of homogeneous catalysis.[10−12] Beginning in 1959,[13] reports on the generation of Cp′−metal−oxo complexes from the controlled oxidation of low valent metallocenes and metal−carbonyl precursors have been especially plentiful (Cp′ = Cp, η-C_5H_5; Cp* = η-$C_5(CH_3)_5$).[14−20] More recently, the use of Cp−metal−nitrosyl complexes as precursors for the generation of oxo-derivatives has

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Table 1. Characterization Data for the Cp′Mo(NO)$_2$(CH$_2$X) Complexes

	CpMo(NO)$_2$(CH$_2$Cl)	CpMo(NO)$_2$(CH$_2$Br)	CpMo(NO)$_2$(CH$_2$I)	Cp*Mo(NO)$_2$(CH$_2$Cl)	Cp*Mo(NO)$_2$(CH$_2$I)
^{1}H NMR, δ (CDCl$_3$)	5.98 (5H, s)	5.98 (5H, s)	5.97 (5H, s)	1.94 (15H, s) (Cp*)	1.92 (15H, s) (Cp*)
	4.30 (2H, 2)	4.06 (2H, s)	3.40 (2H, s)	3.98 (2H, s) (CH$_2$)	3.03 (2H, s) (CH$_2$)
^{13}C NMR, δ (CDCl$_3$)	102.2 (Cp)	102.7 (Cp)	103.2 (Cp)	111.5 (Cp*)	111.5 (Cp*)
	37.4 (CH$_2$),	26.5 (CH$_2$)	−7.5 (CH$_2$)	9.75 (Cp*)	9.71 (Cp*)
	$^1J_{C-H}$ = 148 Hz			44.2 (CH$_2$),	−1.8 (CH$_2$)
				$^1J_{C-H}$ 144 Hz	
ν_{NO}, cm^{-1} (CH$_2$Cl$_2$)	1738, 1648	1747, 1654	1746, 1651	1710, 1625	1715, 1630
anal.: calcd (obsd)					
C	26.64 (26.90)	22.87 (22.76)	19.90 (19.92)	38.80 (39.05)	30.58 (30.86)
H	2.59 (2.55)	2.24 (1.99)	1.93 (1.88)	4.99 (5.24)	3.94 (4.17)
N	10.35 (10.18	8.89 (8.55)	7.74 (7.65)	8.22 (8.19)	6.48 (6.51)
mass spec, *m*/*e* (%), (^{95}Mo)	272 (12%, M$^+$)	316 (13%, M$^+$)	364 (67%, M$^+$)	337 (2%, M$^+$)	434 (61%, M$^+$)
	237 (100%)	237 (100%)	334 (100%)	266 (100%)	404 (100%)
mp, °C	63−64	67−68	64−65	95−98	100−105

Table 2. Summary of the Crystallographic Data for the Cp′Mo(NO)$_2$(CH$_2$X) Complexes (X = Cl, Br, I)

	CpMo(NO)$_2$(CH$_2$Cl)	CpMo(NO)$_2$(CH$_2$Br)	CpMo(NO)$_2$(CH$_2$I)	Cp*Mo(NO)$_2$(CH$_2$Cl)
formula	C$_6$H$_7$N$_2$O$_2$ClMo	C$_6$H$_7$N$_2$O$_2$BrMo	C$_6$H$_7$N$_2$O$_2$IMo	C$_{11}$H$_{17}$N$_2$O$_2$ClMo
crystal system	monoclinic, $P2_1/a$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
a, Å	7.238(2)	7.754(2)	7.822(3)	6.951(2)
b, Å	10.589(3)	8.259(2)	8.406(4)	7.985(3)
c, Å	12.209(5)	8.663(3)	8.964(5)	14.291(6)
α, deg		96.81(2)	98.31(4)	76.92(3)
β, deg	101.73(3)	116.04(2)	115.50(3)	84.28(3)
γ, deg		104.85(2)	104.37(3)	67.55(2)
V, Å^3	916.2(6)	464.4(2)	493.6(4)	714.0(5)
T, K	298	298	298	298
F(000)	528	300	336	344
data colln	$h(+8)$, $k(+12)$, $l(\pm14)$	$h(+8)$, $k(\pm9)$, $l(\pm9)$	$h(+8)$, $k(\pm9)$, $l(\pm10)$	$h(+8)$, $k(\pm9)$, $l(\pm17)$
μ, mm^{-1} (Mo Kα)	1.65	5.60	4.36	1.08
R,[a] R_w[b]	0.0526, 0.0632	0.0465, 0.0566	0.0585, 0.0779	0.0316, 0.0340
GOF	1.14	0.92	0.96	1.34

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

increased.[21−22] The work of Legzdins has been especially helpful in addressing the fate of the NO ligand after attack by O$_2$ and H$_2$O.[23]

Herein we present the novel Cp′Mo(NO)$_2$(CH$_2$X) complexes that react with O$_2$ to produce formaldehyde and the Cp′MoO$_2$X complexes[16,18] (X = Cl, Br, I). We show that the well-known Cp′Mo(NO)$_2$X complexes[24] are produced as intermediates in this process and that they independently undergo oxidation to the Cp′MoO$_2$X products. Remarkably, the Cp′Mo(NO)$_2$−alkyl[25] complexes react with O$_2$ to give the Cp′MoO$_2$−alkyl derivatives by the oxidation of the nitrosyl ligands.[18,19,22]

Results

Formation and Characterization of the Cp′Mo(NO)$_2$(CH$_2$X) Complexes. The repeated dropwise addition of ethereal CH$_2$N$_2$ to a CH$_2$Cl$_2$ slurry of Cu powder and CpMo(NO)$_2$Cl results in the formation of the halomethyl derivative CpMo(NO)$_2$(CH$_2$Cl) (eq 1).

$$\mathrm{Cp'Mo(NO)_2X} \xrightarrow{\mathrm{CH_2N_2/Cu/CH_2Cl_2}} \mathrm{Cp'Mo(NO)_2(CH_2X)} \quad (1)$$

$$\mathrm{Cp'Mo(NO)_2(CH_2Cl)} \xrightarrow{\mathrm{NaI/THF}} \mathrm{Cp'Mo(NO)_2(CH_2I)} \quad (2)$$

Similar conditions lead to the formation of CpMo(NO)$_2$)(CH$_2$Br) and Cp*Mo(NO)$_2$(CH$_2$Cl) from the corresponding halide precursors. The direct formation of the iodomethyl derivatives by the treatment of the Cp′Mo(NO)$_2$I precursors with ethereal CH$_2$N$_2$/Cu powder is especially sluggish. However, stirring the Cp′Mo(NO)$_2$(CH$_2$Cl) derivatives with excess NaI in THF gives essentially quantitative conversion to the Cp′Mo(NO)$_2$(CH$_2$I) derivatives (eq 2).

The air-sensitive green to greenish-yellow halomethyl complexes are freely soluble in organic solvents and are easily recrystallized from pentane at low temperature. As shown in Table 1, each of the halomethyl complexes display characteristic ^{1}H and ^{13}C NMR signals for the coordinated Cp′ and CH$_2$X ligands. Two strong IR absorptions for the [Mo(NO)$_2$] moiety are observed, and each of the complexes shows a significant parent ion in the CI mass spectrum.

The new halomethyl complexes melt under N$_2$ with decomposition at temperatures somewhat lower than their parent halides. The headspace gas contains N$_2$O as the only gaseous product detectable by IR spectroscopy. In control experiments, the headspace above heated and evacuated samples of CpMo(NO)$_2$Cl contains NO, NO$_2$, and N$_2$O as detected by IR spectroscopy.

Structural Analysis. The crystallographic parameters for the new halomethyl complexes together with the data for the related CpMo(NO)$_2$Br, Cp*Mo(NO)$_2$Cl, and Cp*Mo(NO)$_2$(CH$_3$) complexes are presented in Tables 2 and 3. The thermal ellipsoid plot for Cp*Mo(NO)$_2$(CH$_2$I) in Figure 1 is representative of the general structural features of the Cp′Mo(NO)$_2$(L) piano-stool complexes presented in this work. Tables 4 and 5 list a comprehensive summary of the relevant structural features of the complexes using the atom-labeling scheme shown in Figure 1.

The terminal nitrosyl ligands have [Mo−N−O] bond angles ranging from 165.7 to 175.2°. The Cp and Cp*

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Table 3. Summary of the Crystallographic Data for the Cp′Mo(NO)$_2$X Complexes (X = Cl, Br, CH$_3$)

	CpMo(NO)$_2$Br	Cp*Mo(NO)$_2$Cl	Cp*Mo(NO)$_2$(CH$_3$)
formula	$C_5H_5N_2O_2BrMo$	$C_{10}H_{15}N_2O_2ClMo$	$C_{11}H_{18}N_2O_2Mo$
crystal system	triclinic, $P\bar{1}$	monoclinic $P2_1/n$	monoclinic, $P2_1/c$
a, Å	6.933 (2)	12.527(3)	7.601(2)
b, Å	6.937(2)	7.536(2)	14.712(4)
c, Å	9.995(2)	14.413(6)	12.208(2)
α, deg	87.94(3)		
β, deg	71.17(3)	105.91(3)	99.19(2)
γ, deg	70.79(3)		
V, Å^3	428.3(2)	1308.5(7)	1347.5(6)
T, K	298	298	298
F(000)	284	656	624
data colln	$h(\pm 8)$, $k(\pm 8)$, $l(-11)$	$h(+14)$, $k(+8)$, $l(\pm 17)$	h,$(+8)$, $k(+16)$, $l(\pm 13)$
μ, mm^{-1} (Mo Kα)	6.15	1.658	0.939
R,[a] R_w[b]	0.0388, 0.0527	0.0249, 0.0351	0.0359, 0.0459
GOF	0.84	0.81	1.13

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

ligands are bound symmetrically to the metal with an essentially constant Mo−Cp′$_{centroid}$ distance. The Mo−C(6) bond distances for the four halomethyl complexes are constant within experimental error and are not significantly different from the Mo−C(6) distance in Cp*Mo(NO)$_2$(CH$_3$). The [Mo−C(6)−X] bond angles are nearly constant and the [Cp$_{centroid}$−Mo−C(6)−X] torsion angle ranges from 64° in CpMo(NO)$_2$(CH$_2$Cl) to 80° in Cp*Mo(NO)$_2$(CH$_2$Cl). The Mo−C(6) bond in the halomethyl and methyl complexes nearly eclipses the C(4)−H(4a) or C(4)−C(14) bonds on the Cp′ ring, with the nonbonded C(6)−C(4) approach ranging from 3.03 to 3.06 Å. In the case of Cp*Mo(NO)$_2$Cl, the Mo-Cl bond is approximately staggered between the two nearest C−CH$_3$ bonds of the Cp* ligand.

Reactivity of CpMo(NO)$_2$(CH$_2$Cl) with Ag$^+$. Treatment of CpMo(NO)$_2$(CH$_2$Cl) with AgBF$_4$ in CD$_2$Cl$_2$ for 1 h results in the precipitation of AgCl and the appearance of a single new Cp ^{1}H NMR signal at δ 6.19. New multiplet signals at δ 1.22 and 0.88 characteristic of oligomeric hydrocarbons are also observed. The IR spectrum of this mixture shows the ν_{NO} absorptions of the starting complex to be replaced by ν_{NO} absorptions at 1780 cm^{-1} and 1687 cm^{-1} attributed to the solvated [CpMo(NO)$_2$]$^+$ species (eq 3).[26] Treatment of CpMo(NO)$_2$(CH$_2$Cl) in CD$_2$Cl$_2$ with AgBF$_4$ in the presence of 10 equiv of cyclohexene produces only a trace amount of norcarane as detected by ^{1}H NMR spectroscopy.

$$\mathrm{CpMo(NO)_2(CH_2Cl)} \xrightarrow{\mathrm{AgBF_4/CD_2Cl_2}} [\mathrm{CpMo(NO)_2{-}solvent}]^+/\mathrm{BF_4}^- + \mathrm{AgCl(s)} + {-}(\mathrm{CH_2})_x{-} \quad (3)$$

Reaction of CpMo(NO)$_2$(CH$_2$Cl) with O$_2$. Over a 12 h period, the introduction of 1 equiv of dry O$_2$ into the headspace of a 5-mm NMR tube containing a CD$_2$Cl$_2$ solution of CpMo(NO)$_2$(CH$_2$Cl) results in the gradual disappearance of the starting ^{1}H NMR signals at δ 5.98 and 4.30 and the simultaneous development of new signals at δ 9.71 and 6.05 that are attributable to CH$_2$O and CpMo(NO)$_2$Cl, respectively (eq 4). Continued exposure to excess O$_2$ results in a color change from green to yellow-brown, the development of a flocculent precipitate, and the evolution of a brown headspace gas. The ^{1}H NMR spectrum shows a single new resonance from CpMoO$_2$Cl (δ 6.66), and IR spectroscopy of the headspace gas shows the presence of NO$_2$.

$$\mathrm{CpMo(NO)_2(CH_2Cl)} \xrightarrow{\mathrm{CD_2Cl_2/O_2}} \mathrm{CpMo(NO)_2Cl} + \mathrm{CH_2O} \xrightarrow{\mathrm{CD_2Cl_2/O_2}} \mathrm{CpMoO_2Cl} + 2\mathrm{NO_2} \quad (4)$$

Inside an evacuated gas IR cell, crystalline CpMo(NO)$_2$Cl evolves NO and traces of N$_2$O after standing at 100 °C for 1 h. The exposure of microcrystalline CpMo(NO)$_2$Cl to a 1:10 O$_2$/N$_2$ mixture at 1 atm inside the gas IR cell results in strong IR absorptions from NO$_2$ together with smaller amounts of NOCl and N$_2$O. Following a 1−3 min induction time, a CD$_2$Cl$_2$ solution of pure CpMo(NO)$_2$Cl undergoes a reaction with O$_2$ to give yellow CpMoO$_2$Cl (^{1}H NMR: δ 6.66) together with the visible evolution of a brown gas identified by IR spectroscopy as NO$_2$ (eq 5). The induction period is shortest when the reaction vessel is capped immediately after introduction of O$_2$.

$$\mathrm{CpMo(NO)_2Cl} \xrightarrow{\mathrm{CD_2Cl_2/O_2}} \mathrm{CpMoO_2Cl} + \mathrm{NO_2} \quad (5)$$

Exposure of microcrystalline CpMo(NO)$_2$(CH$_2$Cl) to a 1:10 O$_2$/N$_2$ gas mixture at 1 atm inside a sealed gas-IR cell results in a gradual color change from green to yellow and the evolution of NO$_2$, NOCl, N$_2$O, and CH$_2$O headspace gases as monitored by IR spectroscopy. A similar treatment with a ^{18}O$_2$/N$_2$ mixture produces a mixture of the ^{16}O/^{18}O isotopomers of NO$_2$, NOCl, and CH$_2$O but only the ^{16}O isotopomer of N$_2$O (eq 6). The

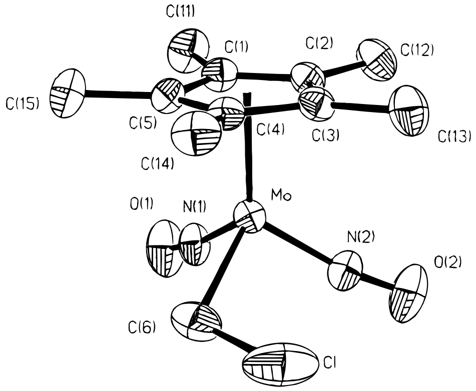

Figure 1. Thermal ellipsoid plot of Cp*Mo(NO)$_2$(CH$_2$Cl) with numbering scheme (30% probability level).

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Table 4. Selected Geometric Data for the Cp′Mo(NO)$_2$(CH$_2$X) Complexes (X = Cl, Br, I, H)

feature	CpMo(NO)$_2$(CH$_2$Cl)	CpMo(NO)$_2$(CH$_2$Br)	CpMo(NO)$_2$(CH$_2$I)	Cp*Mo(NO)$_2$(CH$_2$Cl)	Cp*Mo(NO)$_2$(CH$_3$)
Cp′$_{cent}$−Mo, Å	2.04	2.04	2.05	2.02	2.03
Mo−N(1), Å	1.824(7)	1.828(10)	1.821(10)	1.820(4)	1.815(6)
Mo−N(2), Å	1.830(7)	1.823(8)	1.819(8)	1.824(3)	1.806(5)
N(1)−O(1), Å	1.167(10)	1.185(14)	1.180(15)	1.185(6)	1.160(9)
N(2)−O(2), Å	1.173(9)	1.170(12)	1.161(11)	1.168(4)	1.186(7)
Mo−C(6), Å	2.192(10)	2.200(9)	2.197(9)	2.187(5)	2.170(7)
C(6)−X, Å	1.783(9)	1.953(12)	2.154(12)	1.810(5)	
∠, deg					
Mo−N(1)−O(1)	173.9(7)	175.2(6)	175.2(5)	168.9(4)	169.7(6)
Mo−N(2)−O(2)	174.2(7)	173.4(6)	174.5(6)	170.4(4)	172.9(4)
∠, deg					
Mo−C(6)−X	113.1(5)	112.5(5)	113.0(5)	112.3(3)	
∠, deg					
N(1)−Mo−N(2)	93.3(3)	92.5(4)	92.2(4)	94.7(2)	95.0(2)
N(1)−Mo−C(6)	97.7(4)	93.9(4)	94.5(4)	97.7(2)	98.9(3)
N(2)−Mo−C(6)	93.8(3)	96.0(4)	95.6(4)	96.7(2)	96.2(2)
∠, deg					
Cp$_{cent}$−Mo−N(1)	125.9	128.9	129.5	122.4	122.4
Cp$_{cent}$−Mo−N(2)	125.8	125.0	124.4	124.5	124.7
Cp$_{cent}$−Mo−C(6)	113.1	112.5	112.5	115.1	113.9
torsion ∠, deg					
Cp′$_{cent}$−Mo−C(6)−X	63.6	76.1	74.8	80.0	

Table 5. Selected Geometric Data for CpMo(NO)$_2$Br and Cp*Mo(NO)$_2$Cl

feature	CpMo(NO)$_2$Br	Cp*Mo(NO)$_2$Cl
Cp′$_{cent}$−Mo, Å	2.01	2.02
Mo−N(1), Å	1.821(6)	1.829 (4)
Mo−N(2), Å	1.823(6)	1.833 (4)
N(1)−O(1), Å	1.178(9)	1.179 (5)
N(2)−O(2), Å	1.183(9)	1.153 (5)
Mo−X, Å	2.555(1)	2.412 (1)
∠, deg		
Mo−N(1)−O(1)	168.9(7)	167.1(3)
Mo−N(2)−O(2)	167.1(6)	165.7(4)
∠, deg		
N(1)−Mo−N(2)	92.0(3)	93.5(2)
N(1)−Mo−X	101.5(2) (X = Br)	103.1(1) (X = Cl)
N(2)−Mo−X	102.0(2) (X = Br)	102.8(1) (X = Cl)
∠, deg		
Cp$_{cent}$−Mo−N(1)	120.2	119.8
Cp$_{cent}$−Mo−N(2)	121.1	118.8
Cp$_{cent}$−Mo−X	115.8	115.3

residue contains a mixture of the $^{16}O/^{18}O$ isotopomers of $CpMoO_2Cl$ as the only identifiable organometallic products.

$$\mathrm{CpMo(NO)_2(CH_2Cl)(s)} \xrightarrow{^{18}O_2} \underset{\text{mixture of }^{16}\text{O}/^{18}\text{O isotopomers}}{\mathrm{CpMoO_2Cl}} + \mathrm{NO_2} + \mathrm{NOCl} + \mathrm{CH_2O} + \mathrm{N_2{}^{16}O} \quad (6)$$

As monitored by ^1H NMR spectroscopy, the treatment of a $CHCl_3$ solution of $CpMo(NO)_2Cl$ with an excess of NO_2 or O_3 gas results in the immediate generation of $CpMoO_2Cl$ in a ca. 80% spectroscopic yield (eq 7). The treatment of $CpMo(NO)_2(CH_2Cl)$ with NO_2 or O_3 gives a similar result together with the additional appearance of CH_2O (δ 9.71) in the ^1H NMR spectrum (eq 8). N_2O is the only new gaseous product detected by IR spectroscopy when solid samples of $CpMo(NO)_2Cl$ or $CpMo(NO)_2(CH_2Cl)$ are treated with NO_2. The exposure of the $Cp'M(NO)_2X$ or $Cp'M(NO)_2(CH_2X)$ complexes to excess N_2O does not produce any detectable reaction within 24 h (M = Cr, Mo).

$$\mathrm{CpMo(NO)_2Cl} \xrightarrow{[Ox]} \mathrm{CpMoO_2Cl} + \mathrm{N_2O} \quad (7)$$

$$\mathrm{CpMo(NO)_2(CH_2Cl)} \xrightarrow{[Ox]} \mathrm{CpMoO_2Cl} + \mathrm{CH_2O} + \mathrm{N_2O} \quad (8)$$

$$[\mathrm{Ox}] = \mathrm{NO_2} \text{ or } \mathrm{O_3}$$

Reaction of CpMo(NO)$_2$(CH$_3$) with O$_2$. As monitored by ^1H NMR spectroscopy, the treatment of $CpMo(NO)_2(CH_3)$ in CH_2Cl_2 with excess O_2 gas results in the disappearance of the starting complex and the generation of $CpMoO_2(CH_3)$ (δ 6.33 and 1.46) in a 75% spectroscopic and 60% isolated yield (eq 9). Low-intensity hydrocarbon-like resonances at δ 1.22 and 0.88 are also visible. This reaction occurs after a 1−3 min induction period, with the shorter time being observed when the reaction vessel is capped. A similar treatment of $CpMo(NO)_2(CH_2CH_3)$ or $Cp^*Mo(NO)_2(CH_3)$ with O_2 gives the corresponding $Cp'MoO_2(R)$ derivatives as the only identifiable organometallic products in 47% and 40% isolated yields, respectively. The exposure of microcrystalline $CpMo(NO)_2(CH_3)$ to a 1:10 O_2/N_2 gas mixture at 1 atm inside a sealed gas-IR cell results in a gradual darkening and the formation of NO_2 as the only gaseous product visible in the IR spectrum of the headspace gas. The residue contains $CpMoO_2(CH_3)$ as the only identifiable organometallic product.

$$\mathrm{Cp'Mo(NO)_2(R)} \xrightarrow{O_2/CD_2Cl_2} \mathrm{Cp'MoO_2(R)} + \mathrm{NO_2} \quad (9)$$

$$\mathrm{R} = \mathrm{CH_3},\ \mathrm{CH_2CH_3}$$

Reaction of CpCr(NO)$_2$(CH(CH$_3$)Br) with O$_2$. The treatment of a $CDCl_3$ solution of $CpCr(NO)_2(CH(CH_3)Br)$ with O_2 gas leads to the disappearance of the ^1H NMR signals of the starting material and a corresponding increase in the signals from $CpCr(NO)_2Br$ (δ 5.72) and $O{=}CH(CH_3)$ (δ 2.19 (d) and 9.77 (q)) (eq 10).

$$\mathrm{CpCr(NO)_2(CH(CH_3)Br)(s)} \xrightarrow{^{18}O_2} \mathrm{CpCr(N^{16}O)_2Br} + {}^{18}\mathrm{O{=}CH(CH_3)} \quad (10)$$

After 36 h, this reaction is quantitative by ^1H NMR spectroscopy. When solid $CpCr(NO)_2(CH(CH_3)Br)$ is exposed to a 1:10 O_2/N_2 gas mixture at 1 atm in a sealed

Table 6. Oxidation Potentials for Selected Cr and Mo Complexes

complex[a]	oxidn pot, V[b]	complex[a]	oxidn pot, V[b]
$CpCr(NO)_2Cl$	1.22 ($E°'$)[c]	$CpMo(NO)_2(CH_2Br)$	0.94 (E_{pa})
$CpMo(NO)_2Cl$	1.02 ($E°'$)	$CpCr(NO)_2(CH_3)$	1.09 (E_{pa})
$CpCr(NO)_2(CH_2Cl)$	1.24 (E_{pa})[d]	$Cp^*Mo(NO)_2(CH_3)$	0.82 (E_{pa})

[a] 1.0×10^{-3} M in CH_2Cl_2, 0.2 M Bu_4NPF_6 supporting electrolyte; $v = 1$ V/s. [b] Versus ferrocene/ferrocenium couple. [c] Midpoint potential (partially reversible). [d] Peak anodic (irreversible).

gas cell, the solid becomes gummy and acetaldehyde is detected in the headspace by IR spectroscopy. The use of $^{18}O_2$ leads to the formation of $^{18}O{=}CH(CH_3)$ and the IR spectrum of the reaction residue reveals ^{16}O-labeled $CpCr(NO)_2Br$ to be the only isotopomer present (eq 10).

Electrochemical Potentials. The oxidation potentials for the Cr and Mo congeners of $CpM(NO)_2Cl$, $CpM(NO)_2(CH_2Cl)$, and $Cp'M(NO)_2(CH_3)$ are listed in Table 6. The oxidation waves for the $CpM(NO)_2Cl$ complexes are partially reversible, permitting the determination of the midpoint potentials $E°$. The remaining complexes undergo irreversible oxidation in CH_2Cl_2, leading only to the determination of their E_{pa} (anodic peak) values.

Discussion

Characterization of the Mo−Halomethyl Complexes. Similar to the well-known reactivity of selected main-group[27] and transition metal halides,[3,4,7,9,28–30] $CpMo(NO)_2Cl$ and $CpMo(NO)_2Br$ react with diazomethane to give the corresponding $CpMo(NO)_2(CH_2Cl)$ and $CpMo(NO)_2(CH_2Br)$ derivatives (eq 1). This conversion is much more sluggish than that seen for the $Cp'Cr(NO)_2X$ complexes,[3,4] requiring 3−4 times as much CH_2N_2 together with repeated addition of fresh Cu powder before the Mo halides are completely consumed. The conversion of the $Cp'Mo(NO)_2I$ complexes to the $Cp'Mo(NO)_2(CH_2I)$ derivatives with the diazomethane/Cu method is extremely slow. Fortunately, the metathesis of Cl^- for I^- occurs efficiently when $CpMo(NO)_2(CH_2Cl)$ is treated with excess NaI in THF (eq 2).

The IR spectral features of the Mo−halomethyl complexes indicate the halomethyl ligand to be intermediate in donor/acceptor properties between halide and methyl ligands. The average ν_{NO} values for the halomethyl complexes are 10−15 cm^{-1} lower energy than their corresponding parent halides and 15−20 cm^{-1} higher in energy than the corresponding methyl complexes. The 25−30 cm^{-1} lower ν_{NO} values in the $Cp^*Mo(NO)_2(CH_2X)$ complexes is a direct indication of increased metal to NO back-donation caused by the stronger Cp* donor (*vide infra*).[31]

The NMR spectroscopic features of the (CH_2X) moiety of the $Cp'Mo(NO)_2(CH_2X)$ complexes reflect trends similar to organic alkyl halides.[32] The ^1H NMR signal of the $-CH_2X$ group is steadily deshielded as the electronegativity of X increases from H to I to Br to Cl. A similar trend is observed in the ^{13}C spectrum except that the resonance of the (CH_2I) carbon occurs at higher field than the (CH_3) carbon. The 6−7 ppm shift of the methylene ^{13}C NMR signals to low field upon changing Cp to Cp* is opposite to the trend in the ^1H NMR spectrum. A similar trend is observed in the $Cp'Cr(NO)_2(CH_2X)$ complexes.[4] With the expectation that the Cp* ligand is more electron releasing to the metal, it is likely that this trend is associated with the paramagnetic shielding effect becoming more dominant as seen in metal carbonyl complexes.[33] Although the $^1J_{C-H}$ values for $CpMo(NO)_2(CH_2Cl)$ (148 Hz) and $Cp^*Mo(NO)_2(CH_2Cl)$ (144 Hz) are slightly larger than the 127 Hz value observed for $Cp^*Mo(NO)_2(CH_3)$, they still fall in the range typical for primary alkyl chlorides.[32]

X-ray Structural Analysis. The series of structurally characterized $Cp'Mo(NO)_2(L)$ complexes presented here permits a detailed analysis of the structure/bonding parameters within this group of 18-electron molybdenum complexes and a comparison to related group 6 dinitrosyl complexes.[4,30b,34]

A direct comparison of the structures of $CpMo(NO)_2Br$ and $Cp^*Mo(NO)_2Cl$ to the halomethyl and methyl derivatives (Tables 4 and 5) shows that the [Mo−N−O] bond angles are significantly more linear in the halomethyl complexes. There is little difference in the [N(1)−Mo−N(2)] bond angles, but the $[Cp'_{cent}{-}Mo{-}N]$ bond angles are somewhat more acute in the halide complexes. Since the trends in the ν_{NO} values suggest an increase in donor character from halide < CH_2X < CH_3, it is apparent that the entire $[Mo(NO)_2]$ geometry rather than just the [Mo−N−O] bond angles should be considered in assessing the relative donor power of ligands. Any trends in the Mo−N and N−O distances for the complexes presented are too small (relative to the error of the experiments) to be helpful for interpreting the relative extent of back-donation into the NO π^* levels. Nevertheless, the [Mo−N−O] bond angles in $Cp^*Mo(NO)_2(CH_2Cl)$ and $Cp^*Mo(NO)_2(CH_3)$ are 4−5° smaller than in $CpMo(NO)_2(CH_2Cl)$. $Cp^*Mo(NO)_2Cl$ has the smallest [Mo−N−O] bond angles in the entire series. Thus, the donor power of the Cp* ligand is apparently translated into the $[M(NO)_2]$ π^*-framework and results

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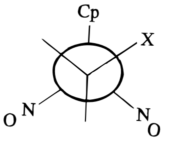
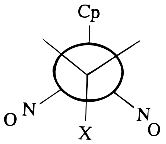
in more acute [Mo−N−O] angles. The geometry in the halide complexes may be a reflection of considerable halide π-donation into the [Mo(NO)$_2$] moiety.[35] The Mo−Cp′$_{centroid}$ distances are not significantly different between the Cp and Cp* complexes presented.

The basic parameters of the Cp′Mo(NO)$_2$(CH$_2$X) complexes are essentially constant. The Mo−C(6) bond length varies only slightly between the halomethyl complexes and is the same as the Mo−C(6) bond length in Cp*Mo(NO)$_2$(CH$_3$). This data together with a relatively low $^1J_{C-H}$ value for the −CH$_2$Cl ligand argues for a simple [Mo−CH$_2$Cl] bonding interaction over one described by a [Mo=CH$_2$$^+Cl^-$] resonance form.

The most curious feature of the four new Mo−halomethyl complexes is their similar adoption of a *gauche* conformation of the halide substituent relative to the Cp ligand (**A**). Table 4 shows the torsion angle [Cp$_{cent}$−Mo−C(6)−X] to increase from 64° for CpMo(NO)$_2$(CH$_2$Cl) to 76 and 75° for CpMo(NO)$_2$(CH$_2$Br) and CpMo(NO)$_2$(CH$_2$I), respectively. This trend together with a comparable torsion angle of 80° Cp*Mo(NO)$_2$(CH$_2$Cl) is consistent with increasing steric demands of the halides and the Cp* ligand. The equivalence of the methylene protons in the ^{1}H NMR spectrum down to −90 °C does not argue for a strongly locked *gauche* solution conformation observed for Cp*Ru(NO)(CH$_2$Cl)$_2$ by NOE ^{1}H NMR spectroscopy.[6] While the *anti* orientation (**B**) in the Cp*Cr(NO)$_2$(CH$_2$I) and [CpCr(NO)$_2$(CH$_2$PPh$_3$)]$^+$ complexes was presumed to be reasonable on steric grounds,[4] it is possible that the longer metal−carbon bond lengths in the Mo complexes (both Mo−Cp and Mo−CH$_2$) make the *gauche* conformation more stable for the Mo complexes. Steric demands are likely to be further amplified in the Mo complexes by the more acute [N−M−N] and [N−M−C] angles as compared to the corresponding Cp′Cr(NO)$_2$ analogues.[4]



A



B

Reactivity of the Halomethyl Complexes With Ag$^+$. Halide abstraction from CpMo(NO)$_2$(CH$_2$Cl) produces IR and ^{1}H NMR spectra consistent with the generation of a solvent-stabilized [CpMo(NO)$_2$]$^+$ species together with intractable hydrocarbon (polymethylene) residues (eqs 3 and 4).[36] The fact that some norcarane is formed when cyclohexene is present suggests that a transient [CpMo(NO)$_2$(=CH$_2$)]$^+$ species is generated. Attempts to observe a methylene complex by ^{1}H NMR spectroscopy at low temperature have been unsuccessful.

Previous work from our group on CpCr(NO)$_2$(CH$_2$Cl) showed that Cl$^-$ abstraction with Ag$^+$ leads to the formation of [(C$_5$H$_4$CH$_3$)Cr(NO)$_2$]$^+$ in good yield.[3,4] This process is proposed to occur via an intramolecular migration of the methylene moiety into a Cp C−H bond in a putative [CpCr(NO)$_2$(=CH$_2$)]$^+$ species. The absence of any detectable intramolecular CH$_2$ migration into a C−H bond of the η^5-C$_5$H$_5$ ligand when the Cp′Mo(NO)$_2$(CH$_2$X) complexes are treated with Ag$^+$ may be a consequence of the longer Mo−ligand bonds. The distance between C(6) and the closest Cp′ skeletal carbon atom in the Mo−halomethyl complexes is 0.13−0.15 Å longer than the corresponding distances in the related Cp*Cr(NO)$_2$(CH$_2$I) complex. In addition, the longer Mo−ligand bonds may increase the favorability of the *gauche* conformation of the halomethyl ligand. If steric interactions between the CH$_2$X ligand and the [CpMo(NO)$_2$] moiety are lower in the *gauche* conformation (*vide supra*), the CH$_2$X ligand may spend much less time in an *anti* conformation that is best oriented for CH$_2$ migration into a C−H bond of the Cp ligand (**A**). Halide abstraction from the *gauche* conformation would produce a [Mo=CH$_2$] conformation that is unfavorable for a smooth migration into the Cp C−H bond (**B**).

Reactivity of Cp′Mo(NO)$_2$X and Cp′Mo(NO)$_2$(CH$_2$X) With O$_2$. Although the aerobic conversion of the [CpW(NO)$_2$] moiety to the [CpWO$_2$] moiety has been demonstrated,[21b] the air-sensitivity of the CpMo(NO)$_2$X complexes has remained unclear until now. The original report of CpMo(NO)$_2$Cl claims the complex to be considerably air-sensitive,[37] but a more recent report points to its air-stability.[24a] CpMo(NO)$_2$Cl is prone to NO loss upon thermolysis under vacuum. The exclusive formation of small amounts of N$_2$^{16}O even when ^{18}O$_2$ is present suggests the operation of an intramolecular reductive NO-coupling process where N$_2$O is trapped as a kinetically inert product.[38] The evolution of NO in the presence of O$_2$ leads to the formation of highly oxidizing NO$_2$. We show that NO$_2$ independently reacts rapidly with the Cp′Mo(NO)$_2$ complexes to give the corresponding Cp′MoO$_2$ derivatives. The induction times for the O$_2$ reactions are consistent with the increasing buildup of NO$_2$ concentration as the reaction proceeds. Thus, a more rapid reaction can be expected in closed vessels.

The experimental data suggest that the family of Cp′Mo(NO)$_2$L complexes are significantly more susceptible to chemical oxidation than their Cr congeners. From the data in Table 6, it is apparent that the Mo complexes oxidize at ca. 0.2−0.3 V lower potential than their Cr congeners under electrochemical conditions.[39]

Our present work clearly shows that the treatment of the Cp′Mo(NO)$_2$(CH$_2$X) complexes with O$_2$ leads to the initial formation of CH$_2$O together with the regeneration of the parent Cp′Mo(NO)$_2$−halide complexes (eq 4). This shows that the [Mo−CH$_2$X] moiety is more sensitive to oxidative attack than the [Mo−NO] moiety. Because of the subsequent reactivity of the nitrosyl ligands, a direct assessment of initial O$_2$ attack is

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(36) There are now numerous examples of complexes containing weakly coordinating ligands (e.g., BF$_4$$^-$, PF$_6$$^-$, RX); see ref 17 and the following: (a) Beck, W. A.; Schloter, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1214. (b) Sünkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 231. (c) Legzdins, P.; Martin, D. T. *Organometallics* **1983**, *2*, 1785. (d) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599. (e) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766 and references therein. (f) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405. (g) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.

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difficult. Experiments using ^{18}O show the formation of both $^{16}O{=}CH_2$ and $^{18}O{=}CH_2$, but this could result from the action of ^{18}O-labeled NO_2 causing nitrosyl oxidation. However, the reaction of $CpCr(NO)_2(CH(CH_3)Br)$ with $^{18}O_2$ to give only $^{18}O{=}CH(CH_3)$ and the nearly quantitative regeneration of $CpCr(N^{16}O)_2Br$ as the sole isotopomer suggests that O_2 can directly attack at the methylene carbon and does not necessarily scramble into the NO ligands prior to CH_2 oxidation (eq 10). Nevertheless, an intramolecular O atom transfer between a coordinated NO_2 (or possibly $NO(O_2)$ peroxynitrite) ligand and the CH_2 moiety of the halomethyl ligand cannot be completely ruled out.[40] Intramolecular O atom transfer between *cis*-coordinated NO and NO_2 ligands is a well-known process[41] and has been characterized in the closely related $CpCr(NO)_2(NO_2)$ system.[42]

In contrast to the $Cp'Mo(NO)_2(CH_2X)$ derivatives, the reactivity of the alkyl complexes $CpMo(NO)_2(CH_3)$, $CpMo(NO)_2(CH_2CH_3)$, and $Cp^*Mo(NO)_2(CH_3)$ with O_2 shows that the Mo−C bond is surprisingly resistant to oxidative attack when a labile α-substituent is not present (eqs 8 and 9). The formation of the $Cp'MoO_2$−alkyl products in fair to good yields indicates that the oxidation process leads to a preferential activation of the NO ligands. In the case of the 16-electron $Cp'M(NO)R_2$ complexes, attack by O_2 or H_2O leads to the loss of one M−C bond and the formation of $Cp'MO_2R$ products.[22] Whereas the formation of $Cp'MO_2R$ products with β-hydrogens on the R group has not been possible from the 16-electron $Cp'M(NO)R_2$ complexes,[22b] the formation of $CpMoO_2(CH_2CH_3)$ from $CpMo(NO)_2(CH_2CH_3)$ shows that the presence of β-hydrogens does not affect the oxidation of the dinitrosyl complexes.

Summary

A combined spectral and structural study shows the CH_2X ligands in the new $Cp'Mo(NO)_2(CH_2X)$ complexes to have donor properties intermediate between a halide and an alkyl ligand. The failure of the $CpMo(NO)_2(CH_2X)$ complexes to give the $[(\eta\text{-}C_5H_4CH_3)Mo(NO)_2]^+$ cations upon treatment with Ag^+ may be the result of the CH_2X ligand being less constrained to an *anti*-conformation that is favorable for methylene migration. The limited cyclopropanation of cyclohexene is evidence for some generation of a transient $[CpMo(NO)_2{=}CH_2)]^+$ species. Finally, the Mo−CH_2X bonds are much more prone to chemical oxidation than the Mo−CH_2R bonds in related $Cp'Mo(NO)_2$−alkyl complexes. The alkyl and halide derivatives are very sensitive to oxidative loss of the NO ligands. We are continuing to explore the possibility of the role of peroxynitrite intermediates in this chemistry.

Experimental Section

Standard Schlenk techniques were employed in all syntheses. The nitrogen reaction atmosphere was purified by passing through scavengers for water (Aquasorb, Mallinckrodt) and oxygen (Cu catalyst, Chemical Dynamics, So. Plainfield, NJ). Oxygen gas (Matheson) was dried through a column of Aquasorb before use. $^{18}O_2$ gas was used as received from Isotec. Reagent grade solvents were purified by distillation from appropriate drying agents.[43] Chemical reagents were used as received from Aldrich. SiO_2 (Baker, 60−200 mesh) was activated by drying under vacuum for 24 h (10^{-5} Torr). Neutral alumina III was prepared by adding 6% H_2O (by weight) to neutral alumina I obtained from Aldrich. Routine filtrations were performed through Analytical Filter Pulp (Schleicher and Schull).

Infrared spectra were recorded using a Mattson Polaris Icon FT-IR spectrometer. Gaseous samples were examined in a 10 × 2.5 cm cylindrical gas cell that was fitted with KBr windows, a vacuum stopcock, and a 14/20 ground joint for the attachment of a 5-mL sample bulb. Typically 10−15 mg of solid complex was loaded into the sample bulb and the cell was evacuated and then refilled to 1 atm with a 1:10 O_2/N_2 gas mixture (or $^{18}O_2$). Reagent gases (NO, NO_2, N_2O) were obtained from Matheson and used for reference purposes. Ozone was generated using an OREC Model 03V5-O ozonater (Ozone Research and Equipment Corp, Phoenix, AZ). ^{18}O-labeled aldehydes, NO_2, and NOCl were identified on basis of their significantly lower absorption energies as compared to authentic ^{16}O-labeled materials.

The ^1H and ^{13}C NMR spectra were recorded using a Bruker WP-270 spectrometer at 270 and 67.9 MHz or a Varian Associates XL-300 spectrometer at 300 and 75.4 MHz, respectively. Residual solvent peaks were used as internal standards (7.24 ppm [^1H] and 77.0 ppm [^{13}C] for $CDCl_3$; 7.15 ppm [^1H] and 128.0 [^{13}C] for C_6D_6; 5.32 ppm [^1H] for CD_2Cl_2). Mass spectra were obtained with a Finnigan 4610 GC−mass spectrometer using chemical ionization (methane). Melting points were measured with a Mel-Temp device (Laboratory Devices) in sealed capillaries prepared under N_2 and are uncorrected. Combustion analyses were performed by Robertson Laboratories, Inc., Madison, NJ.

Diazomethane (CH_2N_2) was generated using the “alcohol free” method from Diazald (Aldrich).[44] Diazoethane was prepared from the slow addition of 3.0 g of solid 1-ethyl-3-nitro-1-nitroguanidine (Aldrich) to an ice-cooled mixture of 80 mL of Et_2O and 50 mL of 50% aqueous KOH. *Caution: Diazoalkanes are exceedingly toxic, and solutions have been known to explode unaccountably! All work must be carried out in a well-ventilated fume hood behind safety shields.* The ethereal diazoalkane solutions were dried over KOH pellets and were stored in a −60 °C dewar until use. The reservoir of ethereal diazoalkane was tapped with 0.5 mm i.d. Teflon cannula tubing (Rainin Corp.) and the solution was peristaltically pumped (Haake Buchler Model No. 426−2000) using a 20-cm section of 1.6 mm i.d. Viton tubing (Cole-Parmer). A second piece of Teflon tubing delivered the solution to the vented reaction vessel through a rubber septum. Cu powder (electrolytic dust) was used as received from Fisher. Authentic formaldehyde was generated by the thermolysis of solid paraformaldehyde. The compounds $CpMo(NO)_2Cl$,[24] $CpMo(NO)_2(CH_3)$,[25] $Cp^*Mo(CO)_2NO$,[45] $CpMo(NO)_2(CH_2CH_3)$,[25] CpCr-

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$(NO)_2Br$,[4] and $Cp^*Mo(NO)_2Cl$,[26] and NOCl[46] were prepared as described in the literature. $CpMo(NO)_2Br$ was prepared from $CpMo(CO)_2NO$[47] and NOBr.[48] Characterization data for $CpMo(NO)_2Br$: ^1H NMR ($CDCl_3$) δ 6.06 (5H, s); ^{13}C NMR ($CDCl_3$) δ 103.8 (Cp); ν_{NO} (CH_2Cl_2, cm^{-1}) 1755 vs, 1670 vs. Anal. Calcd for $C_5H_5N_2O_2BrMo$: C, 19.95; H, 1.67; N, 9.31. Found: C, 19.78; H, 1.58; N, 9.21. MS (CI, CH_4): *m/e* 302 (10%, M^+), *m/e* 223 (100%). Mp 95−98 °C (dec).

Preparation of $Cp^*Mo(NO)_2(CH_3)$. A solution of $Cp^*Mo(NO)_2Cl$ (0.75 g, 2.3 mmol) in 40 mL of CH_2Cl_2 was cooled to −80 °C and treated with 4.0 mL of a 2.0 M solution of $AlMe_3$ in toluene. The initial bright green color darkened upon the addition, and the solution was allowed to stir for 30 min as it slowly warmed to room temperature. The reaction mixture was transferred directly onto a 3 × 6 cm Al_2O_3 III flash chromatography column prepared in CH_2Cl_2. Elution with pure CH_2Cl_2 produced a bright yellow zone that was collected and taken to dryness *in vacuo*. The residue was extracted with 50 mL of warm hexane. Filtration of the extract and concentration to ca. 10 mL gave 0.50 g (1.6 mmol, 70%) of yellow-green $Cp^*Mo(NO)_2(CH_3)$ upon crystallization at −40 °C. ^{1}NMR ($CDCl_3$): δ 1.85 (15H, s, Cp*); δ 0.43 (3H, s, CH_3). ^{13}NMR ($CDCl_3$): δ 113.0 (C_5Me_5); δ 9.7 ($C_5\mathit{Me}_5$); δ 3.2 (Mo-*Me*), $^1J_{C-H}$ = 127 Hz. ν_{NO} (CH_2Cl_2, cm^{-1}): 1699 vs, 1609 vs. Anal. Calcd for $C_{10}H_{15}N_2O_2ClMo$: C, 43.17; H, 5.88; N, 9.15. Found C, 43.27; H, 6.04; N, 9.24. MS (CI, CH_4): *m/e* 308 (26%, M^+); *m/e* 135 (100%). Mp 95−98 °C.

Preparation of Halomethyl Complexes. A mixture of $CpMo(NO)_2Br$ (0.135 g, 0.449 mmol), 10 g of Cu powder, and 90 mL of CH_2Cl_2 was stirred vigorously while ethereal diazomethane was added dropwise (ca. 1 mL/min) for 25 min. The reaction was filtered into a clean Schlenk tube containing 10 g of fresh Cu powder, and diazomethane addition was resumed for 25 min. After repetition of this step 2 more times, no more starting material was detectable in the reaction mixture as assayed by ^{1}H NMR spectroscopy. After a final filtration, the solvent was removed *in vacuo* and the residue was extracted with 2 × 30 mL of warm pentane. Filtration and concentration of the pentane extracts to 10 mL and placement in −40 °C freezer gave 0.130 g (0.413 mmol, 92%) of green, crystalline $CpMo(NO)_2(CH_2Br)$. The preparation of the other $Cp'Mo(NO)_2(CH_2X)$ complexes was carried out under similar conditions with comparable yields from their corresponding $Cp'Mo(NO)_2X$ precursors. The spectral and analytical data for the halomethyl complexes are summarized in Table 1.

Preparation of Iodomethyl Derivatives. A typical preparation for $CpMo(NO)_2(CH_2I)$ follows: $CpMo(NO)_2(CH_2Cl)$ (0.25 g, 0.92 mmol) was stirred magnetically with 5 g of NaI (33 mmol, excess) in 20 mL of THF for 24 h at room temperature. Hexane (40 mL) was added, the solution was filtered, and the filtrate was taken to dryness *in vacuo*. Extraction of the residue with 40 mL of pentane followed by concentration to ca. 10 mL and crystallization at −40 °C gave 0.31 g (0.86 mmol, 93%) of $CpMo(NO)_2(CH_2I)$ as green crystals.

The preparation of $Cp^*Mo(NO)_2(CH_2I)$ was carried out in a similar fashion in 88% yield from $Cp^*Mo(NO)_2(CH_2Cl)$. The analytical and spectral data for the complexes are presented in Table 1.

Formation of $CpMoO_2Cl$ from $CpMo(NO)_2Cl$. $CpMo(NO)_2Cl$ (0.5 g, 1.9 mmol) was dissolved in 100 mL of CH_2Cl_2 and purged with dry O_2 for 2 min with rapid stirring. The vessel was sealed with a stopper, and stirring was continued for an additional 5 min as the initial green color suddenly faded to yellow. The evolution of NO_2 was visible as a brown gas above the solution, and a small amount of flocculent yellow-brown precipitate was observed. After standing for 1 h the reaction mixture was filtered and concentrated to ca 25 mL. Crystallization at −40 °C gave 0.41 g (1.8 mmol, 94%) of $CpMoO_2Cl$ as a brilliant yellow microcrystalline solid that gave satisfactory combustion analysis. Since comparison to the original spectral data was difficult,[16] high-field NMR data and FT-IR data are given here: ^{1}H NMR ($CDCl_3$) δ 6.66 (s); ^{13}C NMR ($CDCl_3$) δ 113.8; IR (KBr, cm^{-1}) 925 (vs), 895 (vs); IR (CS_2, cm^{-1}) 935 (s), 905 (s); $^{16}O/^{18}O$ labeled 925 (s), 872 (s); $^{18}O/^{18}O$ labeled 888 (s), 866 (s). A similar procedure starting from $Cp^*Mo(NO)_2Cl$ produced Cp^*MoO_2Cl in 92% yield.[18a]

Formation of the $Cp'MoO_2$(alkyl) Derivatives. A reaction tube was charged with 0.2 g (0.8 mmol) of $CpMo(NO)_2(CH_3)$, 25 mL of CH_2Cl_2, and a stir bar and then flushed for 1 min with O_2 gas. After the tube was sealed with a stopper, the initial green color changed suddenly after several minutes to an orange-yellow color with formation of a flocculent yellow-brown precipitate, and a brown gas was observed over the solution. After 5 min no unreacted starting complex was detectable by IR and the reaction mixture was filtered and concentrated to 5 mL. Crystallization at −40 °C gave 0.10 g (0.48 mmol, 60%) of $CpMoO_2(CH_3)$ as pale yellow crystals that possessed spectral and analytical characteristics as previously reported.[22b] $Cp^*MoO_2(CH_3)$[18,22b] was prepared in 40% from a similar treatment of $Cp^*Mo(NO)_2(CH_3)$.

$CpMoO_2(CH_2CH_3)$ was prepared by the treatment of a CH_2Cl_2 solution of $CpMo(NO)_2(CH_2CH_3)$ with O_2, yield 47%. ^{1}H NMR ($CDCl_3$): δ 6.29 (s, 5H, (η^5-$C_5\mathit{H}_5$)); δ 2.56 (q, 2H ($C\mathit{H}_2$-CH_3)); δ 1.77 (d, 3H ($C\mathit{H}_3$)). $^{13}C\{^1H\}$ ($CDCl_3$): δ 109.8 (η^5-C_5H_5); δ 22.3 ($CH_2\mathit{C}H_3$); δ 34.6 ($\mathit{C}H_2CH_3$). IR (KBr, cm^{-1}): ν_{MoO} 920 (vs), 891 (vs). MS (^{98}Mo): $[M]^+$ *m/e* 224 (100%), *m/e* 206 (74%), *m/e* 194 (31%). Anal. Calcd for $C_7H_{10}O_2Mo$: C, 37.87; H, 4.30. Found: C, 37.45; H, 4.30. Mp 85−86 °C (dec).

Synthesis of $CpCr(NO)_2(CH(CH_3)Br)$. The procedure reported for the preparation of $CpCr(NO)_2(CH_2Br)$ was followed using diazoethane in place of CH_2N_2, yield 55%. ^{1}H NMR ($CDCl_3$): δ 5.52 (s, 5H, Cp); δ 5.39 (q, 1H, ^3J = 6 Hz, $C\mathit{H}(CH_3)Br$); δ 2.34 (d, 3H, ^3J = 6 Hz, $CH(C\mathit{H}_3)Br$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 101.3 (Cp); δ 63.3 ($\mathit{C}H(CH_3)$; δ 35.5 ($CH(\mathit{C}H_3)Br$). IR (CH_2Cl_2, cm^{-1}): ν_{NO} 1791 (vs), 1686 (vs). Anal. Calcd for $C_7H_9N_2O_2BrCr$: C, 29.49; H, 3.18; N, 9.83. Found: C, 29.24; H, 2.99; N, 9.69. Mp 56 °C.

X-ray Analyses. Suitable crystals were fixed vertically on glass fibers with epoxy cement and centered at room temperature on either a Nicolet R3m/V or a P4 autodiffractometer equipped for graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Unit cells were determined from 25 randomly selected reflections with $15^o \leq 2\theta \leq 30^o$. The structures were solved by Patterson methods, and the remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Hydrogen atoms were generated in idealized positions with fixed (0.08) thermal parameters. All computations used the SHELXTL PLUS package of programs (now distributed by Siemens, Madison, WI) on either a MicroVax or a VAXStation 3100 computer. Tables 2 and 3 contain the summary of the crystal data parameters for the complexes. Complete listings of the bond lengths and angles, fractional coordinates and anisotropic displacement parameters, and H atom coordinates and thermal ellipsoid plots are available as Supporting Information.

Electrochemical Measurements. Cyclic voltammetry measurements were made using JAS Instrument Systems potentiostat (Model J-1600-B) driven by a Hewlett-Packard 3314A function generator. The signals were filtered using a dual channel low pass filter (Stanford Research Systems Inc., Model SR640) and recorded on a Nicolet Model 310 digital oscilloscope.[49] The experiments were controlled by an IBM AT computer via an IEEE interface. To reduce periodic noise, multiple scans at selected sweep rates, sweep ranges, and trigger intervals were collected and averaged.[50] Positive *IR* compensation was employed, and the working electrode was

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a Pt disk electrode ($d = 0.8$ mm). The counter electrode was a stainless steel wire, and the reference electrode was a Ag wire in 0.01 M $AgNO_3$ in 0.1 M Bu_4NPF_6 acetonitrile solution.[51] The working electrode was refreshed between measurements. All measurements were made under an argon atmosphere using 1×10^{-3} M sample concentrations in CH_2Cl_2 that also contained 0.2 M $[Bu_4N][PF_6]$ as the supporting electrolyte.

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Supporting Information Available: Complete details of the X-ray structure determinations for $CpMo(NO)_2(CH_2Cl)$, $CpMo(NO)_2(CH_2Br)$, $CpMo(NO)_2(CH_2I)$, $Cp^*Mo(NO)_2(CH_2Cl)$, $Cp^*Mo(NO)_2(CH_3)$, $CpMo(NO)_2Br$, and $Cp^*Mo(NO)_2Cl$ including tables of collection and refinement parameters, complete bond angles and bond distances, fractional atomic positions, equivalent isotropic and anisotropic thermal parameters, and calculated H atom coordinates and thermal ellipsoid plots (35 pages). Ordering information is given on any current masthead page.

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