

Organometallic Amido Nitrosyl Complexes of Molybdenum and Tungsten¹

Peter Legzdins,* Steven J. Rettig, and Kevin J. Ross

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

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Treatment of Cp*M(NO)Cl₂ (Cp* = η⁵-C₅Me₅; M = Mo, W) with arylamines, ArNH₂ (Ar = phenyl, *o*-tolyl, or *p*-tolyl) affords 18-valence-electron adducts of the type Cp*M(NO)Cl₂NH₂Ar. These adducts can be dehydrohalogenated with a strong base to produce the amido chloro complexes Cp*M(NO)(NHAr)Cl in good yields. These latter complexes can also be prepared by treatment of Cp*M(NO)Cl₂ with 1 equiv of a lithium amide. Interestingly, treatment of Cp*M(NO)Cl₂ with excess primary alkylamines produces directly the amido chloro complexes, Cp*M(NO)(NHR)Cl (R = alkyl). Mixed alkyl amido and alkoxo amido complexes are preparable by sequential treatment of Cp*M(NO)Cl₂ with 1 equiv of an alkylating reagent or lithium alkoxy followed by treatment with excess alkylamine. The solid-state molecular structures of the two representative complexes, Cp*Mo(NO)Cl₂PhNH₂ (1) and Cp*W(NO)(OCMe₃)(NHCMe₃) (18) have been established by single-crystal X-ray diffraction analyses. Crystals of 1 are monoclinic, space group *P*2₁/*c*, with *a* = 8.590(1) Å, *b* = 9.430(2) Å, *c* = 22.386(2) Å, β = 94.16(1)°, and *Z* = 4; the structure was solved by conventional heavy-atom methods and was refined by full-matrix least-squares procedures to *R*_F = 0.030 and *R*_{wF} = 0.029 for 2366 reflections with *I* ≥ 3σ(*I*). Crystals of 18 are also monoclinic, space group *P*2₁/*c*, with *a* = 10.103(2) Å, *b* = 15.372(3) Å, *c* = 13.908(2) Å, β = 103.08(1)°, and *Z* = 4; *R*_F = 0.028 and *R*_{wF} = 0.024 for 2684 reflections with *I* ≥ 3σ(*I*). All new complexes isolated have been characterized by elemental analysis and ¹H and ¹³C NMR, IR, and mass spectroscopies. The IR spectroscopic and electrochemical properties of some complexes are specifically compared and discussed in terms of the relative electron-donating properties of the various ligands when attached to Cp*M(NO) fragments.

Introduction

Previous work in these laboratories has established that the monomeric, 16-valence-electron Cp*M(NO)R₂ complexes [Cp' = Cp(η⁵-C₅H₅), Cp*(η⁵-C₅Me₅); 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-alkoxides or metal-amides in place of the metal-alkyl or -aryl bonds. These complexes should possess metal-ligand bond polarity greater than that of their dialkyl or diaryl congeners and thus should exhibit increased reactivity with polar substrates. Furthermore, they should be weaker Lewis acids than the Cp*M(NO)R₂ systems since the electronic requirements of the metal centers may be somewhat satisfied by M–O or M–N multiple bonding. Consistently, preliminary investigations of the alkoxo alkyl complexes, Cp*M(NO)(OR)(R), and the bis(alkoxo) compounds, Cp*M(NO)(OR)₂, indicate that they are generally more air stable and less reactive toward small Lewis bases than are the corresponding dialkyl or diaryl species.³ Since the net amount of electron density transferred to the metal center from an amide ligand should be less than that from the corresponding alkoxy group, it is reasonable to expect that the presence of amido ligands should result in greater reactivity than that exhibited by the alkoxo species toward Lewis bases while still retaining increased reactivity with polar substrates. In addition,

the study of related Cp*M(NO)(OR)(R), Cp*M(NO)(NHR)(R), and Cp*M(NO)(NHR)(OR) complexes should permit the establishment of the relative reactivities toward various substrates of metal-carbon, metal-nitrogen, and metal-oxygen bonds at the same metal centers. This paper describes the syntheses and characterization of such complexes as well as precursor compounds of the types Cp*M(NO)Cl₂(RNH₂) and Cp*M(NO)(NHR)(Cl).

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions in an atmosphere of purified dinitrogen or argon.⁴ General synthetic and electrochemical procedures routinely employed in these laboratories have been described in detail previously.⁵ The organometallic reagents Cp*M(NO)Cl₂ (M = Mo, W) were prepared by published procedures.⁶ *tert*-Butylamine, allylamine, and aniline (Aldrich) were subjected to two freeze-pump-thaw cycles and were dried over CaH₂ or Na. Lithium diisopropylamide, *o*-toluidine, and *p*-toluidine (Aldrich) were used as received. Lithium amides and alkoxydes were prepared by treatment of the corresponding amine or alcohol with 1 equiv of *n*-BuLi (Aldrich) in hexanes. All R₂Mg·x(dioxane) reagents were made by standard methodology.⁷ The active

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Table I. Numbering Scheme, IR, MS, Color, Yield, and Elemental Analysis Data for Complexes 1-14

compd	compd no.	IR (Nujol) (ν_{NO}), cm^{-1}	MS, $m/z^{a,b}$	color (yield, %)	anal. found (calcd)		
					C	H	N
Cp*Mo(NO)Cl ₂ ·PhNH ₂	1	1651	333 [P ⁺ - C ₆ H ₅ NH ₂]	yellow (84)	45.46 (45.19)	5.23 (5.21)	6.76 (6.59)
Cp*Mo(NO)Cl ₂ · <i>o</i> -MeC ₆ H ₄ NH ₂	2	1650	333 [P ⁺ - (<i>o</i> -MeC ₆ H ₄ NH ₂)]	yellow (83)	46.76 (46.48)	5.57 (5.51)	6.33 (6.38)
Cp*Mo(NO)Cl ₂ · <i>p</i> -MeC ₆ H ₄ NH ₂	3	1652	333 [P ⁺ - (<i>p</i> -MeC ₆ H ₄ NH ₂)]	yellow (87)	45.65 (46.48)	5.50 (5.51)	6.38 (6.38)
Cp*W(NO)Cl ₂ ·PhNH ₂	4	1587	421 [P ⁺ - C ₆ H ₅ NH ₂]	red (75)	45.46 (45.19)	5.23 (5.21)	6.76 (6.59)
Cp*Mo(NO)Cl ₂ ·(CH ₂ CHCH ₂ NH ₂)	5	1646	333 [P ⁺ - CH ₂ CHCH ₂ NH ₂]	yellow (76)	40.09 (40.12)	5.66 (5.70)	7.23 (7.20)
Cp*Mo(NO)(NHPh)Cl	6	1606	390 [P ⁺]	maroon (68)	49.48 (49.43)	5.44 (5.44)	7.30 (7.21)
Cp*Mo(NO)(NH(<i>o</i> -MeC ₆ H ₄))Cl·LiCl	7	1615	404 [P ⁺]	maroon (73)	46.11 (45.87)	5.52 (5.21)	6.04 (6.29)
Cp*Mo(NO)(NH(<i>p</i> -MeC ₆ H ₄))Cl	8	1569	404 [P ⁺]	maroon (79)	50.40 (50.69)	5.61 (5.76)	6.87 (6.95)
Cp*W(NO)(NHPh)Cl	9	1573	476 [P ⁺]	red (73)	40.25 (40.31)	4.45 (4.44)	5.84 (5.88)
Cp*W(NO)(NH(<i>p</i> -MeC ₆ H ₄))Cl	10	1538	490 [P ⁺]	red (74)	41.42 (41.61)	4.72 (4.72)	5.68 (5.71)
Cp*Mo(NO)(NHCH ₂ CHCH ₂)Cl	11	1600	356 [P ⁺]	orange (73)	44.29 (44.27)	6.05 (6.00)	7.74 (7.94)
Cp*Mo(NO)(NHCMe ₃)Cl	12	1604	370 [P ⁺]	yellow (82)	45.49 (45.60)	6.92 (6.83)	7.43 (7.60)
Cp*W(NO)(NHCMe ₃)Cl	13	1540	456 [P ⁺]	orange (80)	37.09 (36.82)	5.52 (5.52)	6.36 (6.13)
Cp*W(NO)(NHCH ₂ CHCH ₂)Cl	14	1545	440 [P ⁺]	red (85)	35.10 (35.43)	5.00 (4.80)	6.20 (6.36)

^a m/z are for the highest intensity peak of the calculated isotopic cluster, i.e. ⁹⁸Mo and ¹⁸⁴W. ^b Probe temperatures between 80 and 180 °C.

Table II. Numbering Scheme, IR, MS, Color, Yield, and Elemental Analysis Data for Complexes 15-25

compd	compd no.	IR (Nujol) (ν_{NO}), cm^{-1}	MS, $m/z^{b,c}$	color (yield, %)	anal. found (calcd)		
					C	H	N
Cp*Mo(NO)(OCMe ₃)(NHCMe ₃)	15	1597	408 [P ⁺]	yellow (84)	53.47 (53.19)	8.60 (8.43)	6.72 (6.89)
Cp*Mo(NO)(CH ₂ CMe ₃)(NHCMe ₃)	16	1596	406 [P ⁺]	orange (73)			
Cp*Mo(NO)(Me)(NHCMe ₃) ^a	17	1595	351 [P ⁺]	red (40)			
Cp*W(NO)(OCMe ₃)(NHCMe ₃)	18	1534	494 [P ⁺]	yellow (75)	43.82 (43.73)	6.97 (6.93)	5.75 (5.67)
Cp*W(NO)(CH ₂ CMe ₃)(NHCMe ₃)	19	1526	492 [P ⁺]	yellow (71)	46.08 (46.35)	7.45 (7.37)	5.52 (5.69)
Cp*W(NO)(CH ₂ CMe ₃)(OCMe ₃)	20	1548	493 [P ⁺]	red (56)	46.17 (46.26)	7.13 (7.15)	3.00 (2.84)
Cp*W(NO)(Me)(NHCMe ₃) ^a	21	1515	436 [P ⁺]	red (48)			
Cp*W(NO)(OPh)(NHCMe ₃)	22	1588	514 [P ⁺]	orange (76)	47.00 (46.70)	5.88 (5.88)	5.45 (5.60)
Cp*W(NO)(OPh)(NHPh)·LiCl	23	1588	534 [P ⁺]	yellow (73)	45.95 (45.82)	4.62 (4.54)	4.69 (4.86)
Cp*W(NO)(<i>o</i> -MeC ₆ H ₄)(NHCMe ₃)	24	1515	512 [P ⁺]	yellow (79)	49.01 (49.23)	6.34 (6.29)	5.19 (5.47)
Cp*W(NO)(NHCMe ₃) ₂	25	1539	493 [P ⁺]	yellow (68)	43.50 (43.82)	7.15 (7.22)	8.36 (8.52)

^a Correct analysis was not obtained (see text). ^b m/z values are for the highest intensity peak of the calculated isotopic cluster, i.e. ⁹⁸Mo and ¹⁸⁴W. ^c Probe temperatures between 80 and 180 °C.

Table III. NMR Data for Complexes 1-5 and 11-14

compd no.	¹ H NMR δ	¹³ C{ ¹ H} NMR δ
1 ^a	7.10 (m, 2H, <i>o</i> -ArH), 6.85 (m, 2H, <i>m</i> -ArH), 6.70 (m, 1H, <i>p</i> -ArH), 5.1 (s (br), 2H, NH ₂), 1.43 (s, 15H, C ₅ Me ₅)	141.03, 129.21, 124.91, 120.00 (Ar), 118.75 (C ₅ Me ₅), 10.04 (C ₅ Me ₅)
2 ^b	7.40 (d, 1H, <i>o</i> -ArH), 7.18 (m, 2H, <i>o/p</i> -ArH), 7.02 (m, 1H, <i>m</i> -ArH), 5.7 (s (br), 2H, NH ₂), 1.43 (s, 15H, C ₅ Me ₅)	141.43, 131.20, 127.19, 123.43, 119.79 (Ar), 119.75 (C ₅ Me ₅), 10.06 (C ₅ Me ₅)
3 ^b	7.41 (d, 2H, <i>o</i> -ArH), 7.23 (d, 2H, <i>m</i> -ArH), 6.2 (s (br), 2H, NH ₂), 2.44 (s, 3H, CH ₃), 1.43 (s, 15H, C ₅ Me ₅)	138.10, 134.83, 129.70, 120.10 (Ar), 118.89 (C ₅ Me ₅), 20.77 (Me), 10.15 (C ₅ Me ₅)
4 ^c	7.29 (m, 2H, <i>o</i> -ArH), 7.15 (m, 2H, <i>m</i> -ArH), 6.98 (m, 1H, <i>p</i> -ArH), 5.21 (s (br), 2H, NH ₂), 1.79 (s, 15H, C ₅ Me ₅)	141.43, 129.21, 124.19, 119.90 (Ar), 115.68 (C ₅ Me ₅), 9.85 (C ₅ Me ₅)
5 ^a	1.92 (s, 15H, C ₅ Me ₅) and other broad peaks ^d (between 8.2 and 3.5 ppm)	118.05 (C ₅ Me ₅), 10.65 (C ₅ Me ₅), and other broad peaks ^d
11 ^b	8.4 (s (br), 1H, NH), 5.8 (m, 1H, -CH=), 5.20 (m, 1H, =CH ₂ trans), 5.12 (m, 1H, =CH ₂ cis), 4.85 (m, 1H, NCH ₂), 4.76 (m, 1H, NCH ₂), 1.91 (s, 15H, C ₅ Me ₅)	136.91 (CH ₂ =CH), 116.96 (CH ₂ =CH), 114.96 (C ₅ Me ₅), 67.05 (CH ₂), 10.25 (C ₅ Me ₅)
12 ^c	9.0 (s (br), 1H, NH), 1.62 (s, 15H, C ₅ Me ₅), 1.33 (s, 9H, CMe ₃)	114.68 (C ₅ Me ₅), 65.04 (CMe ₃), 33.09 (CMe ₃), 10.06 (C ₅ Me ₅)
13 ^c	7.9 (s (br), 1H, NH), 1.64 (s, 15H, C ₅ Me ₅), 1.33 (s, 9H, CMe ₃)	113.01 (C ₅ Me ₅), 64.13 (CMe ₃), 33.45 (CMe ₃), 9.96 (C ₅ Me ₅)
14 ^c	7.3 (s (br), 1H, NH), 5.7 (m, 1H, -CH=), 5.05 (m, 1H, =CH ₂ trans), 4.92 (m, 1H, =CH ₂ cis), 4.85 (m, 1H, NCH ₂), 4.54 (m, 1H, NCH ₂), 1.62 (s, 15H, C ₅ Me ₅)	138.22 (CH ₂ =CH), 116.14 (CH ₂ =CH), 112.82 (C ₅ Me ₅), 65.83 (CH ₂), 9.85 (C ₅ Me ₅)

^a CDCl₃. ^b CDCl₃. ^c C₆D₆. ^d See text.

compositions of all solid lithium and R₂Mg·x(dioxane) reagents were established by hydrolysis of weighed samples and titration of the resulting solutions with 0.100 N HCl using phenolphthalein as the indicator.

General Synthetic Procedures. Many of the new complexes isolated during this work were synthesized using similar methodology. Therefore, their syntheses are grouped according to the method employed, with a representative example being described for each procedure. All solid reagents such as Cp*Mo(NO)Cl₂, R₂Mg·x(dioxane), ROLi, and RNHLi were weighed in a glovebox into a Schlenk tube containing a magnetic stirbar.

The tube was then removed from the glovebox, and all subsequent manipulations were performed on a vacuum line. Unless indicated otherwise, solvents were added via syringe to the reaction vessel. Isolated yields and spectroscopic and physical properties of the new complexes are listed in Tables I and II, and their ¹H and ¹³C NMR data are collected in Tables III and IV.

Preparation of the Amine Adducts, Cp*M(NO)Cl₂·RNH₂ (Complexes 1-5). The synthesis of 1 is described as a representative example. THF (10 mL) was vacuum transferred onto Cp*Mo(NO)Cl₂ (667 mg, 2.00 mmol) maintained at -196 °C, and excess aniline (1 mL) was added. The stirred reaction mixture was warmed slowly (45 min) to room temperature. The solvent was removed in vacuo, the yellow residue remaining was extracted with CH₂Cl₂ (30 mL), and the extract was filtered through a

Table IV. NMR Data for Complexes 15–24

compd no.	^1H NMR δ	$^{13}\text{C}\{^1\text{H}\}$ NMR δ
15 ^a	6.8 (s (br), 1H, NH), 1.71 (s, 15H, C ₅ Me ₅), 1.48 (s, 9H, CMe ₃), 1.34 (s, 9H, CMe ₃)	113.41 (C ₅ Me ₅), 78.71 (CMe ₃), 61.67 (CMe ₃), 34.13 (CMe ₃), 33.66 (CMe ₃), 10.02 (C ₅ Me ₅)
16 ^a	7.6 (s (br), 1H, NH), 1.56 (s, 15H, C ₅ Me ₅), 1.42 (s, 9H, CMe ₃), 1.34 (s, 9H, CMe ₃), 1.09 (d, 1H, CH _A H _B CMe ₃)	110.74 (C ₅ Me ₅), 64.10 (CMe ₃), 56.14 (CH ₂), 36.10 (CMe ₃), 34.52 (CMe ₃), 33.29 (CMe ₃), 9.96 (C ₅ Me ₅)
17 ^a	7.9 (s (br), 1H, NH), 1.58 (s, 15H, C ₅ Me ₅), 1.34 (s, 9H, CMe ₃), 0.62 (s, 3H, Me)	110.36 (C ₅ Me ₅), 62.33 (CMe ₃), 33.31 (CMe ₃), 13.36 (Me), 9.77 (C ₅ Me ₅)
18 ^b	5.7 (s (br), 1H, NH), 1.71 (s, 15H, C ₅ Me ₅), 1.44 (s, 9H, CMe ₃), 1.37 (s, 9H, CMe ₃)	112.12 (C ₅ Me ₅), 79.21 (CMe ₃), 61.11 (CMe ₃), 34.43 (CMe ₃), 33.51 (CMe ₃), 9.85 (C ₅ Me ₅)
19 ^a	6.8 (s (br), 1H, NH), 1.59 (s, 15H, C ₅ Me ₅), 1.42 (s, 9H, CMe ₃), 1.33 (s, 9H, CMe ₃), 1.15 (d, 1H, CH _A H _B CMe ₃), 1.01 (d, 1H, CH _A H _B CMe ₃)	109.72 (C ₅ Me ₅), 62.15 (CMe ₃), 52.77 (CMe ₃), 36.34 (CMe ₃), 34.88 (CMe ₃), 33.30 (CMe ₃), 9.88 (C ₅ Me ₅)
20 ^a	1.97 (d, 1H, CH _A H _B CMe ₃), 1.65 (s, 15H, C ₅ Me ₅), 1.40 (s, 9H, CMe ₃), 1.37 (s, 9H, CMe ₃), 0.97 (d, 1H, CH _A H _B CMe ₃)	112.03 (C ₅ Me ₅), 83.16 (CMe ₃), 61.71 (CMe ₃), 37.05 (CMe ₃), 34.52 (CMe ₃), 32.91 (CMe ₃), 9.89 (C ₅ Me ₅)
21 ^b	7.2 (s (br), 1H, NH), 1.60 (s, 15H, C ₅ Me ₅), 1.36 (s, 9H, CMe ₃), 0.57 (s, 3H, Me)	110.86 (C ₅ Me ₅), 62.86 (CMe ₃), 33.20 (CMe ₃), 11.18 (Me), 10.03 (C ₅ Me ₅)
22 ^a	7.35 (m, 4H, <i>o/m</i> -ArH), 6.86 (t, 1H, <i>p</i> -ArH), 6.7 (s (br), 1H, NH), 1.67 (s, 15H, C ₅ Me ₅), 1.32 (s, 9H, CMe ₃)	141.14, 129.49, 120.56, 119.56 (Ar), 112.79 (C ₅ Me ₅), 62.17 (CMe ₃), 34.21 (CMe ₃), 9.64 (C ₅ Me ₅)
23 ^c	7.9 (s (br), 1H, NH), 7.15 (m, 6H, ArH), 6.9 (m, 4H, ArH), 2.08 (s, 15H, C ₅ Me ₅)	129.34, 122.82, 122.34, 121.20, 120.86, 119.48, 118.99 (Ar), 112.79 (C ₅ Me ₅), 9.64 (C ₅ Me ₅)
24 ^b	7.9 (s (br), 1H, NH), 7.15 (m, 1H, ArH), 6.9 (m, 3H, ArH), 2.04 (s, 3H, Me), 1.85 (s, 15H, C ₅ Me ₅), 1.28 (s, 9H, CMe ₃)	112.02 (C ₅ Me ₅), 33.09 (CMe ₃), 10.29 (C ₅ Me ₅), and other broad peaks
25 ^a	4.4 (s (br), 2H, NH), 1.65 (s, 15H, C ₅ Me ₅), 1.44 (s, 18H, CMe ₃)	110.20 (C ₅ Me ₅), 59.71 (CMe ₃), 34.83 (CMe ₃), 9.92 (C ₅ Me ₅)

^a C₆D₆. ^b CD₂Cl₂. ^c CDCl₃.

column of Celite (2 × 4 cm) supported on a sintered glass frit. The filtrate was concentrated in vacuo to incipient crystallization and was transferred to a freezer (−30 °C) overnight. This cooling induced the formation of yellow blocklike crystals that were isolated from the mother liquor by cannulation and dried in vacuo. Further cooling of the supernate afforded additional product.

Complexes 2–5 were prepared similarly, but complex 4 was isolated as red blocks which became a red-brown powder upon exposure to vacuum, and complex 5 was crystallized from CH₂Cl₂/hexanes.

Preparation of the Amido Chloro Complexes, Cp*M(NO)-(NHR')Cl (Complexes 6–11). Method A: Deprotonation of the Amine Adduct. The synthesis of complex 6 is described as a representative example. THF (10 mL) was vacuum transferred onto a mixture of Cp*M(NO)Cl₂·PhNH₂, 1 (426 mg, 1.00 mmol), and lithium diisopropylamide (108 mg, 1.00 mmol) maintained at −196 °C. The stirred reaction mixture was warmed slowly to room temperature, and solvent was removed in vacuo. The dark red solid remaining was extracted with CH₂Cl₂ (30 mL), and the extract was filtered through a column of Celite (2 × 4 cm) supported on a sintered glass frit. The volume of the filtrate was reduced in vacuo until precipitation commenced, and the mixture was placed in a freezer (−30 °C) overnight. This cooling induced the precipitation of complex 6 as a dark red microcrystalline powder that was isolated from the mother liquor by cannulation and dried in vacuo. Further concentration and cooling of the supernate afforded additional product.

Method B: Amide for Halide Metathesis. The preparation of complex 6 by this method is again described as an illustrative example. THF (15 mL) was vacuum transferred onto a mixture of Cp*Mo(NO)Cl₂ (333 mg, 1.00 mmol) and PhNHLi (136 mg, 1.00 mmol) maintained at −196 °C. The stirred reaction mixture was warmed to room temperature, and the final mixture was worked up in a manner identical to that described in method A.

Complex 11 was synthesized only via method A using Et₂O as the extraction and crystallization solvent. Complex 10 was prepared only via method B utilizing (*p*-CH₃C₆H₄)NHLi (121 mg, 1.00 mmol). Interestingly, when method B was employed to synthesize complex 8 from the reaction of (*p*-CH₃C₆H₄)NHLi and Cp*Mo(NO)Cl₂, the first product complex to crystallize from the final CH₂Cl₂ solution was a purple powder formulated as [Cp*Mo(NO)Cl₂]Li in approximately 5% yield. This salt was

isolated by removing the supernatant solution by cannulation and drying the remaining purple powder in vacuo.

Anal. Calcd for C₁₀H₁₆N₂Cl₂LiMoO: C, 35.42; H, 4.46; N, 4.13. Found: C, 35.10; H, 4.63; N, 4.06. IR (Nujol mull): 1626 (s), 1607 (s), 771 (s) cm^{−1}.

Subsequent concentration and cooling of the supernatant solution afforded complex 8.

Preparation of the Amido Chloro Complexes, Cp*M(NO)-(NHR')Cl (Complexes 12–14). These syntheses involve the deprotonation of unisolated amine adducts and thus resemble method A outlined in the preceding paragraph. The preparation of complex 13 in this manner is presented as a representative example. THF (10 mL) and excess *t*-BuNH₂ (1 mL) were vacuum transferred consecutively onto Cp*W(NO)Cl₂ (420 mg, 1.00 mmol) held at −196 °C. The stirred reaction mixture was warmed to, and maintained at, room temperature for 10 min whereupon it became a thick, orange slurry. Solvent was removed from this slurry in vacuo, the orange solid remaining was extracted with Et₂O (20 mL), and the extract was filtered through a column of Celite (2 × 4 cm) supported on a medium-porosity glass frit. The filtrate was concentrated in vacuo until incipient crystallization and was then stored in a freezer (−30 °C) overnight. These operations resulted in the crystallization of complex 13 as orange blocks that were isolated from the mother liquor by cannulation and dried in vacuo.

Complex 14 was prepared similarly but was extracted with CH₂Cl₂ and was crystallized from CH₂Cl₂/hexanes.

Preparation of Alkoxo Amido Complexes, Cp*M(NO)-(OR)(NHR') (Complexes 15, 18, and 22). The synthesis of complex 15 is presented as a representative example. THF (10 mL) was vacuum transferred onto a mixture of Cp*Mo(NO)Cl₂ (333 mg, 1.00 mmol) and Me₃COLi (82 mg, 0.98 mmol) at −196 °C. The stirred reaction mixture was warmed to room temperature, and stirring was continued until all traces of the dichloro complex had disappeared (30 min). The final purple reaction mixture was refrozen at −196 °C, and excess *t*-BuNH₂ (1 mL) was vacuum transferred into the reaction vessel. Again the stirred reaction mixture was allowed to warm slowly to room temperature. The solvent was removed in vacuo, the orange solid remaining was extracted with Et₂O (20 mL), and the extract was filtered through a column of Celite (2 × 4 cm) supported on a sintered glass frit. The filtrate was taken to dryness in vacuo to obtain

a yellow/brown oil which was triturated with pentane. The pentane was removed by cannulation from the resulting yellow powder, and the powder was dissolved in a minimum of Et₂O (5 mL). Maintaining this solution at -30 °C overnight induced the formation of yellow blocks of 15 that were isolated from the mother liquor by cannulation and were dried in vacuo. Complex 22 was prepared similarly using PhOLi (110 mg/mmol).

Preparation of Alkyl or Aryl Amido Complexes, Cp*Mo(NO)(R)(NHR) (Complexes 16, 19, and 24). These complexes were prepared and worked up in a manner essentially identical to that outlined in the previous paragraph. The only difference was that stoichiometric amounts of R₂Mg·x(dioxane) reagents were used in place of the lithium alkoxides. Thus, use of (Me₃CCH₂)₂Mg·x(dioxane) (330 mg/mmol) produced complexes 16 and 19, and the use of (o-CH₃C₆H₄)₂Mg·x(dioxane) (300 mg/mmol) resulted in the production of complex 24.

Preparation of Cp*Mo(NO)(NHCMe₃)Me and Cp*W(NO)(NHCMe₃)Me (Complexes 17 and 21). These two compounds were prepared in a manner identical to that utilized for the syntheses of the three complexes in the preceding paragraph. (CH₃)₂Mg·x(dioxane) (6.5 mL, 0.16 M in THF, 0.98 mmol of R⁻) added via syringe was employed as the alkylating agent in both cases. Samples of both red compounds were obtained by crystallization from Et₂O.

Preparation of Cp*W(NO)(CH₂CMe₃)(OCMe₃) (20). THF (10 mL) was vacuum transferred onto a mixture of Cp*W(NO)-Cl₂ (420 mg, 1.00 mmol) and (Me₃CCH₂)₂Mg·x(dioxane) (160 mg, 0.98 mmol of R⁻) at -196 °C. The stirred reaction mixture was warmed to room temperature, and stirring was continued until all traces of the dichloro complex had disappeared (30 min). The purple reaction mixture was then treated with Me₃COLi (82 mg, 0.98 mmol), and stirring was continued for 1 h. The final mixture was taken to dryness in vacuo, the remaining red solid was extracted with pentane (2 × 25 mL), and the extracts were filtered through a column of Celite (3 × 3 cm) supported on a medium-porosity frit. Concentration and cooling of the combined filtrates afforded dark red blocks of complex 20.

Preparation of Cp*W(NO)(OPh)(NPh)-LiCl (23). THF (10 mL) was vacuum transferred onto a mixture of Cp*W(NO)-Cl₂ (420 mg, 1.0 mmol) and PhOLi (110 mg, 0.98 mmol) at -196 °C. The stirred reaction mixture was warmed to room temperature and allowed to stir for 15 min. The final purple reaction mixture was refrozen at -196 °C, and a solution of PhNHLi (130 mg, 0.98 mmol) in THF (5 mL) was cannulated into the flask. Again, the stirred reaction mixture was allowed to warm slowly to room temperature. The solvent was removed from the final mixture in vacuo, the remaining red solid was extracted with CH₂Cl₂ (20 mL), and the extract was filtered through a column of Celite (2 × 4 cm) supported on a medium-porosity glass frit. The filtrate was taken to dryness in vacuo to a red/brown oil which was triturated with pentane to induce the formation of a yellow powder. The pentane was removed by cannulation, and the powder was dissolved in a minimum of CH₂Cl₂. Cooling this solution to -30 °C induced the precipitation of a red microcrystalline powder that was isolated by cannulation and dried in vacuo.

Preparation of Cp*W(NO)(NHCMe₃)₂ (25). THF (10 mL) and excess *tert*-butylamine (1 mL) were vacuum transferred consecutively onto Cp*W(NO)Cl₂ (420 mg, 1.00 mmol) at -196 °C. The reaction mixture was warmed to room temperature and was stirred for 18 h. The final light orange solution was taken to dryness, and the resulting residue was redissolved in pentane (20 mL). This solution was filtered through Celite (2 × 4 cm) supported on a medium-porosity frit, and the orange filtrate was concentrated under reduced pressure to incipient crystallization before being placed in a freezer at -30 °C overnight. The yellow flakes of complex 25 which had deposited were isolated by filtration and were dried in vacuo.

X-ray Crystallographic Analyses of Cp*Mo(NO)Cl₂·PhNH₂ (1) and Cp*W(NO)(OCMe₃)(NHCMe₃) (18). Crystallographic data for 1 and 18 appear in Table V. The final unit-cell parameters were obtained by least squares on the setting

Table V. Crystallographic Data^a

compd	1	18
formula	C ₁₆ H ₂₂ Cl ₂ MoN ₂ O	C ₁₈ H ₃₄ N ₂ O ₂ W
fw	425.21	494.33
color, habit	yellow, prism	yellow, prism
cryst size, mm	0.08 × 0.15 × 0.35	0.30 × 0.30 × 0.35
cryst syst	monoclinic	monoclinic
space group	P2 ₁ /c	P2 ₁ /c
a, Å	8.590(1)	10.103(2)
b, Å	9.430(2)	15.372(3)
c, Å	22.386(2)	13.908(3)
β, deg	94.16(1)	103.08(1)
V, Å ³	1808.6(8)	2104(1)
Z	4	4
ρ _{calc} , g/cm ³	1.561	1.561
F(000)	864	984
μ(Mo Kα), cm ⁻¹	10.08	56.17
trans factors (relative)	0.90–1.00	0.88–1.00
scan type	ω-2θ	ω-2θ
scan range, deg in ω	1.25 + 0.35 tan θ	1.26 + 0.35 tan θ
scan rate, deg/min	32	32
data collcd	+h, +k, ±l	+h, +k, ±l
2θ _{max} , deg	55	55
cryst decay, %	negligible	20.0
total no. of reflns	4700	5285
no. of unique reflns	4151	4821
R _{merge}	0.043	0.039
reflns with I ≥ 3σ(I)	2366	2684
no. of variables	208	222
R	0.030	0.028
R _w	0.029	0.024
gof	1.57	1.38
max Δ/σ (final cycle)	0.10	0.01
residual dens, e/Å ³	-0.28 to +0.29	-0.52 to +0.48 (near W)

^a Temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα radiation (λ = 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 eight rescans), σ²(F²) = [S²(C + 4B)]/Lp² (S = scan rate, C = scan count, B = normalized background count, function minimized Σw(|F_o - |F_c||)² where w = 4F_o²/σ²(F_o²), R = Σ||F_o - |F_c||/Σ|F_o|, R_w = (Σw(|F_o - |F_c||)²/Σw|F_o|²)^{1/2}, and gof = [Σw(|F_o - |F_c||)²/(m-n)]^{1/2}. Values given for R, R_w, and gof are based on those reflections with I ≥ 3σ(I).

angles for 25 reflections with 2θ = 25.6–38.0° for 1 and 26.6–29.9° for 18. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for 1 and decreased uniformly by 20.0% for 18. The data were processed⁸ and corrected for Lorentz and polarization effects, linear decay (for 18), and absorption (empirical, based on azimuthal scans for three reflections).

Both structures were solved by heavy-atom methods, the coordinates of the heavy atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The NH-CMe₃ group of 18 was 2-fold (82:18) orientationally disordered about the N-C bond. A group occupancy factor for the major component was refined with the constraint that the total occupancies sum to 1.00. All non-hydrogen atoms of both complexes except the low-occupancy disordered methyl carbon atoms (C(16A–18A)) of 18 were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in idealized positions (C-H = 0.98 Å, B_H = 1.2B_{bonded atom}). Corrections for secondary extinction were applied for both structures, the final values of the extinction coefficient being 4.7(2) × 10⁻⁷ for 1 and 8.1(5) × 10⁻⁸ for 18. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 9. Selected bond lengths and angles appear in Table VI and Table VII, respectively, and final atomic coordinates and equivalent isotropic thermal parameters are given

(8) TEXSAN/TEXRAY structure analysis package. Molecular Structure Corp., 1985.

(9) International Tables for X-Ray Crystallography; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.

Table VI. Selected Bond Lengths (Å) with Esd's in Parentheses for Cp*Mo(NO)Cl₂-PhNH₂ (1) and Cp*W(NO)(OCMe₃)(NHCMe₃) (18)

1		18	
Mo(1)-N(1)	1.762(3)	W(1)-N(1)	1.916(4)
Mo(1)-C(1)	2.409(4)	W(1)-C(1)	2.413(5)
Mo(1)-C(2)	2.326(4)	W(1)-C(2)	2.463(6)
Mo(1)-C(3)	2.352(4)	W(1)-C(3)	2.439(6)
Mo(1)-C(4)	2.421(4)	W(1)-C(4)	2.362(6)
Mo(1)-C(5)	2.441(4)	W(1)-C(5)	2.344(6)
Mo(1)-N(2)	2.283(4)	W(1)-N(2)	1.939(4)
Mo(1)-Cp ^a	2.06	W(1)-Cp ^a	2.085
O(1)-N(1)	1.196(4)	O(1)-N(1)	1.237(7)
N(2)-H(1)	0.96(5)	W(1)-O(2)	1.916(4)
N(2)-H(2)	0.78(3)	W(1)-N(2)	1.939(4)

^a Cp refers to the centroid of the pentamethylcyclopentadienyl ligand.

Table VII. Selected Bond Angles (deg) with Esd's in Parentheses for Cp*Mo(NO)Cl₂-PhNH₂ (1) and Cp*W(NO)(OCMe₃)(NHCMe₃) (18)

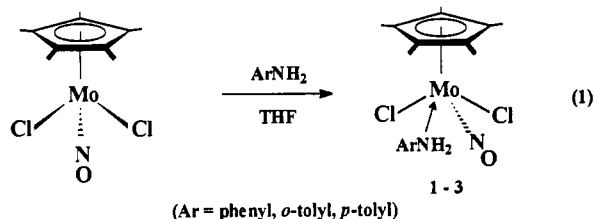
1		18	
N(1)-Mo(1)-N(2)	106.5(1)	N(1)-W(1)-N(2)	100.4(2)
N(1)-Mo(1)-Cp ^a	119.5	N(1)-W(1)-Cp ^a	119.9
N(2)-Mo(1)-Cp ^a	133.9	N(2)-W(1)-Cp ^a	114.8
Mo(1)-N(1)-O(1)	168.6(3)	W(1)-N(1)-O(1)	169.6(5)
Mo(1)-N(2)-C(11)	117.5(2)	W(1)-N(2)-C(15)	138.5(4)
Cl(1)-Mo(1)-N(1)	89.3(1)	O(2)-W(1)-N(1)	102.2(2)
Cl(2)-Mo(1)-N(1)	84.8(1)	O(2)-W(1)-N(2)	108.0(2)

^a Cp refers to the centroid of the pentamethylcyclopentadienyl ligand.

in Table VIII. Hydrogen atom parameters, anisotropic thermal parameters, complete tables of bond lengths and bond angles, torsion angles, intermolecular contacts, and least-squares planes are included as supplementary material. Views of the solid-state molecular structures of complexes 1 and 18 are displayed in Figures 1 and 2, respectively.

Results and Discussion

Synthesis. One of the simplest known methods for the formation of metal-nitrogen bonds involves the treatment of metal halides with amines.¹⁰ Consequently, as the first route to the desired amido nitrosyl complexes, we investigated the reactions of two nitrosyl-containing dihalides, namely Cp*M(NO)Cl₂ (Cp* = η⁵-C₅Me₅; M = Mo, W), with both aryl- and alkylamines. We soon discovered that exposure of these dichloro complexes to excess arylamines, ArNH₂ (Ar = phenyl, *o*-tolyl, or *p*-tolyl), results in the formation of 18-valence-electron, 1:1 adducts in high yields (e.g. eq 1). Related amine adducts of



rhenium, namely the cationic [CpRe(NO)(PPh₃)(RNH₂)]⁺, have been recently reported by Gladysz and co-workers.¹¹ The solid adduct complexes 1-4, yellow for Mo and red/brown for W, are both thermally stable and air stable. Even in the presence of excess amine, these adducts show no tendency to undergo dehydrohalogenation to form the

Table VIII. Final Positional and Equivalent Isotropic Thermal Parameters (Å²) for Cp*Mo(NO)Cl₂-PhNH₂ (1) and Cp*W(NO)(OCMe₃)(NHCMe₃) (18)

atom	x	y	z	B _{eq} ^a	occ
Complex 1					
Mo(1)	0.15006(4)	0.06148(4)	0.12218(1)	3.14(1)	
Cl(1)	0.2421(1)	-0.0293(1)	0.02833(4)	3.90(5)	
Cl(2)	-0.0581(1)	0.1883(1)	0.17017(6)	5.80(6)	
O(1)	-0.0435(4)	-0.1923(4)	0.1362(1)	6.2(2)	
N(1)	0.0261(4)	-0.0869(4)	0.1251(1)	4.1(2)	
N(2)	0.0390(4)	0.2082(4)	0.0501(2)	4.1(2)	
C(1)	0.3110(5)	0.1938(5)	0.1951(2)	4.1(2)	
C(2)	0.2600(4)	0.0635(5)	0.2202(2)	3.8(2)	
C(3)	0.3295(4)	-0.0499(5)	0.1914(2)	3.7(2)	
C(4)	0.4223(4)	0.0079(5)	0.1481(2)	4.1(2)	
C(5)	0.4092(5)	0.1582(5)	0.1494(2)	4.2(2)	
C(6)	0.2752(6)	0.3383(5)	0.2172(2)	6.0(3)	
C(7)	0.1701(6)	0.0485(6)	0.2757(2)	5.9(2)	
C(8)	0.3190(5)	-0.2052(5)	0.2075(2)	5.3(2)	
C(9)	0.5369(5)	-0.0727(6)	0.1132(2)	6.6(3)	
C(10)	0.4959(5)	0.2595(6)	0.1125(2)	7.2(3)	
C(11)	0.1257(4)	0.3341(4)	0.0353(2)	3.5(2)	
C(12)	0.1120(4)	0.4553(5)	0.0694(2)	4.0(2)	
C(13)	0.1936(5)	0.5758(5)	0.0552(2)	4.6(2)	
C(14)	0.2871(5)	0.5745(5)	0.0084(2)	5.2(2)	
C(15)	0.3000(5)	0.4547(6)	-0.0252(2)	5.1(2)	
C(16)	0.2193(5)	0.3331(5)	-0.0115(2)	4.3(2)	
Complex 18					
W(1)	0.30094(2)	0.256875(13)	0.29892(2)	3.029(9)	
O(1)	0.4163(6)	0.1795(3)	0.1396(4)	6.5(3)	
O(2)	0.1840(4)	0.1679(2)	0.3294(3)	3.6(2)	
N(1)	0.3746(5)	0.2054(3)	0.2116(4)	4.2(2)	
N(2)	0.4574(4)	0.2658(3)	0.4088(3)	3.8(2)	
C(1)	0.2890(7)	0.4135(3)	0.3045(6)	4.4(3)	
C(2)	0.1812(8)	0.3844(4)	0.3450(5)	4.4(3)	
C(3)	0.0894(7)	0.3393(4)	0.2714(5)	4.2(3)	
C(4)	0.1390(7)	0.3391(4)	0.1859(5)	3.6(3)	
C(5)	0.2653(7)	0.3854(4)	0.2060(5)	4.0(3)	
C(6)	0.4057(9)	0.4712(5)	0.3546(7)	8.0(5)	
C(7)	0.1652(10)	0.4048(6)	0.4495(6)	8.6(5)	
C(8)	-0.0416(8)	0.2979(5)	0.2825(7)	6.8(4)	
C(9)	0.0710(8)	0.3033(5)	0.0852(5)	5.8(4)	
C(10)	0.3482(8)	0.4068(5)	0.1313(6)	6.5(4)	
C(11)	0.1620(8)	0.0770(4)	0.3027(5)	4.7(3)	
C(12)	0.2939(10)	0.0277(4)	0.3313(7)	7.8(5)	
C(13)	0.0621(10)	0.0431(5)	0.3619(7)	7.8(5)	
C(14)	0.1026(11)	0.0700(5)	0.1939(6)	9.3(5)	
C(15)	0.6038(6)	0.2398(5)	0.4334(5)	4.8(3)	
C(16)	0.6484(9)	0.2017(9)	0.3459(10)	8.2(7)	0.82(1)
C(16A)	0.601(4)	0.140(3)	0.417(3)	5.0(9)	0.18
C(17)	0.6272(11)	0.1750(9)	0.5153(11)	9.4(8)	0.82
C(17A)	0.659(5)	0.254(3)	0.543(3)	6.4(9)	0.18
C(18)	0.6916(10)	0.3190(7)	0.4668(11)	8.8(7)	0.82
C(18A)	0.665(6)	0.286(4)	0.365(5)	9(1)	0.18

$$^a B_{eq} = (8/3)\pi^2 \sum U_{ij} a_i^* a_j^* (a_i a_j)$$

corresponding arylamido complexes.¹² Nevertheless, such transformations can be effected in moderate to good yields for the molybdenum complexes by employing a strong base such as LDA at low temperatures in THF (eq 2). These arylamido complexes, 6-8, may also be synthesized in one step by reaction of the dichloro complex with 1 equiv of the appropriate lithium amide reagent (eq 3).

Interestingly, during the synthesis of complex 8 via the lithium amide route (eq 3), a dark purple complex, [Cp*Mo(NO)Cl₂]Li, is isolable as a byproduct in low yields (5%). This product is interesting from a mechanistic point of view since all the metathetical reactions 3 proceed via transient purple solutions. The purple color persists for short periods of time (ca. 30 s) and then quickly darkens

(10) See for example: Jones, C. J.; McCleverty, J. A.; Neaves, B. D.; Reynold, S. J. *J. Chem. Soc., Dalton Trans.* 1986, 733.

(11) Dewey, M. A.; Knight, D. A.; Klein, D. P.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* 1991, 30, 4995.

(12) Analogous pyrazolylborate complexes undergo facile dehydrohalogenation: McCleverty, J. A.; Denti, G.; Reynolds, S. J.; Drane, A. S.; El Murr, N.; Rae, A. E.; Bailey, N. A.; Adams, H.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* 1983, 81.

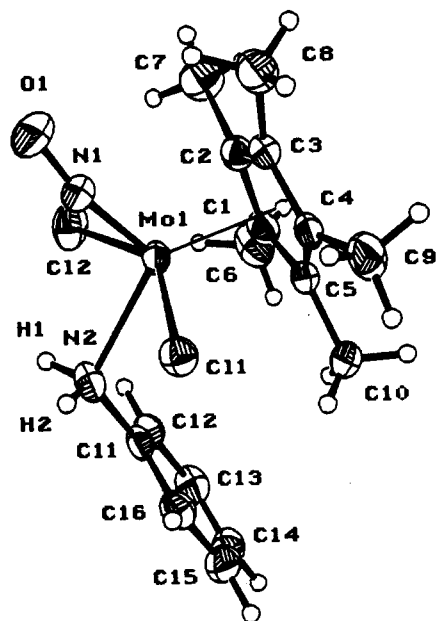


Figure 1. View of the solid-state molecular structure of $\text{Cp}^*\text{Mo}(\text{NO})\text{Cl}_2 \cdot \text{PhNH}_2$ (1). Probability ellipsoids at the 33% level are shown for the non-hydrogen atoms.

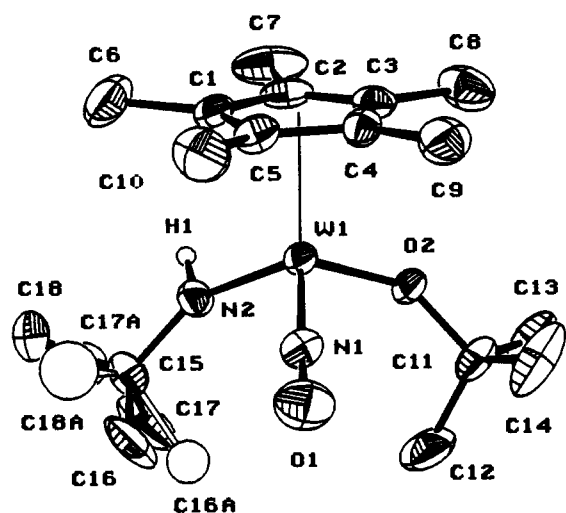
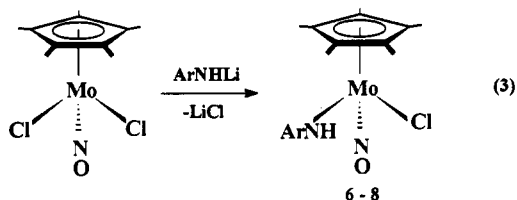
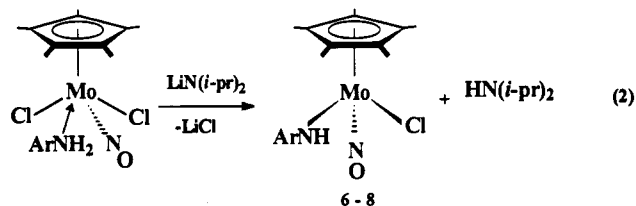


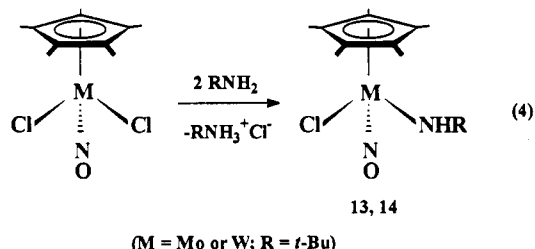
Figure 2. View of the solid-state molecular structure of $\text{Cp}^*\text{W}(\text{NO})(\text{OCMe}_3)(\text{NHCMe}_3)$ (18). Probability ellipsoids at the 33% level are shown for the non-hydrogen atoms.



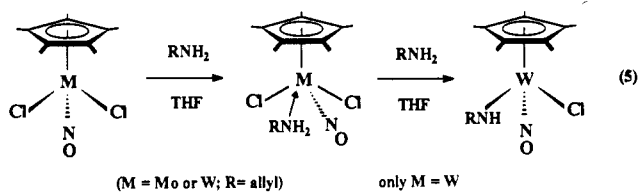
to the characteristic deep red of the final product complexes. The isolation of the radical anion as its lithium salt is consistent with the mechanistic proposal that these metatheses proceed by initial electron transfer to form an

organometallic radical anion which then undergoes ligand substitution.¹³ Similar radical anionic intermediates have been detected by ESR spectroscopy during alkylation reactions of $\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2$.¹³

The reactions of an alkylamine, $t\text{-BuNH}_2$, with the $\text{Cp}^*\text{M}(\text{NO})\text{Cl}_2$ precursors proceed in a somewhat different manner and afford amido chloro complexes directly (eq 4). As outlined in the Experimental Section, reactions 4



proceed via transient yellow solids that are quite insoluble in cold THF. No attempt was made to isolate these transient complexes which are most likely the amine adducts of the dichlorides (cf. eq 1) that subsequently undergo dehydrohalogenation in the presence of excess amine to afford the final products. The observation that Lewis base adducts of 16-electron $\text{Cp}^*\text{M}(\text{NO})\text{X}_2$ compounds have much lower solubilities than their precursors has been previously noted.¹⁴ This difference in reactivity of the arylamines versus the alkylamines can be attributed to the greater basicity of the latter species.¹⁵ Interestingly, the reaction between allylamine and $\text{Cp}^*\text{Mo}(\text{NO})\text{Cl}_2$ affords the allylamine adduct and not the expected allylamido complex, the tungsten congener of which is indeed obtained with $\text{Cp}^*\text{W}(\text{NO})\text{Cl}_2$ (eq 5). The reason



for this exceptional behavior is unclear at present. It should be noted, however, that ¹H NMR spectroscopy indicates that the adduct is stereochemically nonrigid in solutions at ambient temperatures, and the fluxional processes operative may well involve interaction of the metal center with the pendant unsaturation in the allyl group.

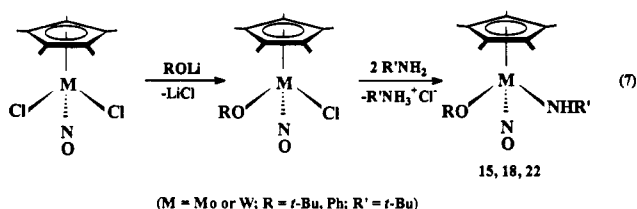
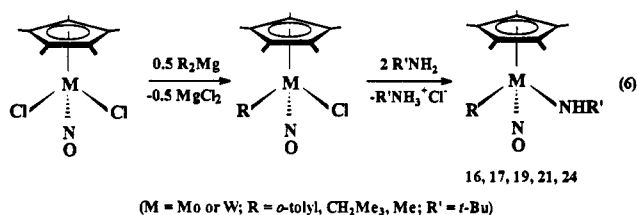
The amido chloro complexes 6–14 were initially desired as synthetic precursors to novel alkyl amido and alkoxy amido complexes. Unfortunately, treatment of several amido chloro complexes with alkylating reagents produces only low yields of the desired alkyl amido complexes. These low yields may well reflect the existence of a competing reaction involving reduction of the starting material by the alkylating agent (vide infra). Similarly, reactions of the amido chloro complexes with lithium alkoxides result in low isolated yields of the desired alkoxy amides. Fortunately, these difficulties may be circumvented by introducing the ligands into the metal's coordination

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

(14) Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* 1988, 7, 2394.

(15) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; Chapter 8.

sphere in the opposite order. The requisite alkyl chloro precursor complexes can be generated by reaction of the dichlorides with 1 equiv of R^- under controlled conditions.¹⁶ Subsequent in situ treatment of these alkyl chloro complexes with excess alkylamine produces the desired alkyl amido complexes in good isolated yields (eq 6). The alkoxo



amido complexes are preparable in a similar manner, the generation of the alkoxo chloro precursor being followed by treatment with excess alkylamine (eq 7). The product complexes resulting from conversions 6 and 7 are yellow to red solids which are quite air sensitive in both solution and the solid state. The methyl derivatives, 17 and 20, have not yet been isolated in an analytically pure state. ^1H NMR spectroscopy reveals that these species are consistently contaminated with approximately 5% of the corresponding amido chloro complex which cannot be removed by crystallization. Also, complex 16 proves to be too hydrolytically unstable to be obtained as an analytically pure species. The hydrolytic instability of analogous alkyl derivatives of molybdenum has been recently documented.¹⁷

Characterization of the New Complexes. The salient features of the IR and NMR spectra of the amine adducts 1–5 are presented in Tables I and III, and these data are consistent with the formulation of these compounds as four-legged piano-stool molecules. The parent peaks in the mass spectra of these complexes (Table I) are assignable to the precursor dichloro complex resulting from loss of the amine. Complex 1 was subjected to an X-ray crystallographic analysis because it is the first crystalline 1:1 adduct of a $\text{Cp}^*\text{M}(\text{NO})\text{Cl}_2$ complex that we have been able to isolate, since such 1:1 adducts are generally obtained as mixtures of cis and trans isomers.¹⁸ In addition, the results of the structural analysis of complex 1 allow a comparison of its intramolecular dimensions with those of the base-free dichloride.⁶

A view of the solid-state molecular structure of 1 is shown in Figure 1. A comparison of the intramolecular parameters of 1 with those of the base-free dichloro dimer reveals that there has been a weakening of the N–O bond (1.196(4) vs 1.174(7) Å) with concomitant strengthening of the Mo–N bond (1.762(3) vs 1.781(5) Å) upon coordination of

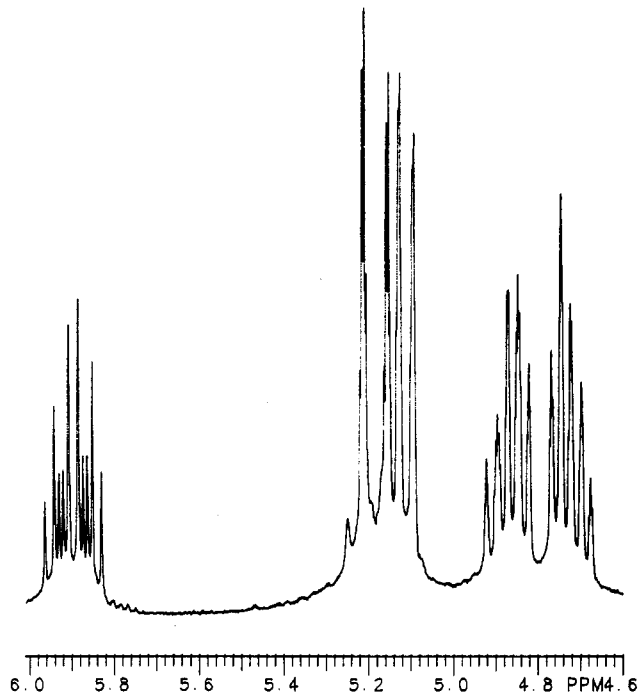


Figure 3. Low-field region of the ^1H NMR spectrum of $\text{Cp}^*\text{Mo}(\text{NO})(\text{NHCH}_2\text{CH}_2)\text{Cl}$ (11) (300 MHz, CDCl_3).

the Lewis base. As expected, the donor amine occupies a trans position relative to the nitrosyl ligand in the adduct complex 1. This transoidal disposition of these ligands is to be expected because the NO ligand is a strong π -acceptor ligand¹⁹ whereas the amine is a good σ -donor ligand. The other metrical parameters exhibited by 1 (Table VII) are comparable to those of the dichloro precursor.

The ^1H and ^{13}C NMR data for the amido chloro complexes $\text{Cp}^*\text{M}(\text{NO})(\text{NHR})\text{Cl}$ (11–14) are listed in Table III; the related amido compounds $\text{Cp}^*\text{M}(\text{NO})(\text{NHR})\text{X}$ (15–24) are collected in Table IV. In general, the IR and NMR data are consistent with these complexes possessing three-legged piano-stool molecular structures. Nevertheless, the NMR data of a few of these compounds merit some discussion. For instance, the ^1H NMR spectrum of complex 11, $\text{Cp}^*\text{Mo}(\text{NO})(\text{NHCH}_2\text{CH}_2)\text{Cl}$ (a portion of which is shown in Figure 3), is interesting in that the allyl group does not give rise to the standard allylic coupling pattern²⁰ because the methylene protons of the allyl group are diastereotopic. Instead, five different signals attributable to five magnetically different protons of the allyl group result from this inequivalency. The ten-line multiplet (lowest field multiplet of Figure 3) assignable to the central proton of the allylic moiety consists of an overlapping doublet of doublets of doublets of doublets ($^3J_{\text{HH}} = 6.5, 6.5, 10, 16$ Hz). The 10- and 16-Hz couplings are the expected order of magnitude for cis and trans alkene coupling;²¹ hence the two other splittings are assigned to coupling of the signal with the two diastereotopic methylene protons. Finally, it may be noted that the NMR data of complex 24 are interesting since the signals in both the ^1H and ^{13}C spectra are significantly broadened. This broadening may well be due to hindered rotation of

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the aryl group, a phenomenon that has been observed previously in related systems.¹⁶

The arylamido complexes Cp*M(NO)(NHAr)Cl (6–10) prove to be difficult to characterize by NMR spectroscopy since they decompose rapidly in solutions at room temperature. In most cases, the complexes decompose to a number of species, as judged by the number of resonances attributable to a Cp* ligand. Fortunately, the thermal decomposition of the phenyl complexes are relatively cleaner, and so the products of these decompositions were subjected to a mass spectroscopic analysis. For example, as the tungsten complex 9 decomposes in C₆D₆, its color changes from dark red to yellow, and ¹H NMR monitoring of this process indicates the formation of a single Cp*-containing product. A low-resolution mass spectrum of the residue from the yellow solution reveals the highest *m/z* envelope to be centered at *m/z* 386 as well as a peak at *m/z* 174. The isotope pattern of the *m/z* 386 feature matches with that expected for a species having the composition Cp*W(NO)(D)Cl, and the *m/z* 174 signal may be assigned to the secondary amine (C₆H₅)(C₆D₅)NH. This evidence is consistent with C–D bond activation and elimination of an elaborated amine having occurred. We are currently endeavoring to perform these thermal decompositions on a preparative scale so that we may confirm the operative processes.

The extent of electron donation from the amido ligand to the metal centers in these latter complexes can be inferred from IR spectroscopic properties (Table I). For instance, the amido chloro complexes 10 and 13 as Nujol mulls exhibit ν_{NO} bands at 1538 and 1540 cm⁻¹. These values may be compared with those found for representative alkyl chloro complexes such as Cp*W(NO)(CH₂-SiMe₃)Cl and Cp*W(NO)(CH₂CMe₃)Cl which as Nujol mulls exhibit ν_{NO} bands at 1599 and 1582 cm⁻¹.¹⁶ This decrease in ν_{NO} of approximately 50 cm⁻¹ upon exchanging an alkyl group for an amide ligand indicates the existence of significant electron donation from the amide ligand to the metal center. Thus, these amido complexes are best viewed as 18-valence-electron complexes containing amido ligands functioning as formal 3-electron donors. The IR data of the mixed complexes are also useful for effecting a comparison of the electron-donating properties of the various ligands. These data indicate that the largest effect on ν_{NO} occurs when either an alkyl or a chloro ligand is replaced by an amido group. Furthermore, an alkyl group has an effect on ν_{NO} comparable to that of an alkoxide group, as can be seen by a comparison of the Nujol mull spectrum of Cp*Mo(NO)(CH₂CMe₃)(NHCMe₃) (ν_{NO} = 1596 cm⁻¹) to that of Cp*Mo(NO)(OCMe₃)(NHCMe₃) (ν_{NO} = 1597 cm⁻¹). Hence, in these systems the relative electron-donating properties of the ligands generally diminish in the order amido > alkoxo \approx alkyl > chloro. A similar trend has been observed in related systems by McCleverty and co-workers.²²

We have also performed a preliminary cyclic voltammetry study of the redox properties of complexes 13, 19, and 18 as representative examples of three classes of amido nitrosyl compounds, namely an amido chloro, an alkyl amido, and an alkoxide amido complex, respectively. The reduction features of complexes 13 and 19 are quasi-

reversible in THF and occur at E° = -0.70 and -2.1 V vs SCE, respectively. Complex 18, on the other hand, exhibits an irreversible reduction at $E_{\text{p,c}}$ = -2.6 V vs SCE. These potentials thus indicate that the ease of reduction of these complexes is 13 > 19 > 18, a trend reflective of the differing electron densities extant at the metal centers and fully in accord with the electron-donating abilities of the ligands inferred from the relevant IR data (vide supra).

The structural analysis of one of these mixed-ligand complexes should allow a crystallographic comparison of the relative π -electron-donating abilities of the two ligands. Consequently, the alkoxo amido complex 18 was subjected to a single-crystal X-ray crystallographic analysis in order to examine this competitive π -electron donation at the same metal center. The results of this analysis are summarized in Tables V–VIII, and a view of the solid-state molecular structure of 18 is shown in Figure 2. The intramolecular dimensions of complex 18 can be most profitably compared to those of the analogous bis(alkoxide) complex, Cp*W(NO)(OCMe₃)₂.³ In general, the metrical parameters of the two complexes are quite similar, but the most interesting comparison involves their W–O bond lengths. The average W–O bond length in the bis(alkoxide) species is 1.896(5) Å, while the W–O bond length in 18 is 1.916(4) Å. While not conclusive by any means, this slight (but statistically significant) lengthening of the W–O bond in 18 may well reflect the better π -donation from the amide ligand in 18 (W–N bond length of 1.939(4) Å) than from the alkoxide group.

Epilogue

The two sets of complexes 15 and 16 and 18–20 contain mixed-ligand species only differing in the nature of the moiety α to the metal (CH₂, NH, and O). Thus, these complexes prepared during this work should allow a systematic comparison of the reactivity of metal–carbon, metal–nitrogen, and metal–oxygen bonds at the same metal center.²³ For example, we have to date determined that complex 20 reacts with *p*-tolyl isocyanate to give insertion preferentially into the metal–oxygen link rather than the metal–carbon link in a ratio of 22:1.²⁴ Finally, we are also presently investigating the use of the amido chloro complexes as hydroamination catalyst precursors.²⁵

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Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, complete listings of bond lengths and bond angles, torsion angles, and least-squares planes for complexes 1 and 18 and intermolecular contacts for 1 (18 pages). Ordering information is given on any current masthead page.

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